Hydrogeochemistry and Isotope Hydrology of the Komadugu-Yobe Basin, Nigeria, Sahel Region Africa

By

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Declaration

This thesis is the result of the author's original research. It has been created by the author and has not been previously submitted, in part or whole, to any university or institution for any degree, diploma, or other qualification.

Signed: Abdulrahman Shuaibu

Date: 13/12/2024

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Abstract

Groundwater is a critical resource for sustaining domestic, agricultural, and industrial activities in the Komadugu-Yobe Basin (KYB). However, growing pressures from over-exploitation, rapid population growth, pollution from geogenic and anthropogenic sources, and climate variability threaten the long-term sustainability of this vital water source. This thesis employs an integrated approach which combines geochemical modelling, hydrochemical characterization, Geographic Information System (GIS)-based techniques, chemometric analysis, index-based models and environmental stable isotopes analysis to determine the factors influencing groundwater chemistry, recharge mechanisms, and contamination sources, human health risk of heavy metals in KYB, to support Integrated Water Resources Management (IWRM) and help in achieving Sustainable Development Goal 6 (SDG 6) in KYB and the wider Sahel region. Groundwater samples were collected from 240 water points across the Komadugu-Yobe basin during two sampling campaigns (120 each) of wet and dry seasons. The pH, temperature, total dissolved solids (TDS), oxidation-reduction potential (ORP), and electrical conductivity (EC) were assessed in situ using a handheld digital electrical conductivity meter in situ while dissolved oxygen (DO) was measured using a DO meter. Major cations (Na, Ca, Mg, and K) and heavy metals (As, Cd, Cu, Zn, Pb, Ni, Fe, Mn, Cr and Co), were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) while anions (Cl, HCO_3, NO_3, and SO_4) were analyzed using ion chromatography (IC). Total alkalinity and bicarbonate were measured in situ using a HACH digital alkalinity kit by the titrimetric method and in Laboratory using KONE equipment. The stable isotopes of δ^2H and $\delta^{18}O$ were analysed at the IAEA Isotope Laboratory, Vienna and the Isotope Laboratory for the Ministry of Water in Lilongwe, Malawi using Picaro Stable Isotope Analyser.

Hydrochemical analysis revealed that groundwater in the Komadugu-Yobe basin is predominantly of Ca-Mg-HCO_3 water type, constituting about 59 % of the samples. Some groundwater quality parameters exceeded World Health Organization guidelines for drinking water, while Gibbs diagrams identified rock-water interactions as the primary factor influencing groundwater chemistry. The groundwater quality index (GWQI) classified 63 % of samples as excellent and 27% as good for drinking. The study showed a strong interaction between geology, hydrochemistry and groundwater quality during the wet season. A further geochemical and chemometric analysis revealed that chloride and nitrate originated from anthropogenic sources mainly synthetic fertilizers and nitrification processes in pit latrines. Principal Component Analysis (PCA) indicated that groundwater chemistry is primarily influenced by geogenic processes, agricultural activities, industrial processes and mineral weathering. Additionally, hierarchical cluster analysis (HCA) identified the impacts of evaporation and ion exchange processes within the aquifer systems. Groundwater sampled during wet and dry seasons is significantly undersaturated with calcite, dolomite and fluorite minerals and partial pressure of carbon dioxide (pCO_2) exceeded the atmospheric pCO_2 in nearly all samples.

The study also assessed heavy metal pollution and its associated human health risks, highlighting lead, iron, manganese, and cadmium as the main contaminants and pose significant health risks to the local communities in the basin. Index-based models revealed that the groundwater is less polluted in upstream parts and highly polluted in downstream parts of the basin. Human health risk assessments showed that both adults and children are at risk of both carcinogenic and non-carcinogenic health effects from drinking contaminated groundwater. Chemometric analysis suggests that physicochemical parameters and heavy metals likely have different geochemical behaviours and originated from distinct geogenic and anthropogenic sources. Moreover, isotopic analysis of δ^{18}O and δ^{2}H signatures provided insights into groundwater recharge, indicating that local precipitation is the primary source of recharge particularly in areas near Hadejia-Nguru wetland, Hadejia Komadugu Valley, Chalawa George Dam, and Tiga Dam, with seasonal variations in isotopic signatures due to evaporative enrichment before infiltration. The local meteoric water line (LMWL) was defined as $\delta^{2}H = 6.7\ (\pm\ 0.1)\ \delta^{18}O + 4.1\ (\pm 0.4)$ for the KYB, while regional analyses of δ^{18}O and δ^{2}H signatures revealed the influence of the Inter-Tropical Convergence Zone (ITCZ) on isotopic variability. D-excess results highlighted complex recharge processes in both sedimentary and basement aquifers, suggesting that recharge occurs primarily during periods of heavy rainfall with depleted isotopic signatures. D-excess analysis suggests that average precipitation in the entire Sahel region exhibits a general continental effect until the ITCZ meets the Congo Basin and that average precipitation in the entire Sahel region occurs under equilibrium conditions. The findings from this study are essential for policymakers, stakeholders, government agencies, NGOs, and local communities to implement integrated water resources management strategies toward achieving SDG 6 in the Komadugu-Yobe basin and the wider Sahel region.

Preface

The core of this thesis was developed as a series of papers published in peer-reviewed journals, under review, or in preparation for submission to peer-reviewed journals. Each main research chapter consists of its abstract, introduction, methodology, results, discussions, conclusions, and policy recommendations where appropriate. Each of the core chapters consists of a preface of text at the beginning to highlight the links between the chapters, introduce the broad concept, research questions, and specific objectives answered. Each of the core chapters ends with a postface which highlights how the chapter answered the research question and fulfilled the specific objectives as well as providing any additional thesis context where required. The references for the papers and authors' contributions are presented as follows:

Chapter 5

Shuaibu, A., Kalin, R. M., Phoenix, V., Banda, L. C., & Lawal, I. M. (2024). Hydrogeochemistry and Water Quality Index for Groundwater Sustainability in the Komadugu-Yobe Basin, Sahel Region. *Water*, *16*(601), 1–22. https://doi.org/10.3390/w16040601

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List of Abbreviations and Acronyms

APHA	American Public Health Association
cm	Centimetre
CJF	Climate Justice Fund
CR	Carcinogenic Risk
DO	Dissolved Oxygen
EC	Electrical Conductivity
FA	Factor Analysis
GIS	Geographical Information System
GMWL	Global Meteoric Water Line
GNIP	Global Network of Isotopes in Precipitation
GNIR	Global Network of Isotopes in Rivers
GPS	Global Positioning System
GWQI	Groundwater Quality Index
HCA	Hierarchical Cluster Analysis
HRA	Health Risk Assessment
IAEA	International Atomic Energy Agency
IWRM	Integrated Water Resources Management

Kg	Kilogram
KI	Kelly Ratio
Km	Kilometres
KYB	Komadugu-Yobe Basin
LMWL	Local Meteoric Water Line
m	Metres
mm	Millimetre
masl	Metres Above Sea Level
mg/L	Milligrams Per Litre
MR	Magnesium Ratio
NGO	Non-Governmental Organization
NCR	Non-Carcinogenic Risk
ORP	Oxidation and Reduction Potential
PCA	Principal Component Analysis
PI	Permeable Index
PTEs	Potentially Toxic Elements
RWML	Regional Meteoric Water Line
RQ	Research Question

RSC	Residual Sodium Carbonate
SAR	Sodium Absorption Ratio
SDGs	Sustainable Development Goals
SI	Saturation Index
SO	Specific Objective
TCR	Total Carcinogenic Risk
TDS	Total Dissolved Solids
TH	Total Hardness
UN	United Nations
USEPA	United States Environment Protection Agency
V-SMOW	Vienna Standard Mean Ocean Water
WHO	World Health Organization
WMO	World Meteorological Organization
µS/cm	Micro siemens Per Centimetre
%Na	Percentage Sodium

1 Introduction

1.1 Overview

Groundwater is a vital natural resource and plays a crucial role in sustaining water supplies for domestic, agricultural, and industrial activities, especially in arid and semi-arid regions where surface water is often unreliable or seasonally unavailable. (El Ouali et al., 2022; Mohamed et al., 2022). Over one-third of the world's population, mainly in developing nations depends on groundwater for their drinking water supply. (Dippong et al., 2024; Li et al., 2021; Noor et al., 2024). Yet, over-exploitation, increasing contamination, and rapid population growth threaten its long-term sustainability, particularly in developing economies striving to meet their water demands while working towards realizing Sustainable Development Goals (SDGs). In line with Goal 6 of the Sustainable Development Goals (SDGs), which aims to "Ensure availability and sustainable management of water and sanitation for all", and targets 6.1, 6.3, 6.4, and 6.5 which underscored the need to ensure access to safe drinking water, improve water quality, promote sustainable groundwater exploitation, and implement integrated water resources management, respectively (UN, 2017, 2020). This highlights the urgent need for coordinated groundwater research, development, and management.

The Petroleum Technology Development Fund (PTDF) awards overseas postgraduate scholarships to Nigerians to conduct cutting-edge research in engineering, geology, science, and management at prestigious universities worldwide. Its vision, "To serve as a vessel for the development of Indigenous manpower and technology transfer/acquisition in the oil and gas industry, and to position Nigeria as a human resource centre for the West African sub-region and the Gulf of Guinea," emphasizes the importance of fostering knowledge and addressing critical challenges in the oil and gas sector through Indigenous research initiatives. As part of the focus on technology transfer and acquisition, this PhD research was developed to examine the impact of groundwater pollution and hydrochemistry, to understand the geochemical processes influencing groundwater chemistry and recharge mechanisms in aquifer systems. Petroleum exploration activities are predominantly concentrated in the oil-rich southern region of Nigeria, most PTDF-sponsored research has historically focused on the oil-rich southern regions of Nigeria, leaving the northern region marginalized in terms of research and development despite facing significant socioeconomic challenges and health risks related to groundwater contamination.

Subsequently, the PhD titled “Hydrogeochemistry and Isotope Hydrology of the Komadugu-Yobe Basin, Nigeria, Sahel Region Africa” was developed in consultation with PTDF and the representatives from the Hadejia Jama’are River Basin Development Authority (HJRBDA). The Komadugu-Yobe Basin, a critical area for agriculture and food security in Nigeria, faces serious challenges, including Boko Haram insurgencies, banditry, farmer-herder crisis, and severe human health risks from groundwater contamination. My prior research on flood risk and vulnerability assessment in the Hadejia River Basin in 2019 gave me insights into groundwater contamination and related human health risks in the Komadugu-Yobe Basin. My local knowledge and connections in the area made me an ideal candidate to undertake this research. Conducting this study in the region aligns with PTDF’s objectives by offering scientific solutions to pressing regional problems and contributing to national development. Furthermore, the findings not only provide an understanding of groundwater quality and human health risks of groundwater contamination in northern Nigeria but also serve as a framework for addressing similar challenges in the southern region, where contamination from oil and gas exploration, as well as domestic and agricultural activities, are prevalent. This work aligns seamlessly with PTDF’s mission and vision by fostering sustainable solutions and advancing socioeconomic well-being.

Groundwater provides a significant portion of the water needed for various purposes in both rural and urban areas of the Komadugu-Yobe basin (KYB) (Abubakar et al., 2018; Ahmed et al., 2018b; Wali et al., 2019). However, the quality of groundwater in KYB is increasingly affected by a range of anthropogenic activities and geogenic processes including improper domestic waste disposal, agricultural runoff, industrial discharges, mineral weathering, cation exchange processes, and evaporation from shallow aquifers. (Kwaya et al., 2017). Moreover, rapid population growth, intensive agriculture, urbanization, and ongoing armed conflicts in the region have significantly increased water demand, pollution, and the degradation of groundwater quality and quantity in the region. Therefore, conducting a comprehensive hydrochemical assessment and stable isotope analysis is essential to understand the geochemical processes influencing groundwater chemistry, identify sources of contamination, and assess recharge processes. This is critical for safeguarding public health and developing effective, sustainable water management strategies in the basin.

According to Le Coz et al., (2011), the aquifer recharge process and pollution potential in the Komadugu-Yobe basin have been modified over the last three decades due to extensive irrigation farming within the Komadugu-Yobe valley, urbanization, and domestic and industrial discharges. Numerous cases of renal failure have been reported in Yobe State, particularly in communities such as Gashua, Bursari, Biomari, and areas around the Hadejia-Nguru wetlands (Ahmed et al., 2018a; Waziri & Ogugbuaja, 2010). Ahmed et al., (2018a) reported that health centre records from communities around the Hadejia Nguru wetland and towards downstream parts of the Komadugu-Yobe basin indicate that 40 % of admitted patients were diagnosed with chronic kidney disease (CKD), with 70 % of these cases originating from Gashua, Nguru, and Jakusko in Yobe State, as well as certain communities in Jigawa State. It was emphasized that nearly every household has been affected either by losing a family member or relative to the disease or by struggling with the financial burden of renal failure treatment. The kidney disease cases were said to have begun about 20 years ago, in the early 1990s. Available evidence suggests that the disease is not confined to any age group, gender, or ethnic background, affecting individuals of all ages, including children, young adults, and the elderly. However, women appeared to experience more severe impacts than men (Sulaiman et al., 2022). Most people in the communities rely on hospital care or traditional medicine, with the latter being more widely used due to its affordability. Potentially toxic elements (PTEs) and major ions, including lead, cadmium, arsenic, sodium, sulfate, iron, and nitrate, are prevalent in this region and are believed to be the primary pollutants affecting groundwater quality in the basin causing renal failure and other water-related diseases (S. D. Ahmed et al., 2018a; Sulaiman et al., 2022; Waziri et al., 2012; Waziri & Ogugbuaja, 2010). Although, several studies have detected the presence of various contaminants in the groundwater of the basin (Amshi et al., 2019; Dauda & Ali, 2024; Jagaba et al., 2020; Tukur et al., 2018; Usman & Aliyu, 2020; Waziri et al., 2012). However, to date, no comprehensive attempt has been made to characterize hydrochemical processes controlling the groundwater chemistry, identify pollution sources, assess human health risks associated with PTEs, evaluate the general suitability of groundwater for drinking and irrigation, and analyze groundwater recharge mechanisms on a more regional scale.

1.2 Aim and Objectives of the Research

1.2.1 Research Aim

This research aims to investigate the groundwater resources of the Komadugu-Yobe Basin using an integrated approach that combines geochemical modelling, GIS-based techniques, chemometric analysis, index-based models, and stable isotope analysis. This approach seeks to elucidate the key hydrogeochemical processes governing groundwater chemistry, assess its suitability for drinking and irrigation, identify sources and human health risks of groundwater pollution, analyze the chemical speciation and complexation of PTEs, and investigate groundwater recharge mechanisms. The goal is to provide insights that support sustainable management of groundwater resources and underpin integrated water resources management in the Komadugu-Yobe Basin and the wider Sahel region, ensuring water quality and availability in the context of climate change and environmental and anthropogenic influences.

The Komadugu-Yobe Basin in Nigeria was selected as the case study for this PhD research to fulfil the requirements of the scholarship funding provided by the Petroleum Technology Development Fund (PTDF). Additionally, the basin faces persistent challenges of groundwater contamination, and significant socioeconomic issues, and is a region of critical importance for agricultural activities and food security in Nigeria.

*1.2.2 Research Questions (**RQ**) and Specific Objectives (**SO**)*

Four Research Questions (**RQ**) were developed to achieve the overall aim of the research. These research questions and their associated specific objectives are:

RQ1. What are the general hydrochemical characteristics of groundwater in KYB and its suitability for drinking and irrigation purposes?

> *SO1*. Conduct a case study to determine the suitability of groundwater for drinking purposes in KYB.
>
> *SO2*. Conduct a case study on groundwater quality index analysis to classify groundwater potability.
>
> *SO3*. With the aid of Piper trilinear diagram and Chadha plot, identify various groundwater facies and water types in the basin.
>
> *SO4*. Conduct a case study to determine the spatial variation of groundwater quality parameters and the link between geology and groundwater quality in the basin. The distribution of groundwater quality parameters in the basin was determined and used as a

guide in developing effective strategies for sustainable use and management of groundwater in the basin.

SO5. Conduct irrigation water quality analysis in the basin by evaluating various parameters that control irrigation water quality such as sodium percentage (Na %), sodium adsorption ratio (SAR), Magnesium Adsorption Ratio (MAR), soluble sodium percentage (SSP), total hardness (TH), electrical conductivity (EC), residual sodium carbonate (RSC), permeability index (PI) and Kelly's ratio (KR) and irrigation water quality index computation.

RQ2. What role can chemometric analysis and geochemical modelling approach play in assessing geochemical evolution and mechanisms influencing groundwater chemistry as well as the origin/source of chemical constituents in groundwater in the Komadugu-Yobe basin?

SO6. Investigate geochemical evolution and mechanisms governing groundwater chemistry using geochemical modelling.

SO7. Conduct a case study to determine the source extent of chemical parameters in the groundwater using a chemometric analysis approach.

SO8. To explore the impact of climate change/seasonal variability on groundwater quality in the basement and sedimentary quaternary aquifers of the Komadugu-Yobe Basin.

SO9. Develop a conceptual model for geochemical evolution and hydrogeochemical processes of groundwater in the Komadugu-Yobe basin.

RQ3. What are the sources and status of PTEs pollution and their associated health risk in the Komadugu-Yobe basin and how do these PTEs form speciation and complexation reactions in aqueous solution?

SO10. Conduct chemometric analysis and index-based analysis on various PTEs to identify their sources and contamination levels in the basin.

SO11. Model speciation and complexation of some selected PTEs in groundwater of Komadugu-Yobe Basin using Geochemist's WorkBench GWB software.

SO12. Conduct human health risk assessment (non-carcinogenic and carcinogenic) of PTEs in the basin.

RQ4. What role can stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ offer in identifying the origin of groundwater recharge and its mechanisms in the transboundary Komadugu-Yobe basin?

SO13. Conduct stable isotope analysis to understand recharge mechanisms in the Komadugu-Yobe basin.

SO14. Determine the spatial distribution and seasonal variability of stable isotopic signatures in groundwater of the Komadugu-Yobe basin and the wider Sahel region.

1.3 Thesis Structure

This PhD research work discusses the hydrogeochemistry and stable isotope hydrology of the Komadugu-Yobe Basin, Nigeria, Sahel region of Africa for water sustainability. The thesis is composed of 9 chapters (Figure 1.1); an introduction chapter, a literature review, a study area description, a methodology chapter, 4 main research chapters that present the results section, and a discussion, conclusion, and recommendations. Each of the 4 main research chapters (chapters 5-8) is represented as a stand-alone peer-reviewed publication. These papers are linked sequentially to provide cumulative results analysis and discussion. 2 papers have been published in an international peer-reviewed journal and 2 have been submitted and are under review. The thesis chapters are described as follows:

- The first chapter (chapter 1) presents an overview of the thesis, the research aim, and 4 research questions with 14 specific objectives which were answered and fulfilled to achieve the main aim of the research. The thesis structure is also documented in the first chapter.
- Chapter 2 provides literature reviews of previous works on hydrogeochemical investigations. The fundamental principles and basics of groundwater chemistry are well presented in this chapter. Additionally, the chapter illustrates state-of-the-art knowledge of geochemical modelling and stable isotopic analysis of groundwater resources. The recent approaches and key knowledge gaps form the basis of the work. Moreover, additional literature relevant to each research paper was reviewed in the respective chapters 5-8.
- The third chapter (chapter 3) mainly describes the study area. The study area location as well as its physical and hydro-geomorphological characteristics were presented in this chapter. It described the various regional and local geologies, hydrogeological settings, and groundwater recharges of the Komadugu-Yobe basin.
- Chapter 4 (the methodology chapter) provides detailed methodologies adopted toward achieving the study objectives. The laboratory and field methodologies used in the research were well presented. These consist of the materials used, data and sources of data, software, reconnaissance visits, sampling strategies, fieldwork, equipment calibration, groundwater inventories, field measurement of physicochemical parameters, groundwater sampling, sample preservation, storage and transport, quality assurance and quality control, laboratory analysis, statistical analysis, ArcGIS analysis, geochemical modelling, $\delta^{18}O$, and $\delta^{2}H$ isotopes analysis, and finally data evaluation and interpretation.

- Chapter 5 is the first chapter in the results section and aims to answer RQ1 through SO1, SO2, SO3, and SO4. This chapter presents a case study to determine general hydrogeochemical characteristics and water quality index for groundwater sustainability in the Komadugu-Yobe basin utilizing a wet season physicochemical dataset. The link between geology and hydrochemical characteristics, groundwater facies, and groundwater quality index in the basin was established.
- Chapter 6 is the second chapter in the results section and presents the role of chemometric analysis and geochemical modelling in assessing geochemical evolution and mechanisms influencing groundwater chemistry as well as the origin/source of chemical constituents in groundwater in the transboundary Komadugu-Yobe basin. This chapter answers RQ2 through SO6, SO7, SO8 and SO9. Various sources of chemical constituents in the groundwater were determined using principal component analysis and hierarchical cluster analysis. Furthermore, Gibbs plots, evidential plots, bivariate plots, and chloro-alkaline indices revealed hydrogeological processes in wet and dry season groundwater in the basin. Finally, the chapter developed conceptual model for hydrogeochemical processes and discusses the relevance and implication of the study to groundwater sustainability.
- Chapter 7 presents an integrated methodology of chemometric analysis and index-based models to identify various PTE pollution sources and assess their level of contamination and their associated human health risks. It presented the third chapter in the results section and answered RQ1 and RQ3 through SO5, SO10, SO11, and SO12. The speciation of As, NO_3, Fe, Pb, and Fe was modelled using the Pourbaix diagram (Eh-pH modelling in GWB geochemist's workbench software). Various index-based models: Cdeg, HEI, HPI, and mHPI aided the determination of heavy metals pollution levels while the suitability of wet and dry season groundwaters for drinking

(considering both physicochemical parameters and PTEs) and irrigation were evaluated based on GWQI, WPI and IWQI (hydrochemical indices, USSL diagram, Wilcox plot, Doneen's diagram) respectively. Finally, sources/origin of heavy metals pollution in KYB were identified using Pearson's correlation analysis, PCA/FA, and R-mode HCA.

- Chapter 8 answers RQ4 and fulfils SO13 and SO14 and presents the fourth chapter in the results section. A stable isotopic dataset of groundwater from two sampling campaigns covering wet and dry seasons in KYB and a groundwater dataset from 5 major basins in the Sahel region of West Africa were utilized to elucidate rainfall-recharge relationships in KYB and the Sahel region to underpin integrated water resources management. In doing so, the regional meteoric water line for the KYB was developed using rainfall dataset 3 local and 4 regional GNIP stations. Moreover, the precipitation dataset from 15 GNIP stations across the Sahel region enables the development of a regional meteoric water line for the Sahel region.
- Chapter 9: This chapter presents the general discussion of the result of the entire thesis by providing a discussion and summary of the key findings, thesis contribution to knowledge, the implication of the study to groundwater sustainability, the potential of achieving SDG goal 6, and the way forward. It also presents the main conclusions drawn from the research, suggestions, and recommendations for future practice and research.
- References: This section documented the list of all materials cited in the research work.
- Appendices: This section constitutes a list of items that are not essential in the work but play a vital role in achieving the desired objectives.

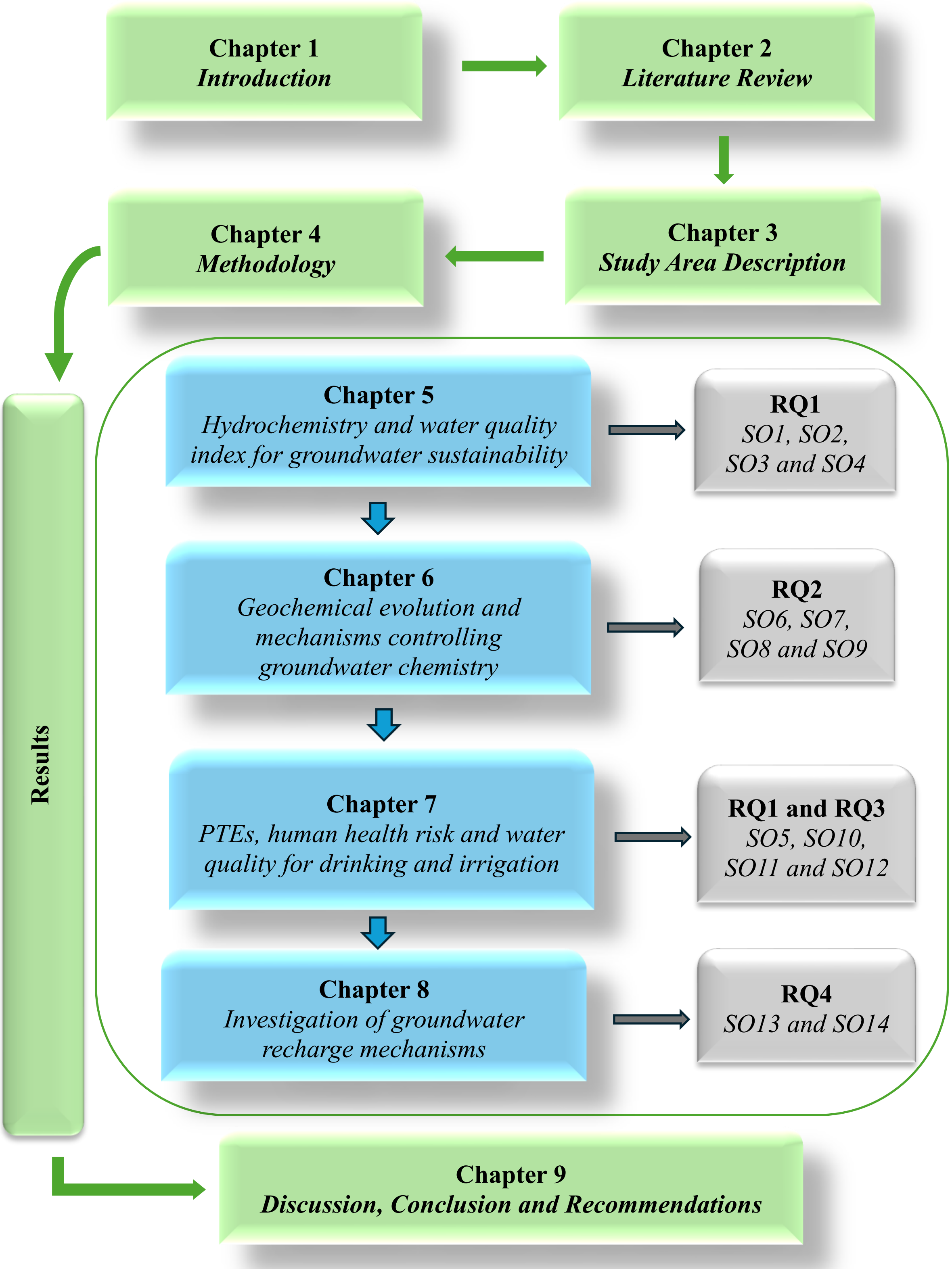

Figure 1.1 Flow diagram of the thesis structure highlighting the research questions and specific objectives addressed in each chapter.

2 Literature Review

The previous chapter presented an overview of the research, outlining the main aim, research questions, and the specific objectives critical to achieving the desired research goal. This chapter provides general literature reviews relevant to the research aim and objectives. It explores the fundamental principles and current state-of-the-art knowledge on the broad thesis topic, whilst highlighting research gaps addressed in the thesis. In the result section, the research chapters (chapters 5-8) comprise a stand-alone, peer-reviewed publication with more detailed literature reviews specific to each study.

2.1 Brief Overview of Global Groundwater Resources

Groundwater constitutes about 98 % of the earth's available freshwater which is about 60 times more than the fresh waters in lakes and streams (Musie & Gonfa, 2023; Omotola et al., 2020; Panaskar et al., 2016; Wali et al., 2019). About one-third of the world's population depends on groundwater for drinking (Noor et al., 2024; Wali et al., 2019). The volume of global groundwater resources is estimated to be about 23 million Km^3 with only 0.3 million Km^3 considered renewable and readily available for consumption because of limitations such as depth, quality and recharge rate (Gleeson et al., 2016). Groundwater is generally considered to be better than surface water due to its lower susceptibility to pollution from anthropogenic activities and its large storage capacity. Groundwater often requires little to no pre-treatment for various purposes. It is increasingly exploited because of its good composition, making it suitable to meet the requirements of a wide range of uses. Omole, (2013) reported that about 75 % of sub-Saharan Africa solemnly depends on groundwater resources for drinking water supply. Moreover, about 40, 70, and 33 % of the earth's groundwater resources are used for irrigation, domestic and industrial purposes respectively (Carrard et al., 2019; Giao et al., 2023; Ingrao et al., 2023; Mark et al., 2016; Musie & Gonfa, 2023). These figures may increase exponentially due to the declining quantity and quality of surface water resources, driven by population growth which heightens the risk of water pollution as well as industrialization, urbanization, and climate change impacts (Odukoya, 2015). Joshi et al., (2018) reported that the global annual groundwater discharge rate is approximately 1,500 km^3, which can vary depending on climate and geography, and it exceeded the typical global groundwater recharge rate. Excessive groundwater withdrawals result from changes in living standards, cultural norms, and population growth as well as climate change which severely affects various regions worldwide (Ingrao et al., 2023; Musie & Gonfa, 2023).

2.2. Groundwater Resources of Nigeria

Groundwater is a vital resource in Nigeria, providing water supply for domestic, agricultural, and industrial purposes. Groundwater is the water stored in the cracks and pore spaces of rocks and sediments within the subsurface of the earth (Pipit et al., 2016). Shallow hand-dug wells and deep boreholes are the main sources of groundwater in Nigeria. Groundwater resources in Nigeria are estimated to be about 87 km^3 which plays a crucial role in meeting water needs in the country, particularly in arid and semi-arid regions with limited surface water resources during dry seasons (Ahmed & Mansor, 2018; Ngene et al., 2021). Nigeria gets its groundwater mostly from basement and sedimentary aquifers across the country, which supply water for domestic, agricultural and industrial purposes (Adelana et al., 2008; Akujieze et al., 2003; Edet et al., 2012; Ighalo & Adeniyi, 2020). Presently, over 60 % of Nigerian citizens depend on groundwater for various domestic purposes (Abioye & Perera, 2019; Omole, 2013; Omotola et al., 2020). Edet et al., (2012) highlighted the heavy reliance on groundwater in both rural and urban areas of Nigeria. Their study identified overexploitation and pollution as major challenges affecting groundwater quality.

Groundwater is widely used for irrigation purposes especially in the semi-arid region of Nigeria (Northern part) (Carter & Alkali, 1996; Sobowale et al., 2014). The demand for groundwater in Nigeria has increased significantly due to inadequate and deteriorating infrastructure, insufficient funding for water and sanitation programs, lack of stringent policies and regulations, inappropriate financial resource management, degradation of available surface water resources from human activities, climate change, and the availability of simple, low-cost technologies for groundwater exploration (Ademiluyi & Odugbesan, 2008; Oni & Aizebeokhai, 2017). While groundwater resources in southern Nigeria have been extensively studied, the northern region that relies most solemnly on groundwater, particularly the northeastern region characterized by semi-arid to arid climate has been underrepresented in groundwater research on pollution, aquifer recharge mechanisms, groundwater sustainability and integrated approach to groundwater resources management. Chapters 5, 6, and 8 fill this gap for the Komadugu-Yobe basin by characterizing the groundwater chemistry, assessing pollution sources, human health risk assessment of heavy metals and identifying groundwater recharge processes.

2.3 Groundwater Pollution

Groundwater pollution is a very serious problem of concern worldwide that poses an impact not only on health but also on socio-economic development (Omonona & Okogbue, 2021; Rajesh et al., 2019). Groundwater pollution may result from inadequate sanitation, indiscriminate use of fertilizers and manures in farmlands, and improper disposal of domestic and industrial wastes (Kurwadkar, 2014; Odukoya & Laniyan, 2014). Singh et al., (2013) highlighted that groundwater pollution results from increased pressure on groundwater, unplanned urbanization, weak exploration policies, and dumping of solid waste and domestic discharges at inappropriate places. Intensive agricultural activities lead to an increase in groundwater pollution by increasing its salinity concentration as well as nutrient concentration (Kurwadkar, 2014; Odukoya, 2015). Moreover, groundwater pollution may arise from natural sources, including soils and geological formations that contain elevated levels of heavy metals and various lithologies, which can leach cations and anions into groundwater systems (Ibrahim et al., 2019). An annual death of about 1.7 million children below the age of 5 years is suspected to be a result of ingestion of contaminated groundwater (Emenike et al., 2018a).

Pollution of groundwater resources in Nigeria arises from varieties of anthropogenic activities, geogenic processes and poor management of effluent from industries (Emenike et al., 2018a; Yusuf & Abiye, 2019). Various sources of groundwater pollution in Nigeria include leachate from landfills, urban development, industrial effluents, over-exploitation of groundwater, hydrogeology, domestic waste and sewage, as well as oil and gas contamination from accidental spills and industrial discharges (Egbueri et al., 2019; Ighalo et al., 2021; Yusuf & Abiye, 2019). Wali, et al., (2021) Reported that groundwater pollution in the northern parts of Nigeria results from salinization and anthropogenic activities coupled with rock weathering and rock-water interaction processes Groundwater contamination in northern, eastern and western parts of Nigeria is mostly attributed to agricultural runoff, industrial effluents, fit latrines, septic tanks, mining activities, insufficient sanitation, excessive extraction, and inadequate waste management (Ighalo et al., 2021). The pollution of groundwater in the coastal areas of Nigeria is attributed to oil exploration activities and effluent discharges from industries (Owoyemi et al., 2019). Egbinola & Amanambu, (2014) argued that groundwater pollution in southern Nigeria primarily results from oil and gas spills, industrial effluents, agricultural runoff, waste disposal, poorly managed septic systems, artisanal mining, and unregulated well construction, all of which contribute to significant water quality degradation.

Previous studies in Nigeria identified groundwater pollution in both northern and southern region (Amshi et al., 2019; Dawoud & Raouf, 2009; Egbueri et al., 2023; Emenike et al., 2018b; Getso et al., 2018; Goni et al., 2019; Mgbenu & Egbueri, 2019; Omeka et al., 2024; Owamah et al., 2023). However, these studies lack a comprehensive analysis of geochemical evolution, various groundwater pollution sources, and their associated impacts on human health, agriculture, groundwater sustainability and socioeconomic development particularly in the northern parts of the country. Chapters 6 and 7 address this gap for the Komadugu-Yobe basin by tracing groundwater pollution sources and their geochemical behaviours using chemometric techniques, evaluating groundwater quality for various purposes and assessing the human health risks associated with heavy metals in groundwater of the basin.

2.4 Groundwater Quality

The quality of groundwater is an issue of concern to scientists and hydrogeologists. The chemical composition of groundwater is the prime factor considered in characterizing and evaluating the quality of groundwater (Rajesh et al., 2019). The chemical reactions which occur between minerals and groundwater within the lithologic structures in the subsurface affected water types (Ewuzie et al., 2021; Rajesh et al., 2019). Moreover, the overall quality of groundwater in terms of domestic, agricultural and industrial applications is significantly influenced by evolution of groundwater (Olofinlade *et al.,* 2018). The quality of groundwater is significantly affected by natural processes, including hydrogeologic conditions, weathering, dissolution, precipitation, lithology, and water-rock interactions, as well as anthropogenic activities such as agriculture, industrial processes, mining, and urban development (Varol, 2020; Zhang et al., 2024). Borehole water in sedimentary regions exhibits low chloride and pH values, indicating a corrosive nature which potentially affects groundwater quality (Aladejana et al., 2021). Assessment and monitoring of groundwater quality is achieved by hydrogeochemical and statistical analysis, as well as water quality indices analysis (Ahmed et al., 2019; Marini, 2006).

2.4.1 Assessment of Groundwater Quality for Drinking

The assessment of groundwater quality for drinking purposes involves the analysis of the chemical composition of groundwater, and remedial actions required for restoring water quality in instances of degradation as well as identifying potential sources of groundwater contamination (Annapoorna & Janardhana, 2015; Goswami et al., 2022). Groundwater quality assessment for drinking purposes is typically performed by juxtaposing each key water quality parameter against the drinking water standard limits (Giao et al., 2023). However, the groundwater quality index (GWQI) calculates a single numerical value from various water quality parameters to assess the suitability of groundwater for drinking and to effectively communicate water quality information (Alrowais et al., 2023; Atta et al., 2022; Batabyal & Chakraborty, 2015; Chen et al., 2019). Omonona & Okogbue, (2021) conducted hydrochemical characterization and evaluation of nitrate contamination to assess the quality of groundwater for drinking in Gboko district, Nigeria. Their study shows that the nitrate contamination of the groundwater is from uncontrolled nitrogen-based fertilizer application, paucity in sanitary facilities and sewages. Troudi et al., (2020) assessed the quality of groundwater for drinking purposes giving special emphasis on salinity and nitrate in shallow aquifers of Guenniche Northern Tunisia using World Health Organization standard limits and groundwater quality index. Atta et al., (2022) employed a water quality index relevant to both WHO standard limits and Egyptian standard limits to identify and assess the suitability of groundwater for drinking in the surroundings of Ismailia canal, Egypt. Batabyal & Chakraborty, (2015) employed hydrogeochemical analysis and water quality index (WQI) to evaluate groundwater quality in a rural area of West Bengal, India. WQI analysis revealed that groundwater is deemed safe for drinking, although it exhibits high iron and chloride concentrations in certain regions.

Hamza et al., (2017) employed the pollution vulnerability index (PVI) and water quality index (WQI) to assess groundwater quality and identify pollutants in Kano City, Northern Nigeria. Similarly, Garba et al., (2021) evaluated water quality for drinking purposes from four different sources in Bauchi metropolis using the Water Quality Index. Several other studies have examined groundwater quality for drinking purposes across Northern Nigeria (Ado et al., 2017;

Amshi et al., 2019; Babagana-kyari et al., 2024; Bernard & Ayeni, 2012; Dawoud & Raouf, 2009; Suleiman et al., 2020; Yerima et al., 2017). There is a lack of sufficient research on how groundwater quality parameters align with drinking water standards, as well as on the analysis of the groundwater quality index in a regional context, particularly in northeastern Nigeria. These issues are thoroughly explored in Chapter 5 for the transboundary Komadugu-Yobe basin.

2.4.2 Assessment of Groundwater Quality for Irrigation

Groundwater is extensively used for irrigation globally, and its quality largely depends on the concentrations of major ions (cations and anions) present. Contaminated groundwater can introduce toxic metals and harmful microbes into the soil and plants, posing risks to agriculture and food safety (Ghosh & Bera, 2023; Ishaku et al., 2016). Agriculture, including both rain-fed and irrigated farming, is the primary occupation of residents in the Komadugu-Yobe basin which contributes significantly to meeting the country's food requirements (Adeyeri et al., 2020; Gana et al., 2019). Ensuring good quality groundwater in the Komadugu-Yobe basin is essential for sustainable irrigation practices. Eyankware et al., (2020) assessed the irrigation water quality in Warri and its environs using the APHA method. The analysis included parameters such as electrical conductivity, soluble sodium percentage, sodium percentage, permeability index, sodium adsorption ratio, residual sodium bicarbonate, Kelly's Ratio, and total hardness. The Gibbs plot and groundwater facies analysis revealed that the groundwater chemistry is predominantly influenced by rock weathering, with the water classified as Na-HCO_3 and Na-Cl types. Abdullahi *et al.,* (2010) evaluated the quality of groundwater for residential and irrigation purposes in Gubrunde, northeastern Nigeria. The dominant water type identified in the study area is Ca-Cl, with a medium salinity hazard. The chemical composition of groundwater in the region varies due to factors such as extensive use of artificial fertilizers, leaching from terrestrial salts, and ion exchange between water and the host rock. Limited studies have assessed groundwater quality for irrigation, particularly focusing on hydrochemical indices and the impacts of salinity and sodicity in northeastern Nigeria. However, Chapter 7 addresses this gap by using irrigation suitability indices, Wilcox and USSL diagrams, as well as the irrigation water quality index to evaluate the suitability of groundwater for irrigation in the Komadugu-Yobe basin.

2.4.3 Hydrochemical Indices for Irrigation Groundwater Quality

The hydrochemical indices utilized in evaluating groundwater quality for irrigation include Electrical Conductivity (EC), Total Dissolved Solids (TDS), Soluble Sodium Percentage (SSP), Sodium Percentage (Na%), Magnesium Hardness (MH), Permeability Index (PI), Sodium Adsorption Ratio (SAR), Residual Sodium Bicarbonate (RSB), Kelly's Ratio (KR), and Total Hardness (TH) (Eyankware et al., 2018, 2020a; Ghosh & Bera, 2023; Ishaku et al., 2011).

Electrical Conductivity (EC)

Electrical conductivity measures the ease with which electric current passes through water. Electrical conductivity is directly proportional to the concentration of dissolved solutes in natural waters. The salinity hazard to crops is best assessed by electrical conductivity. The osmotic activities of crops reduce when salinity is high, hence impairing the absorption of nutrients and water from the soil (Ghosh & Bera, 2023; Ishaku et al., 2011).

Total Dissolved Solids (TDS)

TDS is one of the most important parameters in evaluating groundwater suitability for agriculture. High TDS levels cause water stress around the crop root zone due to salt accumulation in the soil, making it difficult for crops to absorb water (Aravinthasamy et al., 2020; Panaskar et al., 2016).

Total Hardness (TH)

Total hardness or Hardness is the term used to describe water that has limited ability to react with detergents due to its high concentration of dissolved calcium and magnesium ions, which limits its usage (Rajesh et al., 2019; Rawat et al., 2018). Total Hardness is the sum of the concentration of Ca^{2+} and Mg^{2+} concentration in water (Eyankware et al., 2020a; Pivić et al., 2022). High hardness of water leads to scale accumulation in boilers and corrosion of pipelines. Kidney failure may also result from the consumption of hard water (Ahmed et al., 2018a; Ishaku et al., 2011).

Magnesium Hazard (MH)

Magnesium Hazard was introduced by Szabolcs & Darab, (1964) to assess the suitability of irrigation water. Elevated magnesium concentration in irrigation water destroys soil structure. The magnesium hazard is assessed based on the Mg ratio, defined as the ratio of magnesium concentration to the concentration of calcium and magnesium ions. The concentration of Na in irrigated soils is significantly influenced by elevated Mg content. Furthermore, elevated magnesium content in soil renders it alkaline, thereby impacting crop yield (Hosni et al., 2024; Pivić et al., 2022). The concentration of exchangeable Na^{+} in irrigated soils results in an increased level of Mg^{2+} (Rajesh et al., 2019; Rawat et al., 2018).

Permeability Index (PI)

Permeability index is one of the important parameters of irrigation water quality, which is estimated concerning the permeability of the soil. Long-term application of irrigation water typically impacts soil permeability, mostly determined by the concentrations of sodium, calcium, magnesium, and bicarbonate in the soil (Ishaku et al., 2011; Rawat et al., 2018). PI values are classified as I, II, and III. Waters that fall into class I and II are characterized as suitable for irrigation with 75% or more maximum permeability, whereas waters that fall into class III are categorized as unsuitable for irrigation with 25% or less maximum permeability (Rawat et al., 2018).

Sodium Adsorption Ratio (SAR)

Sodium adsorption ratio measures soil sodicity, which assesses its suitability for irrigation. The sodium adsorption ratio increases with sodium content and decreases with higher concentrations of calcium and magnesium in water (Kumar et al., 2021; Rawat et al., 2018). Therefore, it depends upon the concentrations of sodium, calcium, and magnesium. Excessive sodium concentration in soil results in the degradation of soil structure (Rajesh *et al.,* 2019). SAR provides the extent to which soils adsorbed sodium/alkali (Panaskar et al., 2016). The ion-exchange complex of irrigation water may be saturated with Na^+ when it has high Na^+ and low Ca^+ contents which causes the dispersion of clay particles destroying soil structure (Ishaku et al., 2011).

Sodium Percentage (Na%)

Sodium reacts with soil to lower permeability, making it a crucial element in determining the suitability of groundwater for irrigation. When sodium ions are present in irrigation water in high concentration, clay particles in the soil absorb them while dispersing magnesium and calcium. This usually results in reduced soil permeability and poor internal draining capabilities of soils (Ishaku et al., 2011; Panaskar et al., 2016).

Residual Sodium Carbonate (RSC)

The residual sodium carbonate is used to determine the effect of carbonate and bicarbonate on the quality of irrigation water (Ishaku et al., 2011; Rawat et al., 2018). RSC is defined as the ratio of the total concentration of carbonate and bicarbonate to the total concentration of calcium and magnesium in irrigation water (Rawat et al., 2018). High concentrations of sodium bicarbonate and carbonate facilitate the dissolution of organic materials in the soil (Hwang *et al.,* 2017).

Kelly's Ratio

Kelly's ratio is a significant water quality parameter that measures the concentration of sodium ions relative to the concentrations of calcium and magnesium ions in natural waters (Ishaku *et al.,* 2011; Rajesh *et al.,* 2019)**.** Waters with KI < 1 are categorized as suitable for irrigation and those with KI > 1 are deemed unsuitable for irrigation (Hwang et al., 2017; Rawat et al., 2018).

2.5 Geochemistry of Groundwater

The chemical and biogeochemical constituents of groundwater determine the hydrogeochemistry and geochemical processes the groundwater undergoes. Background geochemistry is essential for assessing the hydrochemistry of groundwater and monitoring groundwater quality (Mollema et al., 2013; Nganje et al., 2017). The geochemistry of groundwater largely depends on geogenic processes such as rock-water interactions during recharge, mineral precipitation, prolonged storage in aquifers, interconnections among aquifers and anthropogenic activities (Emenike et al., 2018; Odukoya, 2015). The assessment of geochemical processes and the evolution of water, along with the impact of anthropogenic activities on groundwater, are determined by a hydrochemical study of major dissolved ions in groundwater (Olofinlade et al., 2018; Zhang et al., 2024). Hydrochemical processes, including rock-water interaction, cation exchange, evaporation, mineral dissolution/precipitation, seawater intrusion, oxidation-reduction, and biological activities, significantly influence the hydrochemical evolution of groundwater in aquifer systems (Kumar et al., 2014; Mollema et al., 2013; Omonona & Okogbue, 2021).

The geochemistry of the Lake Chad basin is controlled by geochemical precipitation, clay neoformation and infiltration of water into the quaternary aquifer (Bouchez et al., 2016). Wali et al., (2019) indicated that the primary process governing groundwater chemistry in southern Kebbi is the weathering of rock minerals. Owoyemi et al., (2019) emphasized that the groundwater chemistry of the inland areas of the Niger Delta, Nigeria, primarily results from silicate weathering and ion exchange processes, while that of the coastal areas is predominantly influenced by seawater tidal flushing, silicate weathering, and ion exchange processes. Omonona et al., (2019) revealed that the water of Enyigba-Ameri is neutral to slightly alkaline, influenced by weathering of minerals like Lead, Zinc, and iron, anthropogenic activities, and dissolution of silicate and carbonate minerals. Yet, the geochemical processes controlling groundwater chemistry in northern Nigeria are poorly understood, particularly in the semi-arid northeastern part of the country. Regional hydrochemical analyses which include geochemical modelling and chemometric analyses, have also not yet been conducted. To fill this gap, chapter 6 employed geochemical modelling and chemometric techniques to elucidate the geochemical processes such as carbonate dissolution, evaporation and silicate weathering influencing groundwater chemistry and the impact of anthropogenic and geogenic processes in groundwater of Komadugu-Yobe Basin to have a thorough understanding of the groundwater chemistry.

2.6 Geochemical Evolution of Groundwater

The geochemical evolution of groundwater encompasses the changes in its chemistry as it passes through subsurface strata, interacting with rocks, minerals, and organic matter (Hussainzadeh et al., 2023; Tarasenko et al., 2022; Walter et al., 2023). Geochemical evolution is affected by physical, chemical, and biological processes that alter the concentration of dissolved minerals and gases in groundwater that are vital in groundwater quality assessment and identifying potential contamination sources. The principal processes influencing geochemical evolution include water-rock interactions, redox reactions, ion exchange processes, mineral dissolution and precipitation, evaporation, and anthropogenic activities (Fu et al., 2018; Walter et al., 2023). Geochemical modelling uses mathematical simulation of chemical reactions to characterize the chemical composition and behaviour of groundwater systems. Various processes governing groundwater evolution and the factors affecting groundwater chemistry are most effectively visualized by hydrogeochemical models (Ijioma, 2021). Geochemical models describe and predict how complex natural waters behave in response to various changes in equilibrium and help prevent future contamination of groundwater (Singh et al., 2013).

Piper and Durov diagrams were employed to determine hydrogeochemical facies of groundwater prevalent in the Ogbaru farming district in southeastern Nigeria (Egbueri, 2019). Singh et al., (2013) assessed the impact of seasonal variation and land use changes on groundwater quality in Ganga and Yamuna, India. The result of the WATEQ4F geochemical model revealed high under-saturation concerning halite and brucite, making the water unsuitable for irrigation. Human activities and natural processes were the main drivers of the changes in the hydrogeochemical nature of the groundwater. Emenike et al., (2018) conducted a hydrochemical assessment of groundwater in Abeokuta, Southeastern Nigeria by integrating geospatial and hydrochemical approaches. Their study reveals a mixed water type in the study area and that groundwater contamination is from mineral dissolution in soils and aquifers and anthropogenic activities. Ijioma, (2021) used Piper diagram, Chadha plot, Bivariate cross plots, and Schoeller diagram to describe the chemical behaviour of the groundwater system of Aba and its environs, Nigeria.

Eyankware et al., (2018) evaluated the groundwater quality in an abandoned limestone quarry pit in the Nkalagu region of the southern Benue Trough, Nigeria by employing a geochemical modelling technique. The hydrogeochemical facies analysis in Piper plots indicates that $Ca\text{-}Cl_2$ water type is predominant in the study area. Ukpai et al., (2016) investigated major ion concentrations in groundwater samples from the Upper Cross River watershed and found five distinct alkaline water facies. Stephen et al., (2017) examined the hydrogeochemical facies of groundwater in the upper Cross River Basin, southern Nigeria, to identify different water types by assessing the major ion concentrations in the groundwater. Five hydro-chemical facies of groundwater were identified using aqua-chem analysis: Ca-Mg-Cl-SO_4, Ca-Mg-HCO_3-Cl-SO_4, Ca-Mg-HCO_3, Na-K-HCO_3, and Na-K-Cl-SO_4. Owoyemi et al., (2019) examined the variability in hydrochemical properties and the processes governing the hydrochemical quality of groundwater in Delta State, Niger Delta region of Nigeria. The results indicate that Ca and Mg are the predominant cations in the coastal zone, while Na and Ca are the most prevalent in the inland region. Piper diagrams show Ca-HCO_3, Na-HCO_3, Na-Cl, and Ca-Mg-Cl-SO_4 are the prevalent water facies. Moreover, ionic cross plots, correlation analysis and geochemical modelling indicated that the groundwater chemistry in the inland region is mostly affected by silicate weathering, while that of the coastal region is influenced by ion exchange, silicate weathering and seawater tidal flushing.

The seasonal and spatial evolution of groundwater chemistry remains poorly investigated in the Komadugu-Yobe Basin. To date, there are no comprehensive studies that evaluate the evolution of hydrochemical facies and their relationship with various geological settings across the basin. Moreover, research on the impacts of anthropogenic activities on the geochemical evolution of groundwater is absent in the basin. These issues have been addressed in chapters 5 and 6.

2.7 Potentially Toxic Elements Pollution Analysis

Potentially toxic element pollution in groundwater is of significant concern not only to the environment but public health. The presence of PTEs in groundwater even at very low concentrations has tremendous long-term impacts on ecosystems and human health (Fatunsin et al., 2024; Veluprabakaran & Kavitha, 2023). PTEs are very toxic and do bioaccumulate in the human body when ingested (Aktar et al., 2023; Nordstrom, 2011). Heavy metal pollution originates from industrial effluents, agricultural activities, mining activities, inadequate waste management, urban runoff, and geogenic sources. PTE contamination occurs through leaching, complexation and adsorption, and redox reactions. The impacts of heavy metals in groundwater include severe health risks, including neurological damage, kidney disease, cancer, and developmental issues in children (Ahmed et al., 2018a; Nanayakkara et al., 2019; Waziri & Ogugbuaja, 2010). Groundwater contaminated by PTEs may affect surface water ecosystems and soil quality, leading to reduced agricultural productivity and potential entry of toxins into crops (Fang et al., 2019; Noor et al., 2024; Zhou et al., 2024). Source identification, mechanisms, and degree of PTE contamination are essential for developing sustainable groundwater management and remediation strategies.

Heavy metal pollution and its potential human health risks to adults and children have not been thoroughly studied on a regional scale in the Komadugu-Yobe Basin. However, few studies integrate statistical analysis and spatial mapping to evaluate heavy metal pollution issues in some localities in the basin. Therefore, chapter 7 addressed this gap by providing a comprehensive analysis of PTE pollution, source identification and assessing their associated human health risks for both adults and children on a more regional scale in the Komadugu-Yobe basin.

2.8 Speciation and Complexation of Potentially Toxic Elements in Groundwater

Chemical speciation and complexation refer to the distribution of chemical elements into various molecular and ionic forms in water (Agunbiade et al., 2012; Jacks & Nystrand, 2019; Laxen & Harrison, 1981; Sikakwe et al., 2018). The chemical speciation of elements significantly influences the geochemistry and bioavailability of trace metals in solution. Metals combine with various ligands, such as hydroxides, chlorides, sulfates, bicarbonates, and fluorides, to form complexes in an aqueous environment (Khan et al., 2017; Lenoble et al., 2013). Chemical speciation of PTEs in groundwater is modelled by WATEQ4F, PHREEQC, GWB Workbench, and Visual MINTEQ (Agunbiade et al., 2012; Jacks & Nystrand, 2019; Khan & Umar, 2024). Chemistry in aquatic systems is complex and differs significantly from that of other trace elements with two major species of arsenate and arsenite that vary in degree of mobility and toxicity to humans (Lenoble et al., 2013; Snousy et al., 2021). Sikakwe *et al.,* (2018) conducted modelling of chemical species and complexes of rare earth and trace elements in groundwater in southeastern Nigeria Lenoble et al., (2013) assessed the distribution and chemical speciation of arsenic and heavy metals in Bosnia and Herzegovina using geochemical speciation modelling software (PHREEQC and WHAM-VI). Their results indicated that arsenic predominantly existed as As (V) and iron as Fe (III) in the study area. Khan & Umar, (2024) employed an Eh-pH plot to model the speciation of As and Fe in groundwater during pre-monsoon and post-monsoon seasons. Their results revealed that most of the groundwater in both seasons falls into the field of H_3AsO_3 and Fe^{2+} signifying reducing conditions prevail in the aquifer.

Research on the speciation and complexation of trace elements and their interactions within the groundwater system of the Komadugu-Yobe Basin has not been conducted. Furthermore, there has been no application of advanced geochemical modelling tools such as GWB WorkBench, MINTEQ and PHREEQC to understand the behaviours of trace elements in the groundwater of the basin. These issues have been addressed in chapter 7.

2.9 Epidemiology of renal disease in the Komadugu-Yobe basin

Renal diseases particularly chronic kidney disease (CKD) of known aetiology, have been a major public health issue in northern Nigeria, with an increasing prevalence in the northeastern region including the Komadugu-Yobe Basin (Ahmed et al., 2018a; Oni & Aizebeokhai, 2017; Sulaiman et al., 2022). At least 85% of individuals suffering from kidney-related issues in Yobe State are from Gashua and surrounding areas near the Hadejia-Nguru wetlands. High cases of renal failure have led to many deaths and continue to pose a serious health risk to many residents in the region. Data collected from medical facilities in Gashua indicate that between January and October 2018, as many as 467 cases were recorded (Adamu et al., 2021). Ahmed et al., (2018a) found that 40% of hospital admissions in health centres near affected communities were for CKD, with 70% of cases originating from Yobe and Jigawa States. The deteriorating environmental and socioeconomic conditions significantly contribute to the high level of kidney diseases in the region, with some literature relating these factors to groundwater contamination, environmental pollution as well as limited access to healthcare facilities (Adamu et al., 2021; Oni & Aizebeokhai, 2017; Waziri & Ogugbuaja, 2010).

Heavy metals such as lead, cadmium, and arsenic are prevalent in the region and are considered key pollutants contaminating groundwater, soil, and vegetable crops (Sulaiman et al., 2021; Waziri & Ogugbuaja, 2010). Consuming contaminated water and vegetables grown in the area is considered a primary pathway for heavy metal exposure in humans. A significant portion of the population has suffered, succumbed to, or continues to battle kidney disease. Table 2.1 shows cases of renal diseases in northeastern parts of Nigeria. The renal diseases in northeastern Nigeria affect all age groups, from children to the elderly, without a clear preference for any demographic (Ahmed et al., 2018a; Chiroma et al., 2021). However, community reports indicate that women experience more severe health impacts of renal failure than men, although the reasons for this disparity remain largely unexplored. Moreover, comprehensive epidemiological studies on the region remain understudied, underscoring the need for more scientific investigations to understand the risk factors, prevalence, and human health risks.

Table 2.1 Cases of renal diseases in Northeastern Nigeria (Ahmed et al., 2018a).

Name of Community	Kidney disease incidence
Arki	Kidney diseases exist, number uncertain
Auyo	10 deaths
Dawa	1 death
Gamsarka	1 death; 2 patients in hospital
Ganuwar Kuka	2 patients in hospital
Guri	5 deaths; 1 patient in hospital
Hadejia	Kidney disease exists, number uncertain
Madachi	1 death
Malam Madori	Kidney disease exists, number uncertain
Sabon Gida Gabas	3 deaths
Zugo	Kidney disease exists, number uncertain
Lawan Fannami, Gashua	Several cases and deaths
Lawan Katuzu, Gashua	Several cases and deaths
Lawan Zango, Gashua	Several cases and deaths
Nguru	Several cases and deaths

2.10 Stable Isotopes of Hydrogen and Oxygen in Groundwater Assessment

Stable isotopes of oxygen ($\delta^{18}O$) and deuterium ($\delta^{2}H$) are rare parts of water molecules (H_2O) that vary spatially and temporally over a watershed, serving as a tool for investigating a broad range of processes within the water cycle (Goni, 2006; Gat, 2010; Gibrilla et al., 2017). Stable isotopes are used in estimating groundwater recharge rates. They can also be used as tracers in determining the origin of groundwater, recharge mechanisms, flow direction, relative age of groundwater and information on past climate (Azzaz et al., 2008; Goni, 2006; Maduabuchi et al., 2006). Stable isotopes of water molecules have been extensively used in differentiating modern meteoric waters and palaeometeoric waters and those that get recharged under humid and cooler conditions of Late Pleistocene (Goni et al., 2001; Huneau et al., 2011; Maduabuchi et al., 2006). Isotope geochemistry provides a comprehensive understanding of the geochemical and hydrochemical processes in an aquifer system (Bello et al., 2019; Eissa et al., 2019; Salifu et al., 2017). Understanding groundwater recharge processes is essential for developing sustainable water resource management plans in the context of climatic variability and anthropogenic activities (Bello et al., 2019; Faye et al., 2019; Huneau et al., 2011). Mook, (2000) stated that the distribution of isotopes through the hydrological cycle is influenced by several processes:

- Evaporation: This emits lighter isotopes such as hydrogen (^{1}H) and oxygen-16 (^{16}O) into the atmosphere, leaving enriched heavier isotopes (deuterium (^{2}H) and oxygen-18 (^{18}O)) causing water bodies and soil moisture to become isotopically heavier.
- Condensation and precipitation: This occurs as water vapour rises and cools in the atmosphere, leading to condensation of heavier isotopes that result in isotopically lighter precipitation. This results in the "altitude and temperature effect".
- Isotopic fractionation in clouds (Rayleigh distillation): This occurs when air masses cool and release moisture as they move inland, resulting in a lighter isotopic composition of water vapour.
- Infiltration and groundwater recharge: This entails the incorporation of isotopes from precipitation into groundwater, resulting in the isotopic signature of groundwater reflecting the composition of local precipitation.
- Mixing water sources: This can modify the isotopic signature of water bodies.
- Sublimation and snowmelt: This occurs when snow or ice undergoes a direct transition to vapour, providing insights into seasonal recharge patterns.
- Transpiration: The process by which plants absorb water from the soil, and release water vapor into the atmosphere, resulting in isotopic fractionation.

Goni, (2006) employed stable isotopes to trace meteoric water flow to groundwater in the southwestern Chad basin. Middle and lower aquifer zones showed similar isotope values, indicating the same evolution, while upper aquifer showed variable values, indicating similar water composition in only middle and lower aquifer zones. Maduabuchi et al., (2006) Investigated water sources and ages of waters, the possible modern renewal and the deep groundwater mixing, and paleoclimatic incidences in the aquifers of the Nigerian Chad Sedimentary Basin. They found Na-HCO_3 groundwater, that is slightly to moderately mineralized, replenished by modern meteoric water in the upper aquifer. The middle and lower aquifers exhibited a palaeometeoric origin, with no evidence of mixing with modern waters. Ansari et al., (2018) analyzed isotopic compositions of groundwater, precipitation, river, and canal water to ascertain recharge sources, recharge zones, and groundwater flow within the Ghaggar River basin. Their results indicate that local precipitation is the primary source of groundwater recharge; however, depleted $\delta^{18}O$ and δ^2H signatures suggest recharge contributions from canal seepage and irrigation return flow. Ahmed et al., (2022) examined the historical stable isotopic compositions of hydrogen and oxygen in 1,618 water samples from seven principal aquifer and reservoir systems in Egypt. Their findings indicated that alluvial and coastal aquifers are recharged by modern precipitation, flood waters, and deep aquifers, whereas the Nile Valley and Delta aquifers are recharged by modern rainfall, irrigation canals, and deep aquifers.

The role of stable isotopes in identifying groundwater recharge mechanisms in semi-arid to arid regions affected by seasonal variations and regional climatic factors remains underexplored. Few studies have investigated the role of stable isotopic signatures of groundwater in groundwater recharge mechanisms in some parts of the Komadugu-Yobe Basin. The absence of a Regional Meteoric Water Line (RMWL) for the Komadugu-Yobe Basin and the Lake Chad region hinders the comprehensive interpretation of isotopic data in a regional context. Moreover, research on seasonal and spatial isotopic variations, particularly about climatic factors such as the Inter-Tropical Convergence Zone (ITCZ) and regional orography in KYB and the wider Sahel region is lacking. To address these gaps, Chapter 8 utilizes stable isotope analysis (δ^2H and $\delta^{18}O$) to elucidate groundwater recharge mechanisms, develop the

RMWL for the Komadugu-Yobe basin, Lake Chad region and Sahel region, and investigate seasonal and orographic variations in groundwater recharge processes.

2.10.1 Groundwater Recharge Mechanisms

Groundwater recharge is assessed by various methods such as; isotopes, geochemical tracers, water balance, temperature profiles, water level fluctuations, electromagnetic techniques, and other modelling approaches (Ansari et al., 2018; Eissa et al., 2019; Goni, 2006; Tewolde et al., 2019). Stable isotopes help identify the origin, pathways and dynamics of water recharges as it moves through the hydrological cycle (Faye et al., 2019; Hao et al., 2019). The application of isotope tracers in recharge assessment is increasing and enhancing understanding of groundwater recharge mechanisms (Banks et al., 2021; Hao et al., 2019; Xu et al., 2019).

Tewolde et al., (2019) identified recharge zones and estimated soil evaporation in the Lake Chad basin (LCB) utilizing stable water isotopes and chlorine mass balance approaches. The results identify potential groundwater recharge zones, while soil evaporation was anticipated to correlate with water usage during the early growing period. Bouchez et al., (2016) employed sodium and stable isotope mass balance techniques to evaluate evaporation, transpiration, and infiltration in the Lake Chad basin. The study indicated an evapotranspiration rate of 2070 ± 100 mm/a for the southern pool and 2270 ± 100 mm/a for the northern pool of the basin, with an overall estimate ranging from 100 to 300 mm/a. Fantong et al., (2020) analysed the distribution of major ions, Si, δ^2H, δ^{18}O, trace elements, and rare-earth elements in the Benue River basin. Their results indicate that the recharging of the basin's shallow aquifer occurs by mixing surface water and groundwater between the July and September rainfall. Gibrilla et al., (2017) estimated groundwater recharge dynamics using the characteristics of δ^2H and δ^{18}O in groundwater, rainwater and spring in the Amedzofe area of Ghana. They found a mean annual recharge rate of 125.76 mm/a for groundwater and 300.68 mm/a for spring, respectively, representing 10.70 and 8.39 % of annual rainfall, and recharge occurs in March, June, and

August. Edmunds et al., (1999) analyzed modern hydrological processes and reconstructed the palaeohydrology through hydrogeochemical and isotopic investigation of rainwater, lakes, groundwater aquifers and various other water sources in NE Nigeria. Recharges of the deep aquifers were found to occur between 24 and 18.6 ka BP before the last glacial maximum. The recharge at Manga Grassland is found to be 44 mm/year while regional recharge is 60mm/year mainly from surface water. Furthermore, the shallow water in the region contains significant groundwater resources whereas the deep aquifer waters contain palaeometeoric waters. Salifu et al., (2017) employed hydrogeochemical and environmental isotopic analysis to assess groundwater quality and origin in Gushegu district, Northern Ghana. The groundwater has poor quality due to elevated fluoride, bicarbonate, and electrical conductivity. The stable isotope analysis suggests meteoric origin, however, some samples showed significant evaporation.

3 Description of the Study Area

3.1 The Study Area Setting

The study area is the transboundary Komadugu-Yobe basin (KYB) located in the Southwestern part of the Lake Chad basin. It is a sub-basin of the greater Lake Chad situated in the Northeastern Nigeria and Southwestern Niger Republic, which lies in the Sudan-Sahel region of Africa (Figure 3.1). The basin covers an approximate area of 150,000 Km^2 (Adeyeri et al., 2020; Castelein, 2002). The elevation in the basin varied between 294 m to 1750 m with the highest elevation recorded in Bauchi and Jos Plateau. About 95 % of the basin water contribution in KYB is from Nigeria (Adeyeri et al., 2019). The basin is primarily drained into Lake Chad by the Komadugu Yobe and Komadugu Gana river sub-systems. Two major rivers: the River Hadejia and River Jama'are meet at the Hadejia-Nguru wetlands and form the Yobe River. The Kano highland is the main source of the Hadejia River while the Jama'are River has its source from the Jos Plateau (Bura et al., 2018; Chiroma et al., 2015). The Watari River is at the upstream part of the Hadejia River system. Watari, Tiga and Challawa rivers all together joined upstream of Wudil town to form the Hadejia River. Notable dams in the basin are the Tiga, Watari, and Challawa Gorge dams (Chiroma et al., 2015; Goes, 1999, 2002). These dams are located at the upstream parts of the basin which control about 80 % of flows into the Nadejia-Nguru wetlands. Tiga Dam is mainly used to store water for irrigation in the Kano River Irrigation Project (KRIP). It is also used as a flood control reservoir. Moreover, another irrigation project: the Hadejia Valley Irrigation Project (HVIP) receives water from a barrage constructed below the Tiga dam. The Challawa Gorge dam is mainly constructed to supplement irrigation water in KRIP to HVIP, Water supply to Kano City and as a flood management/control structure (Ahmed et al., 2018). Another large-scale irrigation project in the basin is the Hadejia-Nguru Wetlands (HNW) Conservation Project (Goes, 1999).

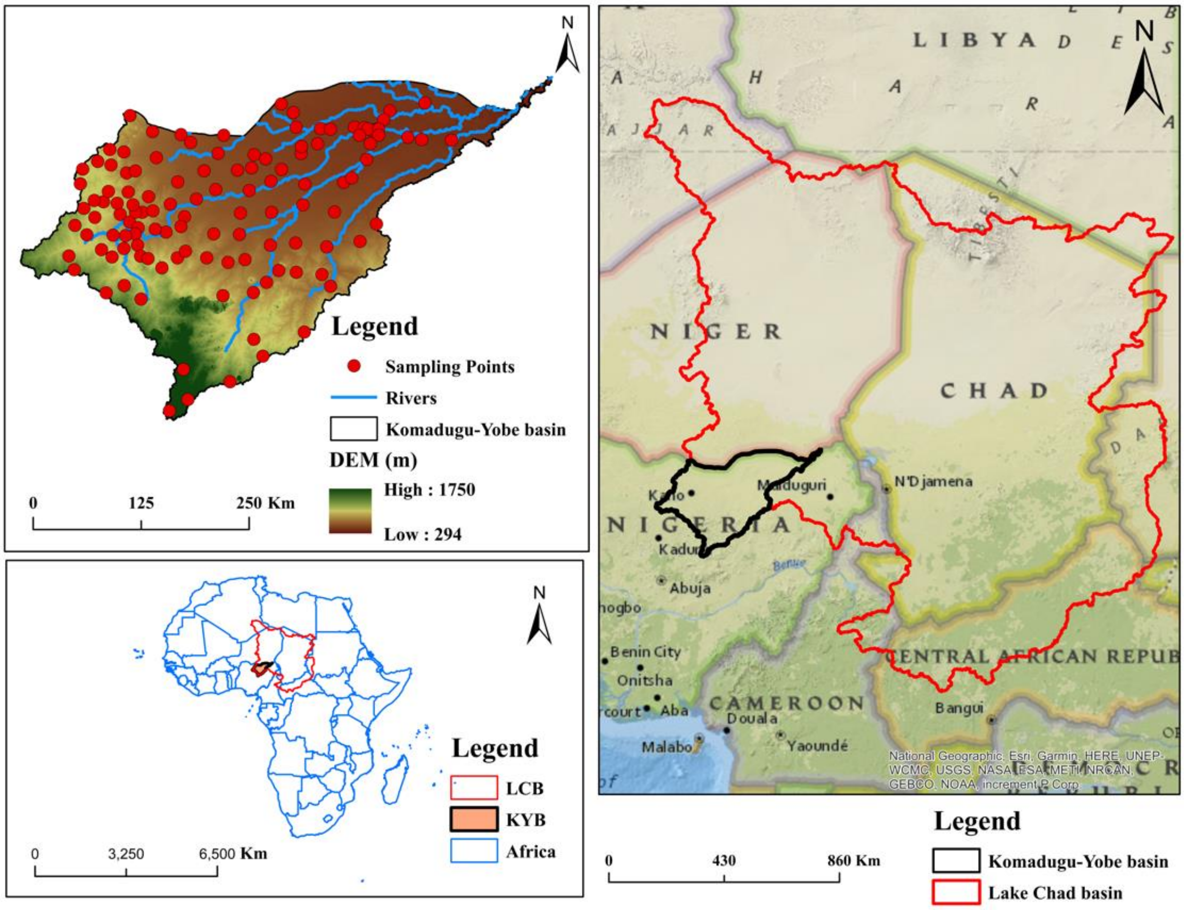

Figure 3.1 Location of Komadugu-Yobe Basin in Africa. LCB: Lake Chad basin. KYB: Komadugu-Yobe basin.

3.2 Climate and Vegetation

The Komadugu-Yobe basin exhibits a semi-arid to arid climate characterized by severe drought, pronounced seasonal variability and significant rainfall fluctuations particularly in the downstream parts of the basin. The basin experiences two distinct seasons: the wet and dry seasons. The wet season is experienced between May and September with peak rainfalls in the month of August while the dry season spans from October to April (Adeyeri et al., 2017; Chiroma et al., 2015). About 80 % of rainfall occurs between June and September. The mean annual rainfall in the upstream part of the basin varies from 1360 mm in Jos to about 900 mm at Kano while it varies from about 600 mm around Hadejia and about 400 mm around Nguru around the middle of the basin. Rainfall amount reduced to a minimal value of less than 300mm toward the downstream parts of the basin (Adeyeri et al., 2020; Ahmed et al., 2018b). Recent studies have highlighted the impact of climate change on the hydrological cycle in the basin (Adeyeri et al., 2017; Adeyeri et al., 2019; Dosio et al., 2022; Shuaibu et al., 2022). For instance, between 1971 and 2017, there has been a notable increase in extreme rainfall events, leading to more frequent and severe flooding, particularly in the downstream parts of the basin (Joshua, 2021; Umar & Gray, 2023).

Climate change studies indicated that these trends are likely to continue, with future scenarios suggesting a rise in both the intensity and frequency of extreme rainfall events (Audu et al., 2021; Joshua, 2021). An average minimum temperature of 12 ^{0}C is recorded between the months of December and January while an average maximum temperature of about 40 ^{0}C is recorded between the months of March and April. The downstream portion of the basin experienced a low amount of rainfall due to semi-arid nature and the high evaporation rate is eminent due to high temperature. This variability in the seasonality of extreme weather events between the upstream and downstream parts of the basin poses challenges for groundwater recharge, as intense rainfall often leads to increased surface runoff reducing groundwater recharges into aquifers (Adeyeri et al., 2019; Audu et al., 2021). Moreover, the basin experiences significant flooding events due to high-intensity rainfall leading to river overflows and inundation of surrounding areas and farmlands which not only disrupt local communities but also alter the natural recharge processes of groundwater systems (Cirella & Iyalomhe, 2018; Enobong et al., 2022; Umar & Gray, 2023). The basin has a moderate relative humidity of 40 % and an annual evaporation rate of 203 mm/year while the annual potential evaporation ranges from 1800 mm to 2400 mm (Adeyeri et al., 2020). The vegetation of the basin is mostly dominated by dense grasslands, shrubs and scattered trees (Adeyeri et al., 2020; Chiroma et al., 2015; Goes, 2002).

3.4 General Geology and Stratigraphy of Lake Chad Basin

3.4.1 The Geology of Lake Chad Basin

The Lake Chad basin sits on the African Continent and is centrally overlaid on the extension of the Cretaceous Benue rift system which outcrops in Nigeria (Burke, 1976; Lopez et al., 2016). The bedrock of the Precambrian basement complex of the Lake Chad basin is overlain by sediment deposits of Palaeozoic to Quaternary ages (Maduabuchi et al., 2006). The configuration of the crystalline basement which outcrops in the eastern, southeastern, southwestern and northern borders of the Lake Chad basin beneath the sediment close to the lake resembles the horst and graben zones (Barber & Jones, 1960; Maduabuchi et al., 2006). The structural geology of the basin consists of faults and folds, which influence groundwater flow and recharge (Olugbemiro et al., 1997; Schuster et al., 2009). The general geology of the Lake Chad basin is presented in Figure 3.2 showing most of the basin area is covered by the Quaternary sediments.

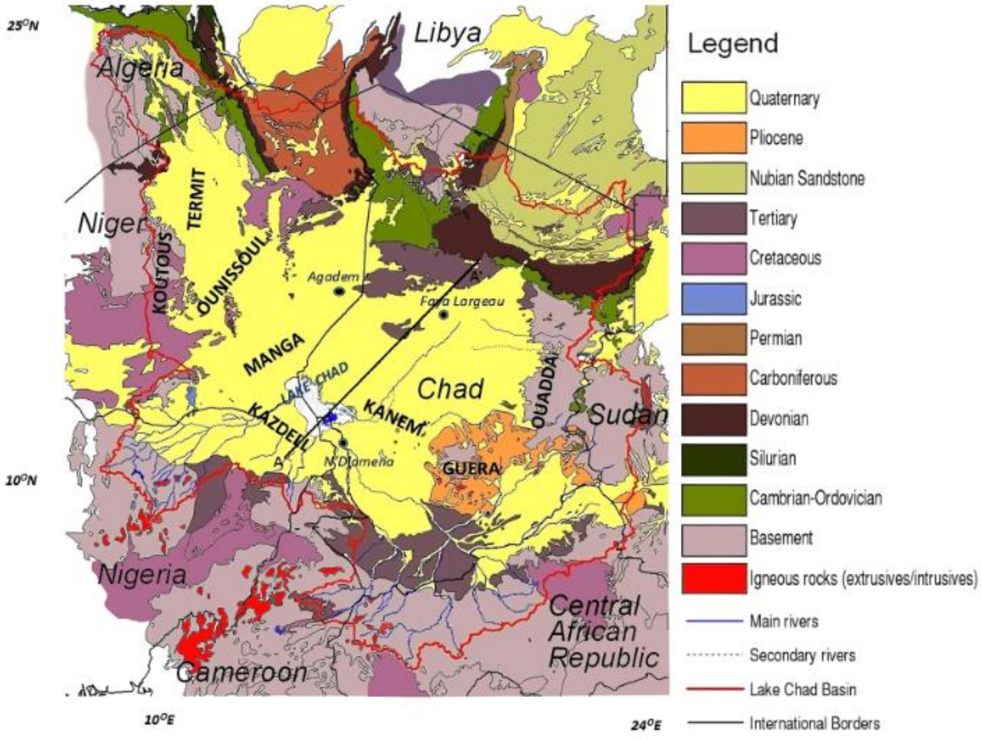

Figure 3.2 General Geology of the Lake Chad Basin (After (Vassolo, 2012)).

3.4.2 Stratigraphy of Lake Chad Basin

The stratigraphy of the Lake Chad basin comprises sediment deposits of varying ages tracing back from the Palaeozoic which is mostly arenaceous deposits, Lower Cretaceous that are of Continental Intercalaire arenaceous deposits, Middle Cretaceous of marine limestones, Continental Hamadien (Continental Intercalaire), Upper Cretaceous (Continental sandstone and Continental Terminal of lacustrine and deltaic river sediments of Mio-Pliocene age). These sediment deposits are overlaid unconformably on the Upper Cretaceous and Basement Complex (Avbovbo et al., 1986; Maduabuchi et al., 2006). The general stratigraphy of the Lake Chad basin consists of three sandy horizons that serves as aquifers which are separated by clays of varying diatomites. (Burke, 1976).

3.5 Hydrogeology of Lake Chad Basin

The Lake Chad Basin is covered mostly by Quaternary sands of different depositional origin (Vassolo, 2012). The Northern part of the basin has an Aeolic deposit with the presence of dunes while the southern part has Fluviatile, Lacustrine and Deltaic depositions that result in various sequences of thin layers of sand and clay with clayey soils being at the surface. The quaternary aquifer of the Lake Chad basin has some dissolved salts concentration in some areas above the permissible limits (Bouchez et al., 2016). The main source of groundwater in the Lake Chad basin is the Plio-Pleistocene Chad formation and the younger Quaternary sediments (Bakari, 2014; Maduabuchi et al., 2006).

The Upper Pliocene aquifer has a thick clay layer of about 280 m that separates it from the lower Pliocene aquifer. Hydraulic conductivity of the Upper aquifer layer ranges from 1 to 100 m day^{-1} (Lopez et al., 2016). The lower Pliocene aquifer is composed of sand and sandstone of 30 m thick that is underlain by sandstones of 150 m of the Continental Terminal. The Lower Continental Terminal aquifer is confined with a thickness range of 100 to 200 m in the Continental Terminal formation (Avbovbo et al., 1986; Lopez et al., 2016). The Upper Pliocene aquifer behaves as an aquitard because it is almost impermeable. This aquitard confines the sandstones of the Lower Pliocene and Continental Terminal from the upper Quaternary aquifer causing artesian conditions mostly in the central part of the basin (Lopez et al., 2016; Vassolo, 2012). The upper aquifer has an approximate yield of 2.5 to 30 L/s. The yield of the middle aquifer is 24 to 32 L/s while the yield of the lower aquifer ranged from 10 to 35 L/s (Akujieze et al., 2003; Edet et al., 2012).

Studies are lacking on the deepest sandstones and sands of cretaceous ages of the Continental Hamadien and Continental Interclaire because of limited data (Akujieze et al., 2003; Avbovbo et al., 1986; Edet et al., 2012; Vassolo, 2012). The upper unconfined aquifer receives recharge largely from precipitation and depositional characteristics of the aquifer. Some indirect recharges occur in the southern part of the basin from surface water percolation from flooded areas, rivers and lakes. The Lower Pliocene and Continental Terminal recharge takes place at their outcrops at the basin border or outside the basin (Avbovbo et al., 1986; Vassolo, 2012). Recharges of about 5 mm/a were estimated for the Massénya and Yaéré swamps. Isotope study in the basin reveals the occurrence of direct recharge in the Northern part of the basin through the percolation of precipitation accumulated in the valleys between the dunes. Nonetheless, low tritium values from the isotopes study signify that recharges occurred in the past at least more than 60 years ago (Vassolo, 2012). Figure 3.3 shows the geology and the stratigraphy of the basin along section AA.

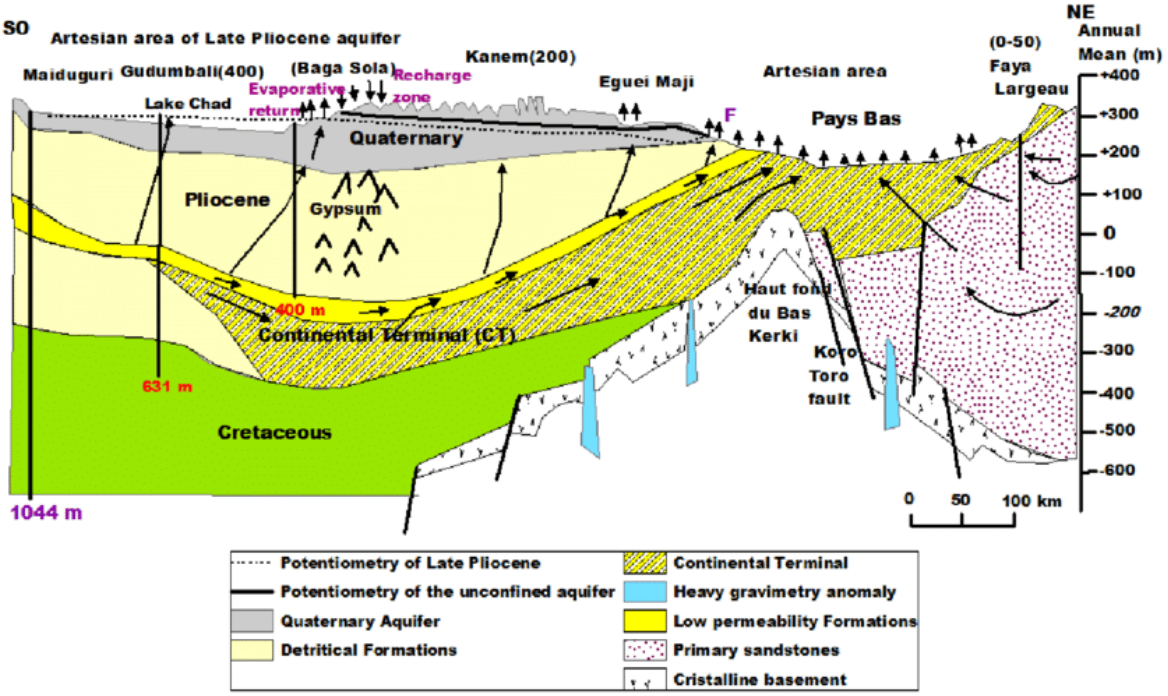

Figure 3.3 Geological Cross-section with depth, drawn along line AA between Maiduguri to the SW and Faya Largeau to the North East of the Lake Chad Basin (After (Schneider & Wolf, 1992))

3.6 General Geology and Stratigraphy of Komadugu-Yobe Basin

3.6.1 The Geology of Komadugu-Yobe Basin

The Komadugu-Yobe basin which is an integral part of Lake Chad Basin is categorized as a rift basin because of the presence of basement tensional force indicators and zigzag fault patterns and the absence of various comprehensive physical features (Avbovbo et al., 1986). The factors controlling the faults are the pre-existing line of weakness that developed during the Pan-African orogenic events or older lineaments (McCurry, 1971). The basin is underlain by basement complex rocks and sedimentary quaternary formations (Figure 3.4) (Bakari, 2014; Genthon et al., 2015).

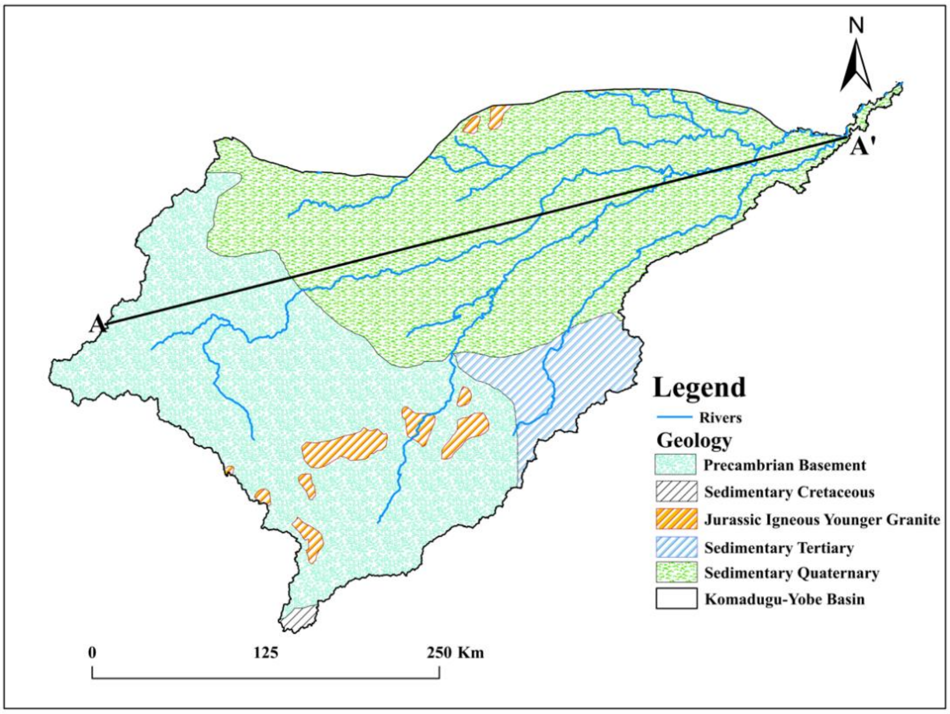

Figure 3.4 Geological Map of Komadugu-Yobe Basin

3.6.2 The Geological Structure of Komadugu-Yobe Basin

The Komadugu-Yobe basin consists of a structure that is predominantly faults and simple symmetrical folds, which are dominant mostly in the northeast-southwest trend. It is difficult to differentiate between intrusive rocks, buried hills and basement horsts in this basin because of the similarities in seismic reflection character (Avbovbo et al., 1986; Goes, 1999). The faults in the basin are mostly in the basement and result in grabens, horsts and other related features. High-angle faults are formed within the underlying sediment in the sub-basin because of the movement along these basement faults (Avbovbo et al., 1986; Obaje et al., 2004). The faults in the basin terminate below the regional angular unconformity that delimits the Cretaceous from Tertiary sedimentation in a cross-sectional view, while two major systems of faults are recognized namely: the laterally persistent northeast-southwest trending faults with a zigzag pattern characteristic of rift systems and the laterally persistent northwest-southeast trending faults that are numerically subordinate to the northeast-southwest trending faults in plan view (Freund & Merzer, 1976). The folds in the basin consist of simple and folded sediments that have low fold frequency and amplitude. The fold frequency decreases towards the northwestern part of the basin whereas the fold amplitude increases in the southeastern parts. The folds in the basin flatten with depth. Many normal faults found in the basement cut across the folds in various directions in the basin. These folds are restricted to a narrow zone in the deeper southeastern section of the basin (Avbovbo et al., 1986).

3.6.3 Lithostratigraphy of Komadugu-Yobe Basin

The Lake Chad basin together with the KYB is underlain by a monotonous, Quaternary, basin and the Chad formation. The sediments below these formations are exposed only at the southern edge of the basin where it merges with the neighbouring Benue trough (Avbovbo et al., 1986). The generalized stratigraphic description of the sediments in the Komadugu-Yobe Basin has been presented by Avbovbo et al., (1986), Obaje et al., (2004), Obaje, (2011), Lopez et al., (2016), and Bura et al., (2018).

The Chad Formation

Chad Formation is the latest formation in the Komadugu-Yobe basin (Wali et al., 2020). The Chad formation present the uppermost Pliocene-Pleistocene formation comprising thick clays of fluviatile and lacustrine that separate three major bodies of sand which correspond to the upper, middle and lower aquifers having lenses of diameter of a few meters thick (Obaje et al., 2004). Various colours of sand and clay layers range from yellow, brown, white and grey colours. Chad formation is made up of light grey colossal claystone, some minor sand and some infrequent pebbly horizon which indicate some ferruginization in the deposits (Ola-Buraimo & Abdulganiyu, 2017; Wali et al., 2020).

Kerri-kerri Formation

Kerri-Kerri formation is characterized by horizontal-laying to moderately plummeting basal conglomerate, sandstone, siltstone, grit and clay that are overlaid on the Maastrichtian Fika

Shale and Gombe Sandstone (Ola-Buraimo & Abdulganiyu, 2017; Wali et al., 2020). Various minerals found in this formation comprised zircon, rutile, kyanite, tremolite, pyroxene, tourmaline, staurolite, limonite, and hornblende, which originated from adjacent basement complex rocks and previous alluvial rocks (Adegoke et al., 1986; Ako & Osundu, 1986; Ola-Buraimo & Abdulganiyu, 2017). The formation is confirmed to be of Paleocene age because of the occurrence of *pollens Monocolpites marginatus* and *Spinizonocolpites baculatus* (Wali et al., 2020).

Bima Sandstone

Bima sandstone is derived from the weathering of basement rocks, and it consists of a sequence of red sandstone and mudstone, which lies unconformably on the basement complex. This formation has Cenomanian age as it is the oldest stratigraphic unit in the Chad basin (Bura et al., 2018; Vassolo, 2012). The Bima sandstone has an average thickness range of 400 and 1000 m below Kadzell and Kanem respectively (Lopez et al., 2016). The Gongila formation underlain the Bima sandstone (Obaje et al., 2004).

Gongila Formation

The Gongila formation is underlain by Bima sandstone. It consists of a deposit of thin to moderately thick interbeds of calcareous grey to dark shales and silty sandstone in a shallow marine environment (Obaje, 2011). An average thickness ranging from 0-800 m was recorded by Avbovbo et al., (1986) From seismic data for this formation.

Fika (Shale) Formation

The Fika (Shale) formation is composed of dark-grey to blue-black shale with sometimes glauconite, gypsum and fine-grained sandstone in the upper part of the formation (Bura et al., 2018; Wali, Dankani, et al., 2020). Fika formation was dated as Turonian-Maastrichtian in age by Obaje, (2011). Obaje et al., (2004) posit that the Fika formation is a blue-black shale of marine origin almost gypsiferous with intercalation of limestone. An average thickness of 430 m was recorded from drilled wells by Obaje, (2011) while Avbovbo et al., (1986) recorded thicknesses ranging from 0-900 m in the basin.

Gombe Formation

The Gombe formation is characterised by intercalations of siltstones, claystones and shales. However, coal seam intercalations are not present in the upper Benue trough (Obaje et al., 2004). The Gombe Sandstone is composed of cross-bedded sandstones and siltstone and is of Maastrichtian age. It also consists of alternating layers of grits and sandstone with a well-developed cross-bedding (Bura et al*.,* 2018). The Gombe Sandstone was deposited in an estuarine/deltaic environment during the Maastrichtian. However, the occurrence of this formation in any significant portion of the basin has been doubtful (Obaje, 2011).

3.6.4 Hydrogeology of Komadugu-Yobe Basin

The main sources of groundwater in the Komadugu-Yobe basin are the Plio-Pleistocene Chad formation and the younger overlying Quaternary sediments. The lithology of the Chad formation that varies lateral and vertically is essentially an argillaceous sequence in which minor arenaceous horizons occur (Edmunds et al., 2002). Groundwater resources in the Komadugu-Yobe Basin are derived from three prominent sandy aquifers of the Chad formation separated by thick clay layers namely: The upper, middle and lower aquifers (Bura et al., 2018; Edmunds et al., 1999). The upper aquifer varies from confined to semi-confined in a few places and mostly unconfined in many places whereas the Lower and the Middle aquifer are confined (Edmunds et al., 2002). The hydrogeological cross-section A-A of the Komadugu-Yobe basin is presented in Figure 3.5.

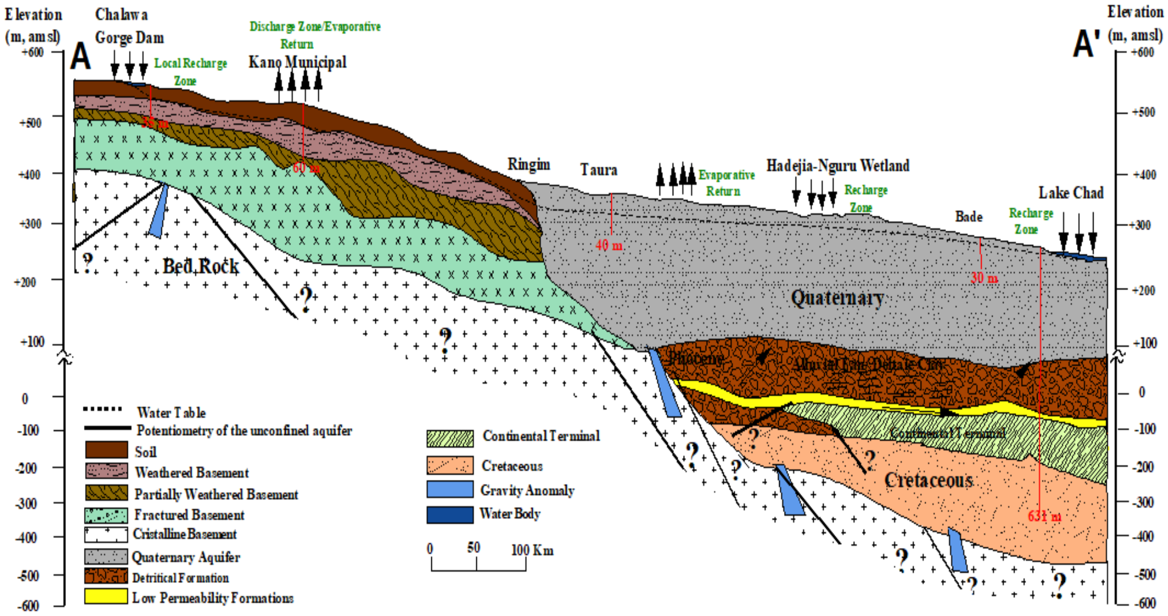

Figure 3.5 Geological cross-section showing various aquifers of Chad formation.

Upper Aquifer

The Upper aquifer is lake-margin deposits, deltaic sediments or alluvial fans and consists of interbedded sands and clays of between 5 to 12 m which has an extensive reservoir of about 500,000 Km^2, overlying most of the region. The Plio-Pleistocene sand and clays of the Chad formation (Upper aquifer) are overlain by the late Pleistocene dunes and have been reactivated at so many times. Water is available in this aquifer under phreatic conditions and occurs at an average depth of 40 to 110 m (Bura et al., 2018; Lopez et al., 2016). The upper aquifer has an approximate yield of 2.5 to 30 L/s (Akujieze et al., 2003). There is the occurrence of longitudinal dunes trending ENE-WSW of the late Pleistocene age in the southern part of the Komadugu Yobe basin that precedes the paranoid dunes (Manga dune system) of the Manga grasslands that overlies the alluvium (Akujieze et al., 2003; Edmunds et al., 2002). The interdune depressions host many saline lakes that are in hydraulic contact with the phreatic aquifer of the dune and occasionally with the deeper aquifer system of the Lake Chad basin (Edmunds et al., 1999). Annual grasses with some perennial grasses are the main vegetation covers of the dunes. However, a few low shrubs are present such as *Caloptris procera, Leptadenia pyrotechnica,* and *Acacia sp*. Some of the ephemeral lakes in the region are used for traditional irrigation cropping and harvesting evaporate minerals where they are saline (Edmunds et al., 1999; Goni et al., 2001).

Middle Aquifer

The Middle aquifer underlies most of the basin area and extended to Niger, Chad and Cameroon which is separated by a thick argillaceous clay layer from the upper aquifer zone. This aquifer has an extremely variable composition of sands, sandy clay and clay materials which range from fine to very coarse-grained, poorly graded and mostly uncemented (Edmunds et al., 1999). The thickness of the aquifer increases slightly from north to east with 31 m being the maximum-recorded thickness. Some of the predominant minerals present are quartz sand, feldspar, iron oxide and micas while carbonate presence was not reported (Bura et al., 2018; Edmunds et al., 1999). This aquifer has a yield of 24 to 32 L/s (Akujieze et al., 2003).

Lower Aquifer

The lower confined aquifer previously known to occur in the Maiduguri area only has now been extended to the fringes of Lake Chad. This aquifer is composed of coarse-grained sands and gravels and occurs at an average depth of about 550 to 600 m and has a variable thickness of about 89 m in some areas of the basin (Barber & Jones, 1960; Bura et al., 2018; Edmunds et al., 1999). The yield of the lower aquifer is 10 to 35 L/s (Edet et al, 2012).

3.7 Groundwater Recharge in Komadugu-Yobe Basin

The Komadugu-Yobe Valley is one of the main areas through which the unconfined quaternary aquifer of the Lake Chad region receives recharges by deep percolation from rivers and wetlands (Le Coz et al., 2011). However, the aquifer recharge process and pollution hazard potential of the basin have been modified over the last three decades because of the extensive irrigation farming within the Komadugu-Yobe valley (Le Coz et al., 2011). The shallow alluvial aquifer that underlies the Yobe floodplain receives recharge through various sources namely: seepage from river channels, infiltration of floodwater, infiltration of excess rainfall or a combination of all three sources (Carter & Alkali, 1996). Goes, (1999) argued that the infiltration of rainfall directly into the ground, infiltration of runoff through riverbeds and infiltration of water through inundated flood plains are the possible processes of groundwater recharge in Hadejia-Nguru Wetland and Hadejia–Jama'are–Yobe River Basin. Sobowale et al., (2014) highlighted that the flooding of the Komadugu-Yobe River system is an important component of groundwater recharge in the Hadejia-Nguru Wetlands areas. Edmunds et al., (2002) estimated recharge rate of 14-49 mm/year in the Komadugu-Yobe Basin. Recharge of 30 -60 mm/year was estimated by Carter & Alkali, (1996) In the Manga Grasslands of the North Eastern Nigeria. Groundwater ages in the middle and lower aquifers was estimated at 24 to 18.6 thousand years (Bura et al., 2018; Edmunds et al., 1999).

4 Methodology

This chapter highlights the materials and methods adopted in the whole thesis. The result section of the thesis was developed as a series of articles published in peer-reviewed journals (chapters 5-8). Each chapter of the result section consists of an article with distinct detailed materials and methods section formatted according to the journal in which it was published.

4.1 Research Materials

4.1.1 Materials

The following are the materials employed in this study to achieve the overall research objectives.

- Global Positioning System (GPS) used for taking coordinate location of sampling locations during fieldwork.
- Water dip meter used for measuring water level in wells, EC meter measures the pH, EC, TDS and water temperature in situ at each sampling location.
- Digital HACK Alkalinity meter with Methyl Orange and Phenolphthalein indicator.
- Containers (fetchers) and a sampling basin used for drawing out water from wells.
- 50 ml polystyrene bottles for collecting groundwater samples.
- Permanent markers used for labelling groundwater samples.
- Cool boxes used for storing groundwater samples at ~4°C before transferring them to the refrigerator.
- Ice boxes used for keeping groundwater samples at ~ 4°C in cool boxes.
- Electric Sellotape for tying the cover of sampling bottles to prevent spillage of samples and entry of air into the sample container.
- Field notebook and pen for recording values of physicochemical parameters and

- Concentrated nitric acid HNO_3 for sample digestion.

4.1.2 Data and Data Sources

Data is the fundamental and essential element of any research. The main types of data used in this research were the groundwater data (for hydrogeochemical and stable isotope), and geospatial data (for geospatial analysis) derived from remote sensing and literature reviews. These datasets include groundwater samples collected from hand-dug wells, tube wells, and boreholes, as well as inventories obtained from two fieldwork campaigns during wet and dry seasons. The topographical maps of the study area were obtained from the Hadejia-Jama'are River Basin Development Authority (HJRBDA). The geological data of the study area were sourced from the United States Geological Survey (USGS) database (https://certmapper.cr.usgs.gov/data/apps/world-maps/), while satellite imagery data, including Landsat 8 OLI (Operational Land Imager) and SRTM DEM (30×30), were acquired from Earth Explorer (https://earthexplorer.usgs.gov). Administrative boundary data were retrieved from DIVA-GIS (https://www.diva-gis.org/), and soil data were obtained from the FAO database (https://data.apps.fao.org/map/catalog/srv/eng/catalog.search?id=14116#/home).

4.1.3 Software Used in the Research

Various software used in this research are ArcGIS 10.8, GWB Geochemist Workbench 17.0, Excel, MiniTab and Origin Pro 23b. These software were used to analyze data, model groundwater, prepare maps and perform GIS and statistical analysis. A brief description of each software is presented below:

- **ArcGIS 10.8**: ArcGIS is a web-based mapping commercial software used for creating, storing, editing, viewing, managing, manipulating and analyzing geographically referenced data. ArcGIS 10.5 was used in creating various geospatial analyses.

- **GWB Geochemist Workbench 17.0:** The GWB package was originally developed at the Department of Geology of the University of Illinois at Urbana-Champaign. The Geochemist's Workbench is software for manipulating chemical reactions, calculating stability diagrams and equilibrium states of natural waters, tracing reaction processes, modelling reactive transport, plotting the results of these calculations, and storing related data.
- **Microsoft Excel 2016**: Microsoft Excel is a spreadsheet developed by Microsoft used to store, view, analyze, and create graphs and model numerical data.
- **Origin Pro 23b**: This is used for scientific data analysis and graphing. It was used to prepare various graphs and figures and to perform data analysis of the groundwater quality parameters and multivariate statistical analysis.

4.2 Research Methods

4.2.1 Reconnaissance Survey

A reconnaissance survey was conducted to have in-depth knowledge about the study area. It is a prerequisite to every field investigation. It was achieved through a walk-over survey, literature reviews, focus group discussions and so on. A detailed literature review, field visit, and several phone calls with the stakeholders in the Komadugu-Yobe basin provide detailed information on the geological and hydrogeological nature of the study area through which the various aquifers and their characteristics were deduced. Information about the hot spot areas and areas bedevilled with insecurity was explored which involved access areas by studying the basin topographic map to save cost and time and to come up with the best mapping and sampling method. During the reconnaissance survey, a visit was paid to the community leaders to enlighten them about the importance of the study and acquaint with the residents of the area and to enquire more about the security challenges in the area for proper development of risk assessment plan of the fieldwork and selecting sampling points and appropriate methods.

4.2.2 Sampling Strategy

240 groundwater samples were collected over the spread of the transboundary Komadugu-Yobe basin in two sampling campaigns (120 samples each) between August 2021 to November 2021 (wet season) and March to April 2022 (dry season). Figure 4.1 presents the methodological flow chart of the study. Three sets of groundwater samples were collected at each sampling point. The first sample was acidified with concentrated nitric acid for cation and PTEs analysis, and the second and the third samples were unacidified for anions and stable isotopes analysis respectively. The size of each sample is 50 ml, 5 sub-samples were collected at each sampling point, one unacidified for Isotope analysis, 2 acidified samples for cations and metals analysis, and 2 unacidified samples for anions analysis. The research study employed composite sampling methods due to the heterogeneity, security issues and contamination history in the basin. The selective sampling for areas known to have groundwater pollution, ease of access sampling method was applied to areas with a history of insecurity, bad terrain and bad roads and random and grid sampling for areas with no history of groundwater water contamination and insecurity issues.

The selective sampling approach was employed in areas around the downstream portion of the basin, including Bade, Yusufari, Nguru, Guri, Auyo, Hadejia, Borsari, Karasawa, and Jakusko, due to their history of groundwater pollution and water-related diseases. Similarly, selective sampling was used in areas around the Kano metropolis and the tertiary geologic formation near Potiskum, Danbuo, Misau, and Darazo, where pollution from industrial activities and dental fluorosis diseases are prevalent. For areas that are not secure and have poorly maintained roads, which pose risks such as car breakdowns or accidents, nearby locations with similar characteristics were sampled using an ease-of-access method, making the sample representative of both areas. Random and grid sampling methods were employed in communities without a history of groundwater contamination to determine their general water chemistry, especially in areas located at the extreme upstream portion of the basin.

***Labelling of Samples**:* All samples collected were labelled using symbols and numbers. The sample bottles each were labelled SXA, SXB, and ISX where X represents the sample location number while A, B and IS represent the acidified samples for metals, normal samples for the major anions and IS for isotopes analysis respectively.

Recording information: Information for each sampling point was documented in the field notebook such as the measured physical parameters, water level, date of sampling, name of sampling point, location coordinates and borehole depths, and various other auxiliary information.

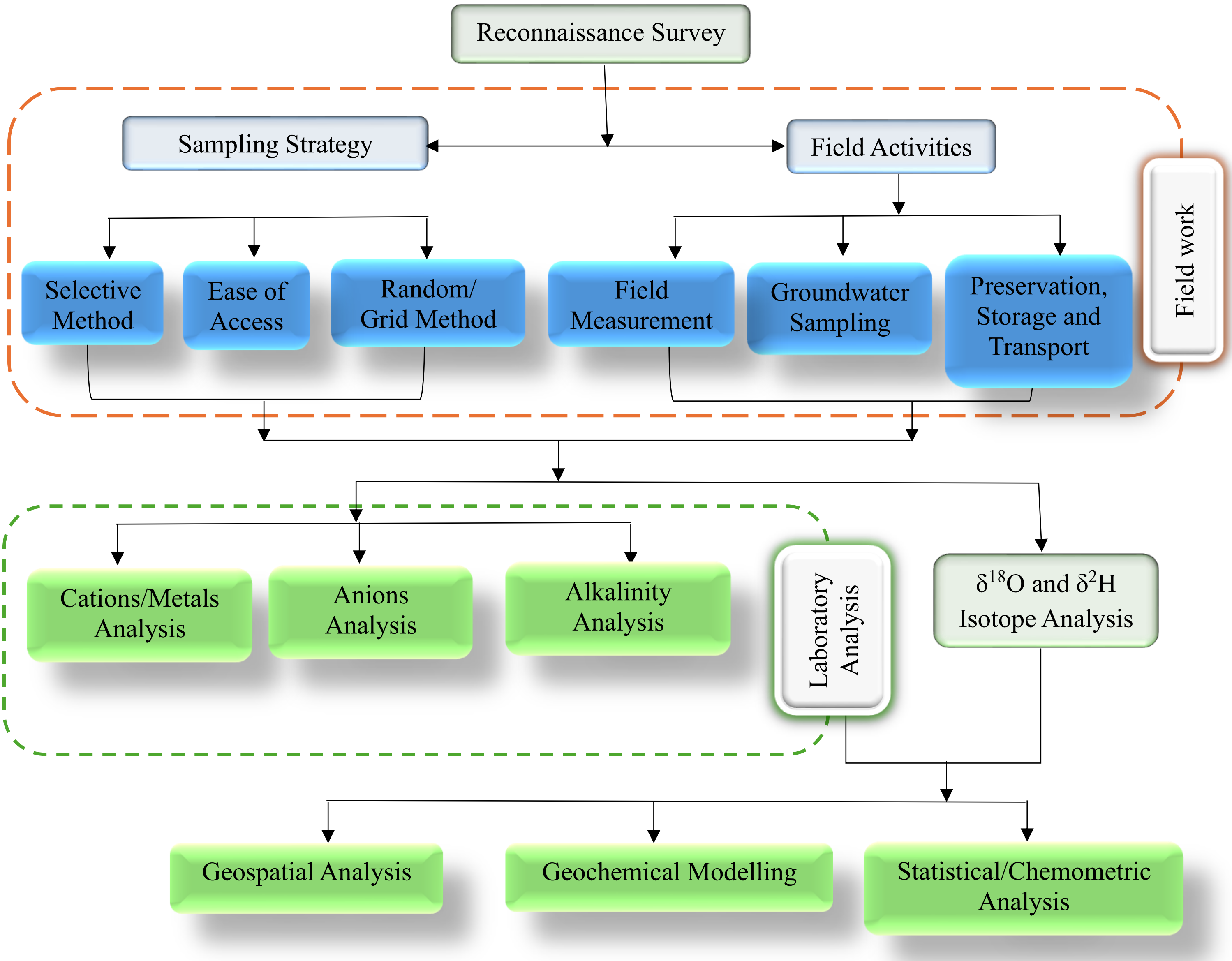

Figure 4.1 Methodological Flow Chart.

4.2.3 Fieldwork

The first fieldwork was conducted from the 28th of August to the 1st of November 2021 during the wet season in Nigeria while the second fieldwork was conducted from 10th March to 7th April 2022. Risk assessment forms for both wet and dry seasons in preparation for travelling to Nigeria and fieldwork were completed and approved (see Appendix C). The various data collected during the fieldwork are listed below;

- Well inventories (well type, well depth, depth to water level and Sampling Location coordinates)
- Physicochemical measurement of total dissolved solids (TDS), electrical conductivity (EC), dissolved oxygen (DO), pH, redox potential (ORP/Eh), total alkalinity and temperature.
- Water samples in 50 ml polystyrene bottles.

4.2.3.1 Equipment Calibration

All the portable handheld equipment was calibrated following the guidelines in the equipment manual at the Kano State water treatment plant before the start of field data collection and tested using raw water and standard solutions (Figure 4.2). Calibration was conducted in the presence of a research assistant to ensure the correct procedure was followed. Subsequently, the handheld equipment was calibrated each morning before measurements began and after multiple measurements in the field to ensure the collection of high-quality data.

Figure 4.2 Equipment calibration at Kano State water treatment plant before the start of field data collection.

4.2.3.2 Field Measurement

Groundwater from wells was pumped for 5 minutes to flush out debris and possible contaminants from the pipe surfaces. Water samples were then collected using a fetcher and transferred into a plastic beaker for physicochemical measurements. The sampler wore new, clean gloves before taking measurements at each location. Physicochemical parameters such as total dissolved solids (TDS), electrical conductivity (EC), temperature and Eh were measured using a digital conductivity meter, while dissolved oxygen was measured using a DO meter. The depths of the wells were measured with a water dip meter, and the coordinates of each sampling location were recorded using GPS (Figure 4.3).

Figure 4.3 Field measurement of physicochemical parameters.

4.2.3.3 Groundwater Sampling

A plastic bucket was rinsed with groundwater twice before being filled with the water. Afterwards, a 20 mL syringe was used to draw water from the bucket, which was then filtered through a 0.45 µm acetate cellulose syringe filter and collected in clean 50 mL polyethylene tubes. The tubes were sealed with electrical tape to ensure watertightness and to prevent leakage and possible cross-contamination of the sampled water.

4.2.3.4 Sample Preservation, Storage and Transport

Preservation of the samples began at the point of collection to prevent contamination and cross-mixing. Samples intended for cation analysis were acidified with two drops of concentrated HNO_3 acid. All samples were stored at a temperature of around or below 4°C in a cooler box with ice packs and then transferred to a refrigerator. The water samples were wrapped in bubble wrap, packed in cool boxes with ice packs, and then couriered to the Civil and Environmental Engineering Laboratory, University of Strathclyde, Glasgow (Figure 4.4).

Figure 4.4 Wrapped groundwater samples in cool boxes before shipping to the Civil and Environmental Engineering Laboratory, University of Strathclyde, Glasgow.

4.2.3.5 Quality Assurance/Quality Control

The fieldwork was conducted according to standard methods to ensure that the quality of the results was not compromised. The following key steps were taken to maintain the appropriate level of quality control and ensure quality assurance:

- The fieldwork was conducted by the standard operating procedures (SOP).
- Equipment was calibrated daily before starting sampling and in between many batches of sample collections. The pH/Conductivity meter and DO meter were calibrated following the guidelines provided in the equipment manual.

- Protective gloves were worn and changed between each sampling location/collection, and equipment was rinsed with water at each sampling location to prevent cross-contamination.
- Samples were stored in cooler boxes with ice packs and refrigerated before being sent to the laboratory.
- The accuracy of the chemical analysis was verified using the ionic balance error equation.
- All field data were thoroughly checked before recording.
- Multiple measurements were taken to ensure accuracy and precision in field measurements.
- A two-person field team was used to facilitate double-checking of the field results.

4.2.4 Laboratory Analysis

The selection of chemical parameters for laboratory analysis in this study was guided by both analytical feasibility and financial constraints. Several potentially toxic elements (PTEs) were initially considered for analysis; however, they were found to be well below the detection limits in preliminary screenings. Therefore, these elements were excluded from further analysis to ensure a focus on quantifiable and relevant datasets. Moreover, rare earth elements (REEs) were also not included in this study due to financial constraints, as their analysis requires specialized analytical techniques, such as inductively coupled plasma mass spectrometry (ICP-MS) which has a lower detection limit compared to Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), which was beyond the available budget. Furthermore, biological analyses were not conducted due to financial limitations and concerns regarding potential sample contamination before shipping to the environmental laboratory of the University of Strathclyde Glasgow, United Kingdom. Chemical parameters such as Na, Ca, Mg, K, As, Cd, Fe, Pb, Mn, Cr, Zn, Cu, Co, Ni Cl, F, SO_4, HCO_3, and NO_3 were chosen in this study to ensure the collection of high-quality relevant data which aligns with the objectives of the study and available research budget.

4.2.4.1 Cations Analysis

The concentrations of various cations and trace elements in 240 groundwater samples, collected during both wet and dry seasons, were analyzed using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, iCAP 6200, Thermo Fisher Scientific) (Chapter 5, 6 & 7) (Figure 4.5). The cations and PTEs analyzed included Na, Ca, Mg, K, As, Cd, Fe, Pb, Mn, Cr, Zn, Cu, Co, and Ni. The filtered, acidified, and preserved groundwater samples in 50 mL tubes, collected from various hand-dug wells and boreholes in the basin, were used for the analysis. A 15 mL portion of each sample was transferred into 15 mL centrifuge tubes for cations analysis. Samples with concentrations above the highest calibration range were diluted and recorded accordingly. The various solutions prepared throughout the cation analysis procedure are presented below:

1. A 2% HNO_3 solution was prepared initially and used to obtain a four-point calibration curve.
2. A 5 ppm Yttrium (Y^{3+}) solution was prepared and used as an internal standard.
3. Calibration blank samples were used for calibration to assess any element carryover effects.
4. Water quality control samples were prepared and analyzed after every 20 samples to monitor instrument performance.
5. Samples with concentrations exceeding the highest standard were diluted to fit within the linear calibration curve.

4.2.4.2 Anions Analysis

The anions analyzed included Cl, F, SO_4, and NO_3. The concentrations of these anions in 240 groundwater samples, collected during both the wet and dry seasons, were determined using Ion Chromatography (IC) (Chapters 5, 6, & 7).

Sample Preparation and Standard Solutions

The filtered and refrigerated groundwater samples were transferred into Peak IC Autosampler sample tubes (12 mL polystyrene, Metrohm) (Figure 4.5). Samples with dissolved ion concentrations exceeding the highest calibration standards were diluted with ultrapure water to fit within the linear calibration curve. Ultrapure water with a resistivity of 18.2 $M\Omega\ cm^{-1}$ was used for cleaning containers and tubes and for preparing stock standard solutions, from which standard solutions of 0.1, 1, 5, and 10 ppm of various analytes were prepared for calibration.

Figure 4.5 Laboratory analysis of major ions and PTEs.

IC Analysis

The equipment used for the analysis included a pre-column (Metrosep A Supp 5 Guard/4.0), a separator (analytical) column (Metrosep A Supp 5), a Metrohm Suppressor Module (MSM), a Metrohm CO_2 Suppressor (MCS), an electrical conductivity detector (Microprocessor-controlled Digital Signal Processing, DSP technology), eluent and sample degassers, and an autosampler (858 Professional Sample Processor) with a 2-channel peristaltic pump. A

Metrohm 850 Professional IC system was employed to analyze six inorganic anions (fluoride, chloride, nitrate, and sulfate) in the water samples simultaneously using a single-column, chemically suppressed IC technique at the Civil and Environmental Engineering Laboratory, University of Strathclyde. The equipment was equilibrated for at least 30 minutes before each run, with electrical conductivity and anion pump pressure monitored throughout. Sample analysis was conducted using the IC system within an acceptable range of pressure and conductivity. A 10 mL portion of each sample was placed into centrifuge tubes and loaded onto the IC system for analysis. The analytes were separated by pumping a mobile phase (eluent) of 1 mM sodium bicarbonate and 3.2 mM sodium carbonate at a flow rate of 0.7 mL/min. The concentrations of the ions present in the water samples were determined using MagIC Net software (Version 3.3) by calculating the peak areas.

4.2.4.3 Bicarbonate Alkalinity

The alkalinity of the water samples was determined using a titration technique with a HACH digital titrator (Model: 16900, HACH International) and 1.6 N and 0.16 N H_2SO_4 cartridges (Figure 4.6).

Figure 4.6 In situ measurement of alkalinity using a HACK digital titrator (Model: 16900, HACH International).

Various materials used are;

1. Digital titrator
2. Stir bar
3. Deionized water
4. Buffers (4.01 and 7.00)
5. 0.16 N sulfuric acid cartridge
6. 1.6 N sulfuric acid cartridge
7. Phenolphthalein indicator powder pillow
8. Bromocresol green-methyl red indicator powder pillow
9. 150 ml glass beaker

10. 100 ml graduated cylinder

The sulfuric acid cartridge was placed in the HACH digital titrator, and the delivery tube was carefully connected. The titrant was then forced out of the delivery tip to expel any trapped air bubbles within the tube. Before starting the titration, potential leaks at the connection between the tip and cartridge were checked, and the tube was rinsed with deionized water. The equipment counter was then reset to zero.

Sample preparation

The preparation of the samples began by grouping them based on their total dissolved solids (TDS) levels to guide the selection of the appropriate titrant molarity. Two groups were created: Group 1 and Group 2. Samples with TDS values below 40 mg/L were placed in Group 1, while Group 2 contained samples with TDS values greater than 40 mg/L. Group 1 samples were titrated with 0.16 M H_2SO_4, while 1.6 M H_2SO_4 was used for titrating group 2 samples.

Procedure

The steps followed during the titration were as follows.

1. A volume (V) in mL of the water sample was added to a 150 mL glass beaker.
2. A phenolphthalein indicator powder pillow was added to the beaker containing the water sample.
3. Starting with the titrator reading at zero, the titrant was gently added to the sample until the solution turned colourless, and the reading was recorded as "A," representing the P-alkalinity.
4. One pillow of bromocresol green-methyl red indicator was added to the solution.

5. The titrant was then added to the sample at the phenolphthalein endpoint until a slight colour change from green to pink was observed, and this reading was recorded as "B," representing total alkalinity.

The concentration of alkalinity was calculated using the following empirical relations:

- The Phenolphthalein Alkalinity was calculated as:

  $CaCO_3$ alkalinity (mg/l) = Multiplier × Total digit used.

- The Bromocresol green-methyl red alkalinity was calculated as:

  $CaCO_3$ total alkalinity (mg/l) = Multiplier ×Total digit used.

Let the $CaCO_3$ alkalinity (mg/l) = X

$CaCO_3$ total alkalinity (mg/l) =Y

and bicarbonate alkalinity = Z

Therefore.

Hydroxide alkalinity = $2X – Y$ and total alkalinity = $X +Y+Z$.

Z = Total alkalinity – $(X+Y)$ = Bicarbonate alkalinity.

4.2.5 ArcGIS Analysis

The spatial distribution of various water quality parameters was created using ArcGIS 10.8 by applying the inverse distance weighting (IDW) method. The generated spatial maps were classified using the manual classification option in ArcGIS (Chapters 5, 6, 7 & 8). The soil and geological maps of the basin were derived by clipping the basin's shapefile from the world digital soil map and the geological map of West Africa.

4.2.6 Geochemical Modelling

Various geochemical modelling techniques were employed in this study, including a combination of box plots, Piper diagrams, Chadha plots, Gibbs diagrams, saturation indices modelling, chloralkaline indices, and Eh-pH plots (Pourbaix diagrams (Chapter 7)). Box plots were primarily used to analyze the distribution of ions and compare them with World Health Organization guidelines for drinking water quality. The Piper diagram and Chadha plots facilitated the identification of different groundwater types and patterns of geochemical evolution. Gibbs plots, scatter plots, Pourbaix diagrams, and saturation indices analysis were used to model the geochemical mechanisms governing groundwater chemistry and the speciation of various ions/PTEs within the groundwater systems (Chapters 5, 6, & 7).

4.2.7 $\delta^{18}O$ and $\delta^{2}H$ Isotopes analysis

The stable isotopes $\delta^{18}O$ and $\delta^{2}H$ of the groundwater samples were analyzed at the International Atomic Energy Agency (IAEA) isotope laboratory in Vienna and the Ministry of Agriculture, irrigation, and Water Development isotope laboratory in Blantyre, Malawi. Groundwater samples from both wet and dry seasons labelled ISX (where X represents the sampling locations), were shipped to the laboratory in a cool box, maintained at a temperature below 4°C, for isotope analysis. The methods for isotope water sampling and analysis described by Banda et al., (2019) were adopted for the groundwater samples from the Komadugu-Yobe Basin. The isotopic interpretation was conducted using bivariate ratio plots of $\delta^{18}O$ vs. $\delta^{2}H$, D-excess vs. $\delta^{18}O$, and geospatial analysis of the stable isotope dataset of groundwater. The analysis involved comparing the regression lines of the samples to both global and regional meteoric water lines. The Global Meteoric Water Line (GMWL), defined as $\delta^{2}H = 8\delta^{18}O + 10$, as established by Craig, (1961) and the Regional Meteoric Water Line (RMWL), derived from rainfall datasets from three local and four regional stations, were used for this comparison (Chapter 8). The isotopic results were then compared with datasets from five major basins within the Sahel region of West Africa. This approach enabled a comprehensive interpretation of isotopic signatures, including groundwater recharge zones, the altitude effect, evaporation, and vapour sources in the basin and the wider Sahel region.

5 Hydrogeochemistry and Water Quality Index for Groundwater Sustainability in Komadugu-Yobe Basin, Sahel Region[1]

5.1 Preface

This chapter presents the first research chapter of the thesis. 120 groundwater samples were collected from the Komadugu-Yobe basin during the wet season of 2021 and analyzed to assess the general hydrogeochemical characteristics of groundwater and its suitability for drinking purposes. This chapter categorically sets out the basic foundational background for subsequent chapters by evaluating the general hydrogeochemistry of groundwater in the basin. Currently, there is limited comprehensive research on the evaluation of groundwater quality that combines hydrogeochemical analysis, water quality index (WQI), and GIS-based approach in a more regional context over the entire basin. This chapter specifically addressed this knowledge gap.

This chapter was written to fulfil research question one (RQ1): What are the general hydrochemical characteristics of groundwater in KYB and its suitability for drinking purposes? This was achieved by first collecting groundwater samples spreading the entire Komadugu-Yobe basin and analysing them for major ions using ICP-OES for cations and IC for anions and employing a methodology that integrates hydrogeochemical characterization, water quality index and geospatial analysis to identify the general hydrogeochemical characteristics of groundwater in the basin. In achieving this, some research gaps are identified (SO1, SO2, SO3, and SO4). Furthermore, it compares various groundwater quality parameters with the WHO, 2018 guideline to determine the suitability of the groundwater for drinking purposes (SO1). It also established the link between geology and hydrochemical characteristics, groundwater facies and groundwater quality index over the entire basin (SO4).

This chapter is a peer-reviewed published article within the special issue of MDPI journal water ‘Effect of climate change and anthropogenic activities on groundwater resources ‘.

Paper reference:

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Author contribution:

Conceptualization (A.S. and R.M.K.) methodology (A.S.) software (A.S., L.C.B., and I.M.L.), validation (A.S., R.M.K., and V.P.), formal analysis (A.S.), investigation (A.S.) resources (A.S.) data curation (A.S.) writing—original draft preparation (A.S.), writing—review and editing (A.S., R.M.K., V.P., L.C.B., and I.M.L.), visualization (L.C.B. and I.M.L.), supervision (R.M.K. and V.P.), project administration (A.S.), funding acquisition (R.M.K. and A.S.).

5.2 Abstract

The assessment of hydrochemical characteristics and groundwater quality is crucial for environmental sustainability in developing economies. This study employed hydrogeochemical analysis, geospatial analysis, and groundwater quality index to assess hydrogeochemical processes and the quality of groundwater in the Komadugu-Yobe basin. The pH, total dissolved solids (TDS), and electrical conductivity (EC) were assessed in situ using a handheld portable electrical conductivity meter. The concentrations of the major cations (Na, Ca, Mg, and K), were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES). The major anions (chloride, fluoride, sulfate, and nitrate) were analyzed via ion chromatography (IC). Total alkalinity and bicarbonate were measured in situ using a HACH digital alkalinity kit by the titrimetric method. Hydrochemical results indicate some physicochemical properties of the groundwater samples exceeded the maximum permissible limits as recommended by the World Health Organization guidelines for drinking water. Gibbs diagrams indicate rock–water interaction/rock weathering processes are the dominant mechanisms influencing groundwater chemistry. Groundwater is predominantly Ca-Mg-HCO_3 water type, constituting 59% of the groundwater samples analyzed. The groundwater quality index (GWQI) depicted 63 and 27% of the groundwater samples as excellent and good water types for drinking purposes, respectively. This study further relates the interaction between geology, hydrochemical characteristics, and groundwater quality parameters. The results are essential to inform a sustainable management strategy and protection of groundwater resources.

Keywords

Groundwater sustainability; geospatial analysis; water quality index; groundwater evolution; sustainable development goal 6 (SDG6)

5.3 Introduction

Safe and sustainable freshwater resources are essential for socio-economic development and the well-being of humanity. Freshwater is vital for drinking, agriculture, sanitation, fisheries, hydropower generation, livestock farming, and recreation (Ganiyu et al., 2021; Kawo & Karuppannan, 2018; Namara et al., 2010; Solangi et al., 2020). The main source of water supply in most developing economies is groundwater from shallow wells (Ganiyu et al., 2018, 2021; Kawo & Karuppannan, 2018; Li et al., 2010; Loh et al., 2020; Mostafa et al., 2017; Rivett et al., 2018; Trabelsi & Zouari, 2019). The semi-arid to arid North-East region of Nigeria relies heavily on groundwater for various uses (Goes, 1999; Goni et al., 2019; Jagaba et al., 2020; Wali et al., 2021). Consequently, it is crucial to ascertain the adequacy of the groundwater in terms of both quantity and quality for sustainable use and management in order to realize Sustainable Development Goal 6 (SDG6). However, impacts of anthropogenic activities pollute groundwater in Nigeria (Balogun et al., 2022; Ocheri et al., 2014; Stephen et al., 2017).

Various human activities such as excessive use of synthetic fertilizer and manure for irrigation purposes, dumping of solid wastes in rivers, leachate from dumpsites, septic tanks, and pit latrines pollute groundwater in the Komadugu-Yobe basin (Wali et al., 2020). Thus, the quality of the groundwater determines its usability (Masood et al., 2021; Omonona et al., 2019).

Groundwater hydrogeochemical analysis provides an in-depth understanding of hydrochemical characteristics and the overall quality of groundwater (Ezugwu et al., 2019; Nalami et al., 2019; Omonona et al., 2019; Wagh et al., 2019; Xiao et al., 2022). The chemistry of groundwater is influenced by geological characteristics, the extent of chemical weathering of different rock formations, rock–water interaction, dissolution rates of various minerals, and the quality of the water that recharges the groundwater system (Adimalla et al., 2018; Kalin and Long, 1993; Kalin, 1995; Li et al., 2010; Marini, 2006). Water quality is assessed and monitored using hydrogeochemical and statistical analysis, as well as the estimation of water quality indices (Ahmed et al., 2019; Marini, 2006). The statistical analysis employed in water quality assessment elucidates the relationships between different water quality parameters. The water quality index (WQI) uses water quality parameters to represent the impact of geogenic and anthropogenic activities on overall water quality (Ahmed et al., 2019; Egbueri et al., 2020; Mgbenu & Egbueri, 2019; Solangi et al., 2020; Tiwari et al., 2017; Vaiphei et al., 2020; Wagh et al., 2019). Many researchers employed the WQI in water quality studies because of its flexibility, adaptability, and simplicity in groundwater quality assessment and monitoring (Adimalla & Taloor, 2020; Aladejana et al., 2021; Ezugwu et al., 2019; Kawo & Karuppannan, 2018; Olasoji et al., 2019; Qasemi et al., 2023; Xiao et al., 2022). The WQI is also used to communicate water quality analysis results in a numerical format for easy communication and presentation to stakeholders, the general public, and government institutions (Aladejana et al., 2020; Olasoji et al., 2019; Qasemi et al., 2023).

A geographical information system (GIS) provides the spatial framework for evaluating water resource changes in space and time, such as water quality and quantity assessment, water pollution risks, and vulnerability mapping at both local and regional levels (Mgbenu & Egbueri, 2019; Panneerselvam et al., 2020; Trabelsi & Zouari, 2019). GISs are widely used for developing groundwater quality maps, which are essential for managing groundwater for various uses (Kawo & Karuppannan, 2018; Solangi et al., 2020; Vaiphei et al., 2020). They are cost-efficient and transform large hydrochemical datasets into spatial information (Panneerselvam et al., 2020; Trabelsi & Zouari, 2019). Geospatial techniques including inverse distance weight (IDW), Kriging, Spilain, and Cokriging interpolation algorithms in ArcGIS, are used to interpret the distribution of water quality parameters (Adimalla & Taloor, 2020; Aladejana et al., 2020; Panneerselvam et al., 2020; Solangi et al., 2020; Vaiphei et al., 2020). The IDW method is commonly employed as it uses a deterministic model approach (Adimalla et al., 2018; Adimalla & Taloor, 2020; Kawo & Karuppannan, 2018; Machiwal et al., 2018; Panneerselvam et al., 2020; Trabelsi & Zouari, 2019; Vaiphei et al., 2020; Wagh et al., 2019).

Management of the water quality is needed for ecosystem health (Ezugwu et al., 2019; Ganiyu et al., 2018) and is critical for environmental quality management (Aladejana et al., 2021). However, access to sufficient quantities of water of adequate quality for the people can be limited, particularly in arid and semi-arid parts of developing countries (Ezugwu et al., 2019; Sebei et al., 2018). Assessment of the quality of available groundwater is essential for proper management and utilization. The quality of groundwater is influenced by various factors including subsurface hydrogeochemical processes, soil characteristics, seasonal variations, natural and anthropogenic activities, climate change, and groundwater recharge processes (Adimalla & Taloor, 2020; Masood et al., 2021; Rivett et al., 2019). Moreover, municipal solid waste, industrial wastewater, and domestic wastewater impact groundwater quality (Al-Jawad et al., 2019; Jagaba et al., 2020). Ganiyu et al., (2018) indicated that WHO estimates 80% of human diseases resulted from poor water quality.

Previous studies within the Komadugu-Yobe basin did not focus on detailed geochemical assessments of the groundwater, though some local studies have been published (Bernard & Ayeni, 2012; Hamidu et al., 2021; Jagaba et al., 2020; Mahammad & Islam, 2021; Suleiman et al., 2020; Usman & Aliyu, 2020). To date, there have been no wide-ranging studies on groundwater quality assessment that integrate hydrogeochemical analysis, WQI, and GIS-based techniques. This study specifically addressed this knowledge gap. This study aims to provide information valuable to stakeholders, government institutions, and decision-makers involved in the sustainable management of groundwater resources in Nigeria and the wider Sahel region.

5.4 Materials and Methods

5.4.1 Study Area Setting

The Komadugu-Yobe basin is situated in the southwestern region of the greater Lake Chad basin. It covers a significant portion of the northwestern and northeastern parts of Nigeria within the Sahel region of Africa (Figure 5.1). The basin covers an approximate area of about 150,000 km^2, with an elevation of 294 to 1750 m above the mean sea level. The Komadugu-Yobe and Komadugu-Gana sub-systems are the primary rivers within the basin. These rivers pass through the Hadejia Nguru wetland before ultimately draining into Lake Chad (Adeyeri et al., 2019; Goes, 2002; Waziri & Ogugbuaja, 2010).

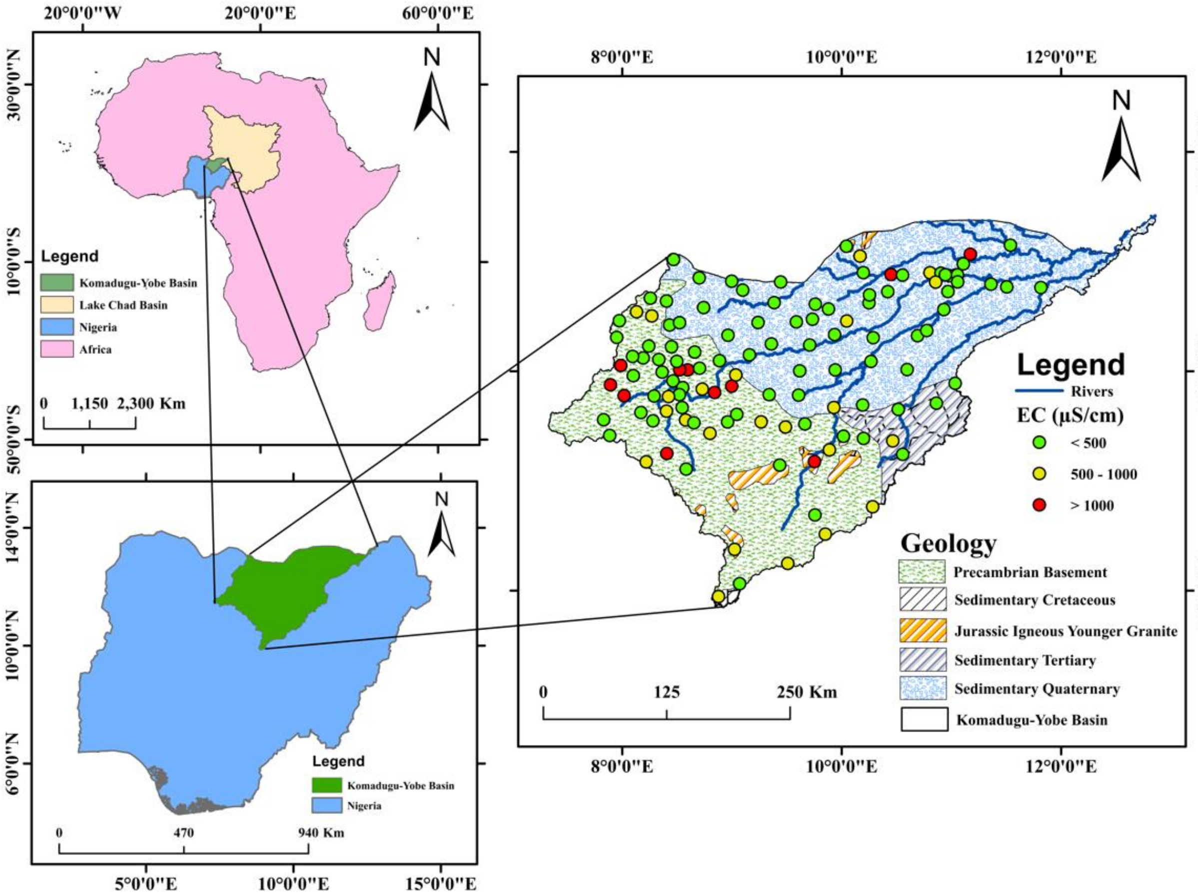

Figure 5.1 Groundwater sampling location, geology type, and electrical conductivity (EC) concentration in Komadugu-Yobe basin.

The basin has a semi-arid and arid climate characterized by severe drought and high rainfall variability. The wet season in the basin commences in May and extends through September and October, with the highest rainfall occurring in the month of August. The dry season spans from October to April (Ahmed et al., 2018b). The mean annual rainfall in the basin varies from a maximum of 1360 mm in Jos and 900 mm at Kano to a minimum of 600 mm and 400 mm around Hadejia and Nguru, respectively. The humidity in the basin is about 40%, and the annual evapotranspiration rate is 203 mm/year (Ahmed et al., 2018b; Waziri & Ogugbuaja, 2010). The basin has higher evaporation rates at the downstream section due to the high temperature. The annual maximum temperatures are recorded between March and April in the basin at 40

◦C with a temperature of around 12 ◦C recorded in the months of December and January. The Komadugu-Yobe basin presently houses more than 20 million people. The wetlands in the Komadugu-Yobe basin provide the inhabitants residing in the basin with various economic activities such as fish production, pastoralism, forestry, trading, and agriculture (Adeyeri et al., 2019). The basin is dominated by dense grasslands, shrubs, and scattered tree-type vegetation (Adeyeri et al., 2020).

5.4.2 Regional Geology and Hydrogeology

The Komadugu-Yobe basin is a rift basin resulting from basement tensional forces, with a zigzag fault pattern and the absence of other comprehensive physical features (Avbovbo et al., 1986). Several factors influence the occurrence of faults including the presence of pre-existing lines of weakness formed during the Pan-African orogenic event (McCurry, 1971). The basin is underlain by basement-complex rocks and sedimentary quaternary formations (Figure 5.1). The main geological structures in the basin are faults and simple symmetrical folds that are predominant in a northeast–southwest trend. The faults are dominant in the basement section and result in grabens, horsts, and other related features. Some high-angle faults are formed within the underlying sediment in the sub-basin because of the movement along these basement faults (Avbovbo et al., 1986). However, the folds in the Komadugu-Yobe basin comprise simple and folded sediments with low fold frequency and amplitude that flatten with depth. The frequency of folds decreases towards the northwestern part of the basin, while the fold amplitude increases in a southeast direction. The stratigraphic sequence of the sediments in the Komadugu-Yobe basin was presented by Avbovbo et al., (1986), Obaje et al., (2004), Obaje, (2011), Lopez et al., (2016), and Bura et al., (2018).

The quaternary Chad formation is the most recent formation in the basin, a Pliocene-Pleistocene deposit with thick clays of fluviatile and lacustrine origin. It consists of light gray claystone, minor sand, and some infrequent pebbly horizons that exhibit ferruginization in the deposits (Bura et al., 2018; McCurry, 1971; Wali et al., 2020). The Keri-Keri formation is characterized by conglomerate, siltstone, grit, sandstone, and clay that overlie the Maastrichtian Fika Shale and Gombe Sandstone. This deposit contains minerals such as zircon, tremolite, pyroxene, rutile, staurolite, kyanite, tourmaline, limonite, and hornblende (Adegoke et al., 1986; Bura et al., 2018; Ola-Buraimo & Abdulganiyu, 2017). The Bima sandstone is situated above the Gongila formation. It is derived from the weathering of basement rocks and consists of a sequence of red sandstone and mudstone (Bura et al., 2018; Wali et al., 2020). The Gongila formation is characterized by the presence of substantial layers of calcareous grey to dark shales and silty sandstone, which were deposited in a marine setting. Furthermore, the Fika formation consists of dark grey to blue-black shale. It has been dated as Turonian-Maastrichtian in age by Obaje, (2011). The upper part of the formation infrequently has glauconite, gypsum, and fine-grained sandstone (Bura et al., 2018).

The Plio-Pleistocene Chad formation and the younger underlying Quaternary sediments are the primary groundwater-bearing units in the basin. Groundwater supply in the basin is provided by the upper, middle, and lower aquifers of the Chad formation, which are separated by thick clay layers. The lower and intermediate aquifers are mostly confined, whereas the upper aquifer is mostly unconfined or partially confined in a few locations (Bura et al., 2018; Edmunds et al., 1999, 2002; Lopez et al., 2016; Vassolo, 2012). According to Akujieze et al., (2003), a yield of 2.5 to 30 L/s is common in the upper aquifer. The yield of the middle and lower aquifers ranges from 24 to 32 L/s and 10 to 35 L/s, respectively (Akujieze et al., 2003; Edmunds et al., 1999). The Komadugu-Yobe Valley serves as the main source of recharge for the unconfined Lake Chad quaternary aquifer, mostly through percolation and wetlands. The processes of aquifer recharge and pollution hazard potential have been impacted due to extensive irrigation farming practices within the basin (Edet et al., 2012; Le Coz et al., 2011). The alluvial aquifer located beneath the Yobe floodplain undergoes recharge through various mechanisms, including seepage from the river channel, infiltration of floodwater, and surplus rainfall. These sources act alone or in combination to replenish the aquifer (Goes, 1999; Le Coz et al., 2011). Carter & Alkali, (1996) estimated a recharge of 30–60 mm/year around the Manga grasslands of northeastern Nigeria. Moreover, recharge of 14–49 mm/year was estimated by Edmunds et al., (2002) in the Komadugu-Yobe basin.

5.4.3 Groundwater Sampling and Field Measurement

A total of 120 groundwater samples were collected from shallow hand-dug wells and boreholes within the Komadugu-Yobe Basin from August to October 2021. The groundwater sampling location is shown in Figure 1. The groundwater sampling was preformed following the standard procedure (APHA, 2012). Groundwater was pumped out of the source for 5 min to flush standing water in the borehole before sampling. Sampling was conducted using 50 mL polyethylene bottles. Samples for cations were filtered using a 0.45µm acetate cellulose syringe filter and acidified with 0.4 mL of concentrated nitric acid (HNO_3^-). Remaining samples were filtered using a 0.45 µm acetate cellulose syringe filter. Samples were sealed to avoid air exposure and stored in ice-packed coolers to maintain a temperature of ~4 ◦C. The samples were shipped to the Department of Civil and Environmental Engineering Laboratory, University of Strathclyde, Glasgow for further analysis. The pH, electrical conductivity, and total dissolved solids were measured in situ with a potable digital electrical conductivity meter (Model 99720 pH/Conductivity meter). The water depth was measured with a dip meter, while the geographic coordinates of each sampling location were recorded using a handheld Global Positioning System (GPS).

5.4.4 Laboratory Analysis

Groundwater samples were analyzed following the standard procedure given by the American Public Health Association (APHA, 2012). A total of 15 mL of groundwater sample was collected in a 15 mL centrifuge tube from 120 samples (acidified) each and analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 6200; Thermo Fisher Scientific) for analysis of the major cations (Na^+, Ca^{2+}, Mg^{2+}, K^+). Ion chromatography (Metrohm 850 Professional IC) was used to analyze the concentration of the major anions (Cl^-, F^-, SO_4^{2-}, NO_3^-) in the groundwater samples. The total alkalinity was analyzed in situ using titration with the HACH digital titrator (Model 16900; HACH International, Loveland, CO, USA).

5.4.5 Accuracy of Chemical Analysis

The ionic balance error (IBE) shown in Equation (5.1) was employed to check the accuracy of the chemical analysis:

$$IBE\% = \frac{\sum c - \sum a}{\sum c + \sum a} \times 100 \tag{5.1}$$

where IBE denotes the ionic balance error; c and a denotes the sum of cations and anions concentrations in milliequivalents per liter (meq/L). The standard threshold limit for the IBE% is ±10. The IBE of the analyzed groundwater samples was between −8.45 and 8.64%.

5.4.6 Geospatial Analysis

ArcGIS 10.8 was used to develop the spatial distribution maps of various groundwater quality parameters and the groundwater quality index. The IDW interpolation approach was used to develop the spatial distribution maps in the spatial analyst toolbox of ArcGIS. This method was used because it follows a deterministic model approach and fits well with real-world parameters (Adimalla & Venkatayogi, 2018; Kawo & Karuppannan, 2018; Vaiphei et al., 2020).

5.4.7 Groundwater Quality Index

The groundwater quality index (GWQI) is a quantitative measure used to determine the suitability of groundwater for human consumption. It involves the aggregation of various water quality characteristics into a single index using mathematical summation (Adimalla et al., 2018; Aladejana et al., 2021; Kawo & Karuppannan, 2018). It is used to elucidate trends in water quality over time. The approach has gained acceptance worldwide and has been employed in assessing the suitability of groundwater for drinking purposes in various regions (Adimalla et al., 2018; Adimalla & Taloor, 2020; Aladejana et al., 2021; Kawo & Karuppannan, 2018).

Groundwater quality index computation involves four main steps: weight assignment for each groundwater quality parameter, relative weight computation, water quality rating scale computation for each parameter, and computation of the sub-index and groundwater quality index as follows:

- Assigning a weight for each groundwater quality parameter: Weights (wi) were assigned to various water quality parameters based on their relative importance to human consumption (Adimalla & Taloor, 2020). Nitrates and fluorides were given the highest weight of 5 due to the vital role they played in groundwater quality evaluation and their significant human health impacts (Aladejana et al., 2021; Vaiphei et al., 2020). Sodium and potassium were given the least weight because they are less significant in groundwater quality assessment. Table 5.1 shows the weights assigned to each groundwater quality parameter.

- Computation of relative weight: Equation (5.2) below was used to calculate the relative weight (Wi):

$$Wi = \frac{wi}{\sum_{i}^{n} wi} \qquad 5.2$$

where Wi is the relative weight; wi denotes the weights assigned for each parameter; n denotes the total number of quality parameters; and i is the ith parameter.

- Water quality rating scale: The rating scale (qi) for each parameter was computed by dividing the determined concentration of each parameter (ci) and its respective water quality standard

(Si) recommended by World Health Organization (WHO, 2018) all multiplied by 100. The qi for all the parameters was computed using Equation (5.3) below:

$$qi = \frac{ci}{Si} \times 100 \tag{5.3}$$

where qi denotes the quality rating; ci denotes the concentration of each groundwater quality parameter in mg/L; and Si is the WHO guideline value for each parameter.

- Sub-index and groundwater quality index computation: The sub-index (SIi) for each parameter and overall groundwater quality index (GWQI) were calculated using Equations (5.4) and (5.5):

$$SIi = Wi \times qi \tag{5.4}$$

$$GWQI = \sum_{i=0}^{n} SIi \tag{5.1}$$

where SIi denotes the sub-index of the ith water quality parameter; qi denotes the quality rating of the ith parameter; n is the total number of water quality parameters; and GWQI is the overall groundwater quality index. The groundwater was classified based on portability in Table 5.2.

Table 5.1 Groundwater quality parameters weighing for groundwater quality index computation.

Parameters	**Units**	**WHO** (WHO, 2018)	**Weight (*wi*)**	**Relative Weight (*Wi*)**
pH	/	6.5–8.5	4	0.095
TDS	mg/L	1000	5	0.119
TH	mg/L $CaCO_3$	500	3	0.071
Na+	mg/L	200	2	0.048
K^+	mg/L	12	2	0.048
Ca^{2+}	mg/L	75	3	0.071
Mg^{2+}	mg/L	50	3	0.071
Cl^-	mg/L	300	4	0.095
HCO_3-	mg/L	250	3	0.071
SO_4^{2-}	mg/L	250	3	0.071
NO_3^-	mg/L	50	5	0.119
F^-	mg/L	5	5	0.119
			$\sum wi = 42$	$\sum Wi = 1$

Table 5.2 Groundwater quality index.

Range of GWQI	**Class of Water**	**Number of Samples**	**% of Samples**
<50	Excellent Water	76	63
50–100	Good Water	32	27
100–200	Poor Water	12	10
200–300	Very Poor Water	/	/
>300	Unsuitable	/	/
	Total	120	100

5.4.8 Hydrochemical Analysis

The water types, hydrochemical facies, and geochemical mechanisms controlling the chemistry of groundwater in the Komadugu-Yobe basin were identified using the Piper trilinear diagram, Chadha plot, and the Gibbs diagrams. The Piper diagram was developed using the Geochemist Work Bench (GWB) software 17.0. The Gibbs diagram and the Chadha plot were developed using Origin Pro 2022. These diagrams have been widely used by several researchers (Adimalla & Taloor, 2020; Vaiphei et al., 2020) to understand the various principal mechanisms controlling groundwater chemistry. The Gibbs diagrams are based on two ratios and are calculated using Equations (5.6) and (5.7):

$$\text{Gibbs ratio—I} = \frac{Cl^-}{(Cl^- + HCO_3^-)} \qquad 5.6$$

$$\text{Gibbs—II} = \frac{Na^+ + K^+}{(Na^+ + K^+ + Ca^{2+})} \qquad 5.7$$

Ionic concentrations in meq/L.

5.5 Results and Discussion

Groundwater quality determines its usability. Various groundwater quality parameters analyzed with their descriptive statistics are presented in Table 5.3. The results of the analyzed groundwater quality parameters were compared with the WHO, (2018) guidelines (Tables 5.1 and 5.3) to determine the suitability of the groundwater for drinking purpose. The geology of the study region was overlaid on the geospatial distribution maps of groundwater quality parameters to relate the interaction between geology and groundwater quality parameters (Figures 5.2–5.4).

Table 5.3 Statistical summary of the physicochemical parameters of groundwater samples of KYB compared with WHO (WHO, 2018) guidelines.

Parameters	Units	Maximum	Minimum	Mean	**WHO** (WHO, 2018)		PAMPL
					HDL	MPL	
pH	/	8.24	5.52	7.2	6.5–8.5	8.5	/
EC	µS/cm	2746	15	462	1000	/	5
TDS	mg/L	1757	10	296	1000	1500	2.5
TH	mg/L $CaCO_3$	704	0.8	138	100	500	2
Na	mg/L	285	2	36	200	250	2.5
K	mg/L	96	0.1	10	12	/	6
Ca	mg/L	220	0.2	39	75	200	2
Mg	mg/L	58	0.1	9.9	50	150	2.5
HCO_3	mg/L	379	1.5	120	250	500	10.8
Cl	mg/L	372	0.7	48	300	600	2.5
SO_4	mg/L	133	0.1	15	250	500	/
NO_3	mg/L	314	ND	42	50	50	30
F	mg/L	2.3	ND	0.3	1.5	1.5	2

Note: HDL: highest desirable limit; MPL: maximum permissible limit; PAMPL: percentage above maximum permissible limit.

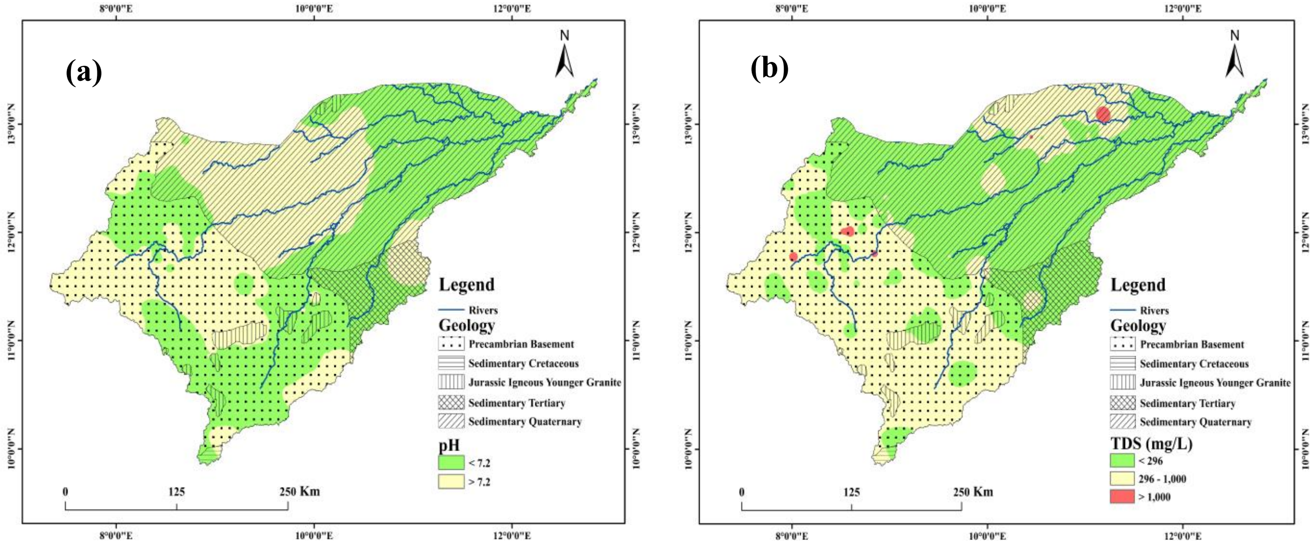

Figure 5.2 Spatial distribution of groundwater quality parameter in Komadugu-Yobe basin. (a) pH; (b) TDS.

5.5.1 Hydrogen Ion Concentration (pH)

pH is an important groundwater quality parameter (Adimalla & Taloor, 2020; Eyankware et al., 2020b). The pH of the groundwater ranged from 5.52 to 8.24 (Figure 5.2a), with an average value of 7.2 (Table 2). About 88 % of the analyzed samples fall between 6.5 and 8.5, the recommended safe limits prescribed by WHO, (2018). Only 12.5 % of the analyzed groundwater samples fell below 6.5 indicating some acidic water. A change in pH leads to change in biochemical reactions (Adimalla & Venkatayogi, 2018). Figure 5.2a shows the eastern part of the basin that is dominated by sedimentary quaternary formation and exhibits the lowest pH values; meanwhile, the western section, dominated by Precambrian basement, has pH values above the mean value. This could be due to the presence of calcite minerals and alkaline ions from feldspar weathering, which raises the pH of groundwater (White et al., 2005). However, the low pH values in the sedimentary quaternary may be related to the extensive use of synthetic fertilizers (urea, GDAP, NPK, etc.) during irrigation, which introduced specific compounds that undergo oxidation reactions, resulting in low pH values in groundwater systems.

5.5.2 Total Dissolved Solids (TDS)

The groundwater in the Komadugu-Yobe basin show variation in concentrations of total dissolved solids (TDSs) (Figure 5.2b). The TDSs of the groundwater samples vary from 10 to 1757 mg/L, with a mean value of 296 mg/L (Table 2). TDSs are the sum of all dissolved inorganic salts of major ions in water (Adimalla & Taloor, 2020). The method prescribed by Davis and DeWiest, (1966) was used to classify the groundwater of the study area based on TDS values (Table 5.4). About 85% of the groundwater sample is desirable for drinking, while 10 and 5% of the groundwater samples are permissible for drinking and useful for irrigation, respectively (Table 5.4). High TDS values above the mean concentration were observed in the Precambrian basement part of the study area. This is an indicator of the dissolution and weathering of carbonates, salts, and sulfate minerals. Other factors that contribute to high levels of TDS in this region include ion-exchange interaction between ions in the groundwater and ions on the mineral surfaces, as well as groundwater flow through rocks, sediments in the subsurface, and water–rock interaction time. TDS values in the sedimentary quaternary, on the other hand, were lower than the mean concentration. However, high TDSs were observed at the downstream fringes of the basin. This could be attributed to high rates of evaporation than rainfall in the region as well as the anthropogenic impacts from agricultural activities and waste disposal.

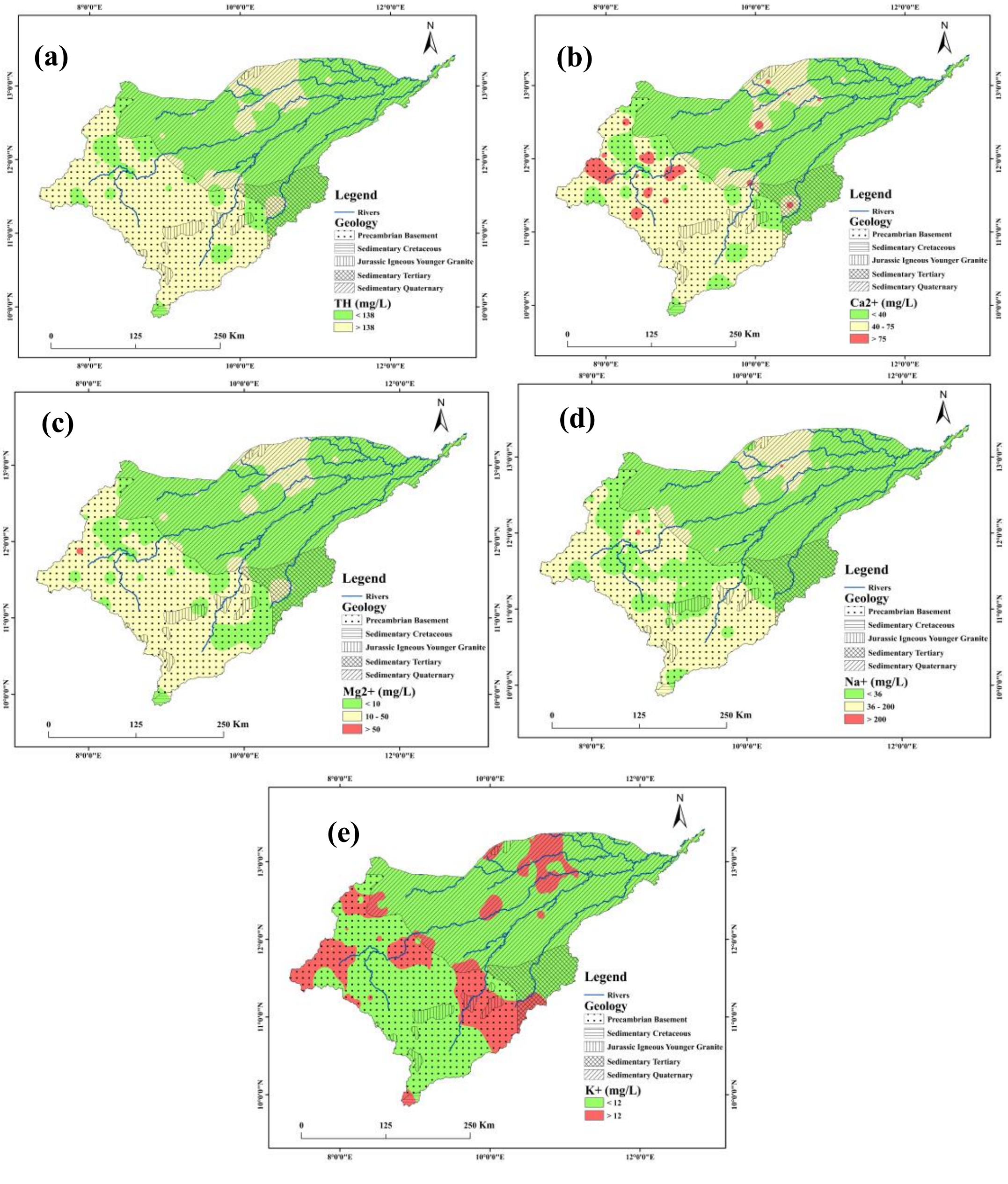

Figure 5.3 Spatial distribution of groundwater quality parameter in Komadugu−Yobe basin. (a) TH; (b) Ca (c) Mg (d) Na (e) K.

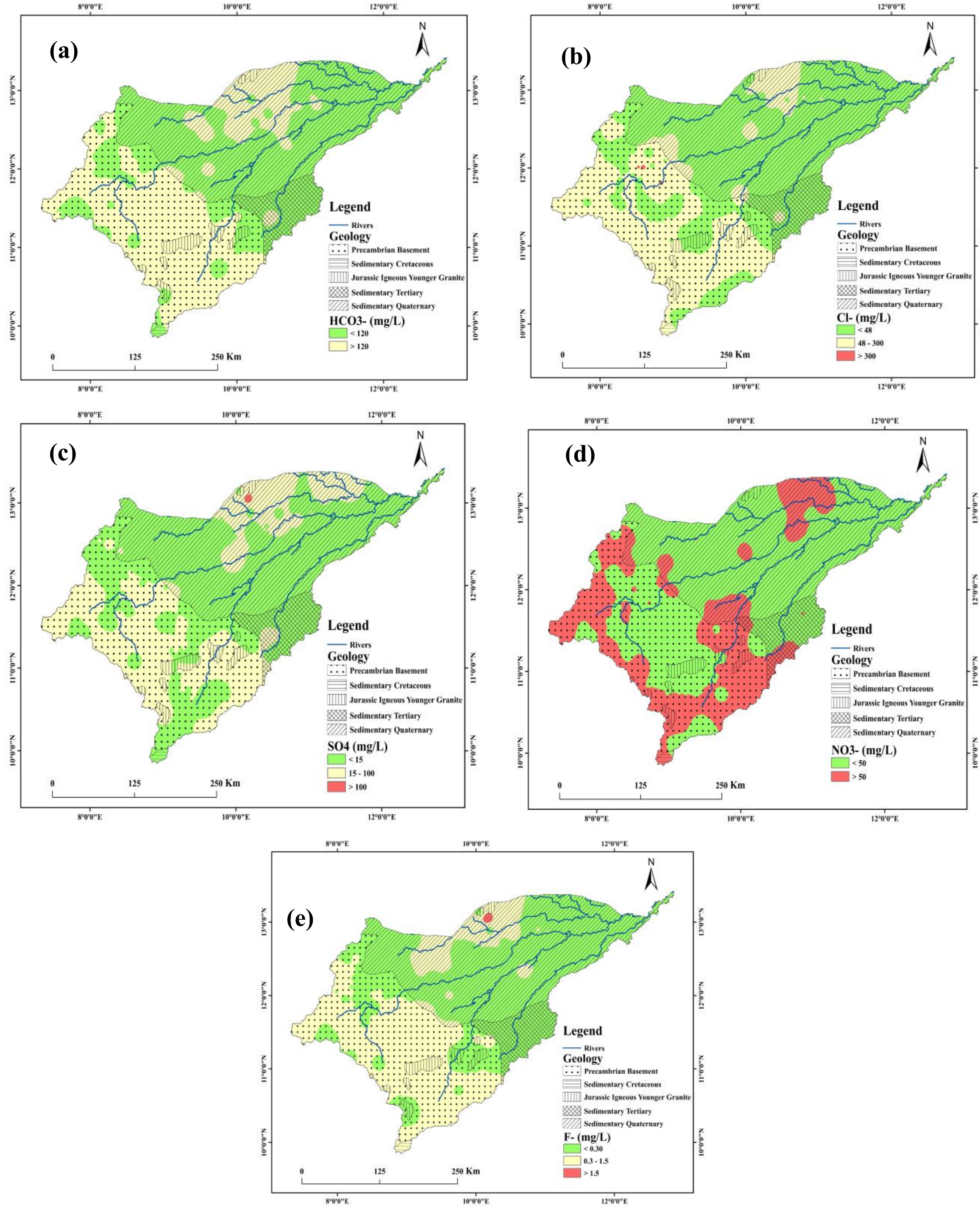

Figure 5.4 Spatial distribution of groundwater quality parameters in Komadugu-Yobe basin. (a) HCO_3 (b) Cl (c) SO_4 (d) NO_3 (e) F.

Table 5.4 Groundwater classification based on TDSs (Davis, and DeWiest, 1966).

TDS (mg/L)	**Class of Groundwater**	**% of Samples**
<500	Desirable for drinking	85
500–1000	Permissible for drinking	10
1000–3000	Useful for irrigation	5
>3000	Unfit for drinking and irrigation	/

5.5.3 Total Hardness of Water (TH)

Ingestion of water with a high concentration (>300 mg/L) of total hardness (TH) may cause renal failure and the likelihood of the formation of kidney stones due to the presence of calcium carbonate, calcium phosphate, and calcium oxalate (Adimalla & Taloor, 2020; Goes, 2002). The TH of groundwater in the Komadugu-Yobe basin varies from 0.8 to 704 mg/L as $CaCO_3$, with a mean value of 138 mg/L as $CaCO_3$ (Table 5.2). About 98 % of the groundwater samples in the study area were below the maximum permissible limit of 500 mg/L (Table 5.2). Sawyer & McCarthy, (1967) classified groundwater based on the concentration of total hardness TH as mg/L of $CaCO_3$ (Table 5.5). The table shows that about 43% of the groundwater samples in the study area are soft water, whereas 13% of the groundwater samples are in the very hard water category. The spatial distribution of TH in the study area is presented in Figure 5.3a. The figure reveals that TH concentrations above the mean value were concentrated in the Precambrian basement part, while the sedimentary quaternary section of the basin is dominated by TH concentrations below the mean value. This may be attributed to the presence of calcite and dolomite minerals in the Precambrian basement part of the study area.

5.5.4 Calcium (Ca) and Magnesium (Mg)

Calcium (Ca) and magnesium (Mg) concentrations in groundwater samples of the study area range from 0.2 to 220 mg/L with a mean value of 39 mg/L and from 0.1 mg/L to 58 mg/L with a mean value of 9.9 mg/L, respectively (Table 5.2). About 2.% of the groundwater samples were above the World Health Organization (WHO, 2018) maximum permissible limit of Mg of 150 mg/L (Table 5.2). Calcium is derived from cation exchange processes and carbonate dissolution (Adimalla & Taloor, 2020). Therefore, Ca variations in groundwater samples could be due to carbonate rock dissolution and ion exchange processes in the Precambrian basement parts of the basin (Figure 5.3b). Figure 5.3c depicts the spatial variation in Mg in the study area. Furthermore, the lower value of Mg concentration in the sedimentary quaternary portion of the basin may be because of the absence of magnesium-bearing minerals in the groundwater of the region. The result also reveals a higher concentration of Ca than Mg, which could be due to the influence of ion exchange mechanisms and dissolution of mafic minerals in the groundwater system (Bloise et al., 2014). This is evident in the Precambrian basement parts of the study area.

5.5.5 Sodium (Na^+) and Potassium (K^+)

Sodium concentration in the groundwater of the study area varies from 2 to 285 mg/L, with a mean value of 36 mg/L (Table 5.2). About 2.5 % of the groundwater samples are above the maximum permissible limit, while 7% of the groundwater samples have concentrations below the mean concentration (Table 5.2). A high Na concentration above 200 mg/L give an unacceptable taste and make water unsuitable for domestic purposes (APHA, 2012; Kawo & Karuppannan, 2018; Vaiphei et al., 2020). The spatial distribution map of Na in the study area is presented in Figure 4d. The concentration of K in the groundwater of the study area varies from 0.1 to 96 mg/L with a mean value of 10 mg/L (Table 5.2). Approximately 6 % of groundwater samples have K concentrations above the WHO, (2018) maximum permissible limit (Table 5.2). Potassium is the most important element for human nutrition, with 10 mg/L in natural water (Adimalla & Taloor, 2020; APHA, 2012). Figure 5.3e shows the spatial distribution of K in KYB, with the sedimentary quaternary Chad formation region characterized by low K concentrations and higher concentrations are dominated in the Precambrian basement portion. This could be attributed to the presence of minerals in the

Precambrian basement such as feldspar which releases K ions into the groundwater during weathering. Relatively low concentrations of sodium were observed in the sedimentary Chad formation parts of the basin, whereas the western part, where the geology is Precambrian basement, has a higher concentration of Na^+ (Figure 5.3d), and low Ca (Figure 5.3b). The cation exchange process of Na with cations on the surface of minerals that replaces Ca with Na and the rock–water interaction in the groundwater system of the basin may be due to the high Na concentration. Moreover, high concentrations of Na and K were observed in the downstream rim of the basin due to intensive agricultural activities and the evaporative nature of the sedimentary quaternary portion of the study area.

5.5.6 Bicarbonate (HCO_3)

The concentration of bicarbonate (HCO_3^-) in the groundwater samples of the KYB varies from 1.5 mg/L to 379 mg/L, with a mean value of 120 mg/L (Table 5.2). Bicarbonate in groundwater is known to have no adverse health effects (Adimalla & Taloor, 2020; Vaiphei et al., 2020). The WHO, (2018) guideline for HCO_3 concentration in drinking water is 250 mg/L. Only 10.8 % of the groundwater have a bicarbonate concentration exceeding the threshold limit of 250 mg/L (Table 5.2). The spatial distribution of bicarbonate concentration shows an elevated level of HCO_3 in the Precambrian basement part, while lower concentrations were observed in the sedimentary quaternary Chad formation region of the study area (Figure 5.4a). The dissolution and weathering of calcite and dolomite minerals increases the concentration of bicarbonate ions in the groundwater in the Precambrian basement. A few spots in the sedimentary quaternary section of the study area show elevated levels of bicarbonate concentrations due to agricultural activities, which enhance the natural contents of bicarbonate ions in the groundwater system (Uddin et al., 2023).

5.5.7 Chloride (Cl) and sulfate (SO_4)

The concentration of chloride (Cl) and sulfate (SO_4) in the groundwater of the KYB varies from 0.7 to 372 mg/L, with a mean concentration of 48 mg/L, and from 0.1 to 133 mg/L, with a mean value of 15 mg/L, respectively (Table 5.2). Excessive chlorine in drinking water imparts a salty taste and signifies contamination from various natural and anthropogenic sources (Adimalla & Taloor, 2020). Chloride concentrations in about 2.5 % of the groundwater samples exceeded the WHO guidelines for drinking water (Table 5.2). However, most of the groundwater samples have Cl concentration above 50 mg/L. These high chloride concentrations may be attributed to pollution from domestic and industrial waste, leachate from dumpsites and septic tanks, animal waste, and agricultural fertilizer (APHA, 2012; Vaiphei et al., 2020). The spatial distribution of chloride concentration in the groundwater of the study area is presented in Figure 5.4b. Low Cl concentration was observed in the sedimentary quaternary Chad formation part of the study area except in a few locations receiving chlorides from agricultural practices and domestic waste, while the Precambrian basement portion is dominated by high Cl concentrations due to infiltration of chloride-bearing pollutant into the groundwater system. The spatial distribution of sulfate concentration in the groundwater of the study area is shown in Figure 5.4c. The WHO, (2018) guideline value for sulfate SO_4 in drinking water is 250 mg/L. All the groundwater samples are below the maximum permissible limit (Table 2, WHO, (2018)) Sulfates in the groundwater of the sedimentary quaternary parts of the basin are from the natural process of evaporation and anthropogenic activities such as artificial fertilizer applications, industrial effluents, and municipal waste. Meanwhile, the sulfate concentration in the Precambrian basement region could be from the dissolution of gypsum and other sulfate-bearing minerals in the groundwater systems (Vaughan, 2006).

5.5.8 Nitrate (NO_3) and Fluoride (F)

Groundwater NO_3 contamination is an important water quality issue globally (Adimalla & Taloor, 2020; Aladejana et al., 2021; Vaiphei et al., 2020; WHO, 2018). Nitrate in the groundwater arises from synthetic fertilizers and organic manures, leachate from dumpsites, septic tanks, landfills, and industrial and municipal waste (Eyankware et al., 2020). The nitrate concentration in Komadugu-Yobe basin varies from ND to 314 mg/L, with a mean value of 42 mg/L (Table 5.2). The maximum permissible limit of NO_3 concentration in drinking water is 50 mg/L (WHO, 2018). Groundwater with nitrate concentrations higher than the maximum permissible limits have been linked to an increased risk of methemoglobinemia (Adimalla & Taloor, 2020; WHO, 2018). About 30 % of the groundwater samples were above the WHO guidelines for nitrate (Table 2). The spatial distribution of nitrate in KYB is presented in Figure 5.4d. It is worth noting that high nitrate concentrations are visible in the Precambrian basement and the sedimentary quaternary formation of the study area. These high concentrations came from various anthropogenic pollutions in the study area as well as denitrification processes in the sedimentary parts of the study area. The concentration of F^- in the groundwater samples varies from ND to 2.3 mg/L, with a mean value of 0.3 mg/L (Table 5.2). About 2 % of the groundwater samples have a F concentration exceeding the maximum permissible limit (Table 2, WHO, (2018)), which renders them unsuitable for drinking purposes. Figure 5.4e shows the spatial distribution of fluoride in groundwater of KYB. The sedimentary Chad formation has groundwater with predominantly low fluoride concentrations, whereas elevated fluoride concentrations were observed in the Precambrian basement part of the basin. The dissolution of fluoride-bearing minerals and geothermal activities could be the possible source of fluoride in the Precambrian basement parts of the basin. Previous studies in Nigeria such as Akpata et al., (2009), Giwa et al., (2021), Malago et al., (2017), and Waziri et al., (2012) have suggested that high fluoride concentrations in northeastern and northwestern Nigeria are due to overexploitation of basement and quaternary aquifers. Ingestion of groundwater with high fluoride concentrations could lead to dental and skeletal fluorosis (Haritash et al., 2018; Yadav et al., 2009). Therefore, there is a need for further study of the risks associated with groundwater fluoride in the study area.

5.5.9 Geochemical Mechanism of Groundwater

Gibbs (Gibbs, 1970) showed that groundwater chemistry is controlled by three main natural processes: rock weathering/rock–water interaction, evaporation, and atmospheric precipitation. A Gibbs plot (Gibbs, 1970) reveals the interaction between groundwater, soil, and host rock (Adimalla & Venkatayogi, 2018; Eyankware et al., 2020; Marandi & Shand, 2018). Figure 5.5 presents the Gibbs plot of the Komadugu-Yobe basin, indicating groundwater chemistry is mainly controlled by rock weathering/rock–water interaction. The Gibbs ratios of the cations and anions of the groundwater varies from 0.2 to 0.95 and 0.1 to 0.9, with an average of 0.5 and 0.2, respectively, and suggest the area is dominated by silicate minerals (Malago et al., 2017; Vaiphei et al., 2020). Only 8% of the groundwater samples indicated precipitation and evaporation, and given the semi-arid climates, some evaporation in the northeastern part of KYB where the geology is sedimentary quaternary may also affect the chemistry of the groundwater.

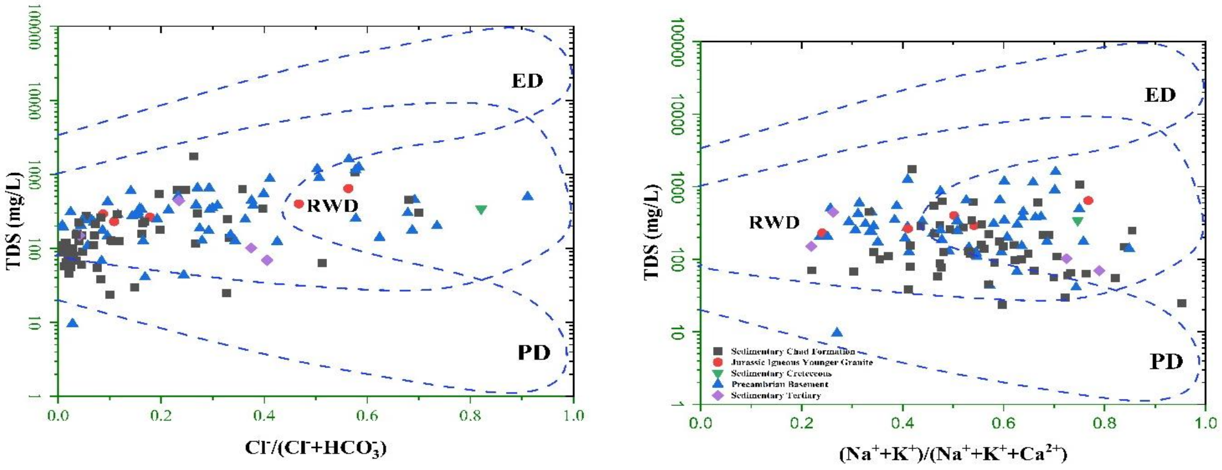

Figure 5.5 Gibbs plots showing the dominant geochemical mechanisms in KYB, (left): anions ratio and (right): cations ratio vs. TDS (mg/L). ED: evaporation dominance. RWD: rock weathering dominance. PD: precipitation dominance.

5.5.10 Groundwater Types and Hydrogeochemical Evolution

5.5.10.1 Piper Plot

The Piper trilinear diagram (Figure 5.6) for the Komadugu−Yobe basin uses major ions to classify groundwater into various hydrochemical types and identify influential factors involved in groundwater chemistry (Adimalla et al., 2018; Waghet al., 2019; Xiao et al., 2022). Figure 5.6 shows the cations of the groundwater are plotted in the calcium and sodium zones, while the anions are mainly plotted in the bicarbonate and chloride zone. About 59% of the groundwater samples were plotted in the Ca-Mg-HCO_3 water type. The order of dominance of the groundwater type in the basin is Ca-Mg-HCO_3 > Na-Cl> Na-HCO_3 > Ca-Mg-SO_4-Cl. This shows that the hydrochemical types resulted from the dissolution of carbonate-rich minerals and the weathering of silicate minerals within the aquifer systems of the Precambrian basement parts of the basin. The presence of a few Na-Cl and Na-HCO_3 water types may be due to rainfed agricultural activities taking place in both Precambrian and sedimentary quaternary parts of the study area. It is strongly believed that Na-HCO_3 enhances the presence and dissolution of fluoride in groundwater systems, particularly in the Precambrian basement geologic formation (APHA, 2012; Vaiphei et al., 2020; Wagh et al., 2019).

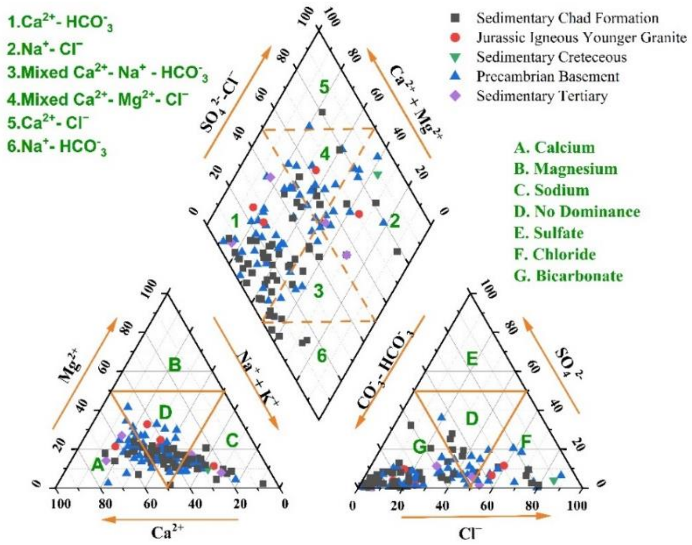

Figure 5.6 Piper diagram showing various water types in Komadugu−Yobe basin.

5.5.10.2 Chadha Diagram

The Chadha diagram was employed to assess the geochemistry of groundwater and various groundwater types in the Komadugu-Yobe basin. The Chadha plot shows the presence of Ca-Mg-HCO_3, Ca-Mg-SO_4-Cl, Na-Cl, and Na-HCO_3 water types in the study area (Figure 5.7). The Chadha diagram is a composite representation that integrates the Piper plot and the extended Durov diagram (Wagh et al., 2019). The Chaha plot best describes the permanent and temporary hardness domains of water (Eyankware et al., 2020). Figure 5.7 reveals that the alkaline earths exceeded the alkali metals and weak acids exceeded strong acids in the groundwater samples of KYB. The Chadha plot shows over half of the groundwater facies belong to the Ca–Mg–HCO_3 water type with temporary hardness dominated in the Precambrian basement parts of the study area. However, Na– HCO_3, Na– Cl, and Ca– Mg– Cl water types were also present in the groundwater of KYB. This could be attributed to dissolution and weathering of calcite and dolomite minerals in the Precambrian basement parts, as well as the influence of evaporation and anthropogenic activities in the sedimentary quaternary Chad formation section of the study area. This result agrees with what was observed in the Piper trilinear diagram (Figure 5.6).

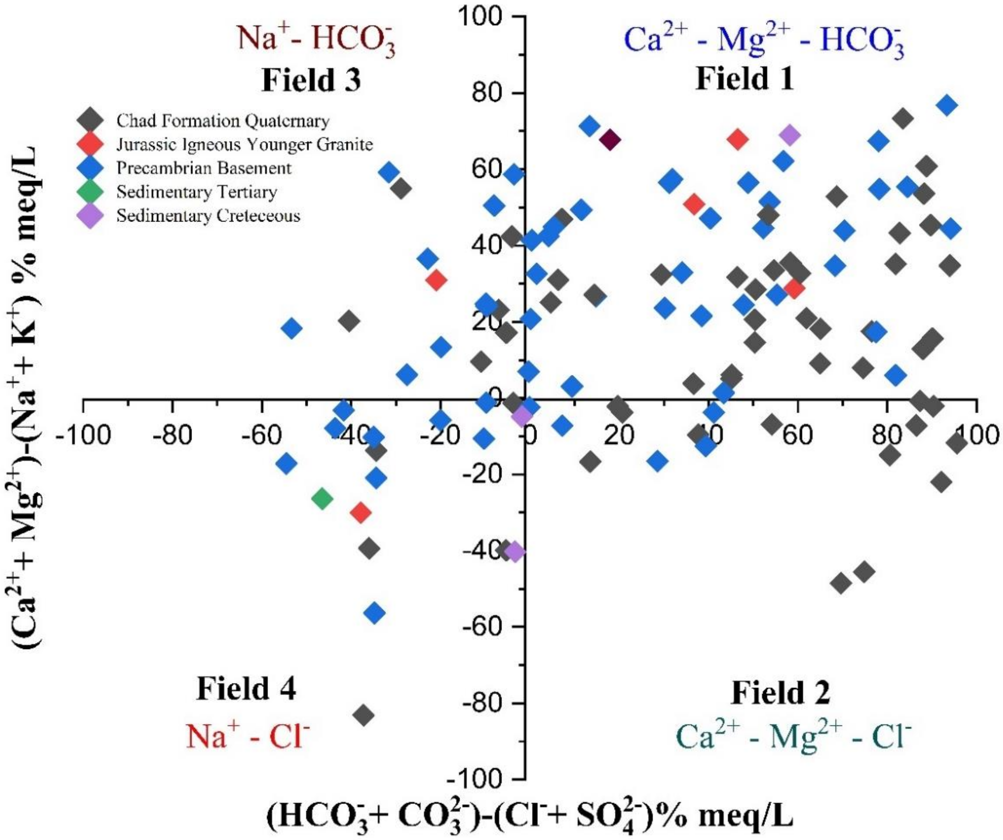

Figure 5.7 Chadha plot showing groundwater evolution in Komadugu-Yobe basin.

5.5.11 Groundwater Quality Index

The spatial distribution of the groundwater quality index in the Komadugu−Yobe basin is presented in Figure 5.8 and varies from 9 to 170, with an average value of 48 (Table 5.6). Groundwater in the study area can be categorized into five classes based on GWQI values: excellent water (GWQI < 50), good water (GWQI = 50–100), poor water (GWQI = 100–200), very poor water (GWQI = 200–300), and unfit for drinking (GWQI > 300) (Adimalla & Taloor, 2020; Vaiphei et al., 2020). The majority of the groundwater in KYB is excellent, constituting about 63%, with good and poor water classes constituting 27% and 10% respectively (Table 5.2, Figure 5.9). It was observed that the poor groundwater quality occurs in the Precambrian basement portion of the basin. This could be attributed to geogenic processes including weathering and dissolution of minerals, as well as anthropogenic pollution resulting from the extensive use of artificial fertilizers, indiscriminate discharge of effluent from local industries, leachates from dumpsites, septic tanks, and pit latrines.

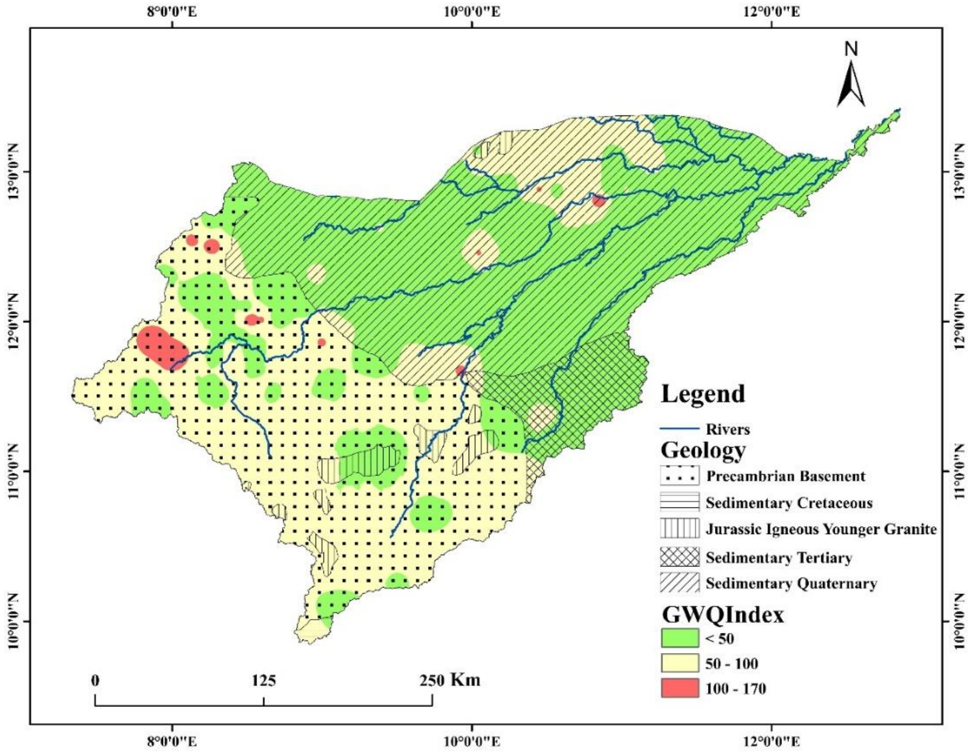

Figure 5.8 Spatial distribution of groundwater quality index in Komadugu–Yobe basin.

Table 5.6 Groundwater quality index (GWQI) in Komadugu-Yobe basin.

Sample Numbers	GWQI	Water Type	Sample Numbers	GWQI	Water Type
L1	79	Good	L63	74	Good
L2	49	Excellent	L64	51	Good
L3	74	Good	L65	125	Poor
L4	104	Poor	L66	76	Good
L5	41	Excellent	L67	9	Excellent
L6	82	Good	L68	62	Good
L7	20	Excellent	L69	15	Excellent
L8	18	Excellent	L70	20	Excellent
L9	24	Excellent	L71	62	Good
L10	82	Good	L72	46	Excellent
L11	39	Excellent	L73	38	Excellent
L12	29	Excellent	L74	61	Good
L13	18	Excellent	L75	41	Excellent
L14	17	Excellent	L76	49	Excellent
L15	19	Excellent	L77	61	Good
L16	14	Excellent	L78	73	Good
L17	156	Poor	L79	37	Excellent
L18	20	Excellent	L80	67	Good
L19	31	Excellent	L81	91	Good
L20	25	Excellent	L82	38	Excellent
L21	19	Excellent	L83	14	Excellent
L22	15	Excellent	L84	79	Good
L23	31	Excellent	L85	52	Good
L24	59	Good	L86	64	Good
L25	91	Good	L87	38	Excellent
L26	134	Poor	L88	15	Excellent
L27	170	Poor	L89	18	Excellent
L28	49	Excellent	L90	15	Excellent
L29	36	Excellent	L91	16	Excellent
L30	28	Excellent	L92	13	Excellent
L31	107	Poor	L93	17	Excellent
L32	150	Poor	L94	107	Poor
L33	14	Excellent	L95	58	Good
L34	37	Excellent	L96	30	Excellent
L35	27	Excellent	L97	14	Excellent
L36	65	Good	L98	14	Excellent
L37	107	Poor	L99	32	Excellent
L38	101	Poor	L100	26	Excellent
L39	23	Excellent	L101	103	Poor
L40	22	Excellent	L102	24	Excellent
L41	38	Excellent	L103	23	Excellent
L42	83	Good	L104	50	Good

Table 5.6 *cont.*

Sample Numbers	GWQI	Water Type	Sample Numbers	GWQI	Water Type
L43	34	Excellent	L105	18	Excellent
L44	64	Good	L106	40	Excellent
L45	49	Excellent	L107	30	Excellent
L46	32	Excellent	L108	33	Excellent
L47	58	Good	L109	28	Excellent
L48	71	Good	L110	52	Good
L49	23	Excellent	L111	25	Excellent
L50	32	Excellent	L112	19	Excellent
L51	39	Excellent	L113	18	Excellent
L52	27	Excellent	L114	24	Excellent
L53	40	Excellent	L115	58	Good
L54	54	Good	L116	16	Excellent
L55	110	Poor	L117	12	Excellent
L56	35	Excellent	L118	11	Excellent
L57	33	Excellent	L119	35	Excellent
L58	72	Good	L120	94	Good
L59	24	Excellent	Maximum	170	/
L60	36	Excellent	Minimum	9	/
L61	33	Excellent	Mean	48	/
L62	84	Good			

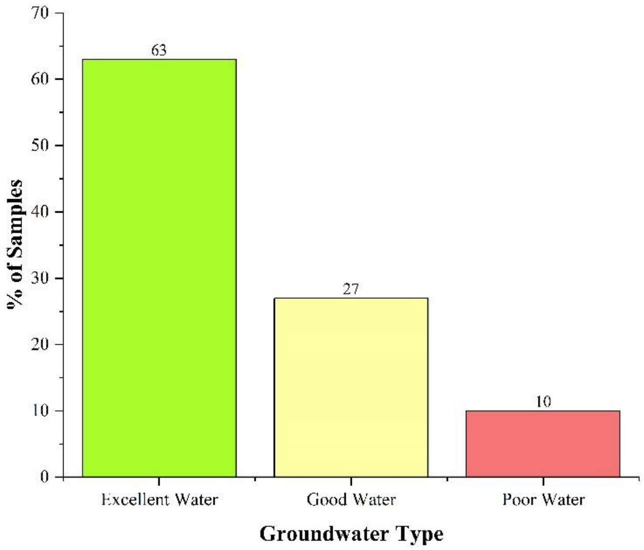

Figure 5.9 Groundwater quality index (GWQI) classification in Komadugu−Yobe basin.

5.6 Conclusion

This study presents the hydrogeochemical characteristics and suitability of groundwater resources for drinking purposes in the Komadugu-Yobe basin, Sahel region. This study analyzed 120 groundwater samples to determine the hydrogeochemical characteristics and overall quality of groundwater in KYB using Gibbs plots, hydrochemical facies plots, and groundwater quality index. The following are the key conclusions from this study:

- The order of the abundance of the major cations and anions in the groundwater samples is: Ca > Na > K > Mg and HCO_3 > Cl > NO_3 > SO_4 > F, respectively. More than 90 % of groundwater samples have Na, Ca, Mg, K, Cl, and SO_4 and total hardness within the WHO, (2018) maximum permissible limits. However, some locations show high F and NO_3 concentrations, largely in the Precambrian basement region and a few locations in the sedimentary formation parts of the study area.

- The chemistry of the major ions in the groundwater samples of the study area is predominantly (92%) influenced by weathering/rock–water interaction.

- Ca-Mg-HCO_3 is the most prevalent hydrochemical facies of groundwater in KYB accounting for more than half (59%) of the groundwater samples. The order of dominance of the groundwater type of the study region is Ca-Mg-HCO_3 > Na-Cl > Na-HCO_3 > Ca-Mg-SO_4-Cl. The Na-HCO_3 groundwater type may promote fluoride dissolution, perhaps contributing to fluoride enrichment in groundwater in some parts of the Precambrian basement complex and the sedimentary Chad formation of the study area. The Piper trilinear plot findings agree with the Chadha diagram results.

- Based on GWQI, the groundwater in the study area is generally of excellent (63%) to good quality (27%) with only 10% exhibiting poor quality. The Precambrian basement complex region of the study basin has the most significant presence of good and poor water quality classes.

5.7 Postface

This chapter has addressed and fulfilled RQ1 “What is the general hydrochemical characteristics of groundwater in KYB and its suitability for drinking purposes?” by publishing a paper in a peer-reviewed journal. The chapter first addressed SO1 “Conduct a case study to determine the suitability of groundwater for drinking purposes by comparing groundwater quality parameters with world health organization drinking water guidelines in KYB”. The suitability of groundwater for drinking purpose was investigated by comparing various water quality parameters with World Health Organization (WHO, 2018) drinking water guidelines. The case study addressed SO2 “Conduct a case study on groundwater quality index analysis to classify groundwater potability”. The groundwater of Komadugu-Yobe basin was categorised into 5 classes from excellent water classes to unsuitable water classes (section 5.5.11). The spatial distribution of groundwater quality parameters was developed using geospatial analysis which shows how quality of groundwater varies over the spread of the basin (SO4). This enabled developing an effective strategy toward sustainable management of groundwater in the study area. This chapter also addressed SO3 “With the aid of Piper trilinear diagram and Chadha plot, identify various groundwater facies and water types in the basin”. The predominant water types were identified and discussed (Section 5.5.10). The Na-HCO_3 groundwater type predominates some parts of Precambrian basement complex and sedimentary quaternary which may promote fluoride dissolution, and perhaps contributing to fluoride enrichment in groundwater.

The next chapter will continue to use Komadugu-Yobe basin as case study and explore an integrated approach of chemometric analysis and geochemical modelling to identify and discuss factors controlling the geochemical evolution of groundwater as well as the hydrogeological processes and origin/source of various chemical constituents present in groundwater of the study area which will enable the development of a simplified conceptual model for hydrogeochemical processes governing the groundwater chemistry in Komadugu-Yobe basin.

6 Geochemical Evolution and Mechanisms Controlling Groundwater Chemistry in Komadugu–Yobe Basin, Sahel Region: An Integrated Approach of Geochemical Modeling and Chemometric Analysis[2]

6.1 Preface

In the previous chapter (chapter 5), we have identified gaps in hydrochemical characterization and water quality analysis and make a case study for a detailed study integrating hydrochemical assessment, water quality analysis and geospatial analysis to ascertain the overall hydrogeochemistry and groundwater quality in Komadugu-Yobe basin. This was achieved by first analysing for major ions in the groundwater samples and employing a methodology that combines hydrochemical characterization and water quality indices analysis. The suitability of groundwater for drinking purposes was investigated by comparing various water quality parameters with WHO, 2018 guidelines. It also highlighted the link between geology and hydrochemical characteristics, groundwater facies and groundwater quality index over the entire basin. It provided basic information required for sustainable management of groundwater resources in the basin.

This chapter will now answer RQ2: "What role can chemometric analysis and geochemical modelling play in assessing geochemical evolution and mechanisms influencing groundwater chemistry as well as origin/source of chemical constituents in groundwater of Komadugu-Yobe basin?". A methodology of geochemical modelling was employed to investigate geochemical evolution and mechanisms controlling the groundwater chemistry (SO6). This was applied to Komadugu-Yobe basin case study where we identified various geochemical mechanisms and hydrochemical processes controlling the chemistry of groundwater. The results indicated rock weathering/rock-water interaction is the dominant mechanism influencing the groundwater chemistry. The research question was also addressed through SO7: 'Conduct a case study to determine the source extent of chemical parameters in groundwater using chemometric analysis approach'. Multivariate statistical analysis involving Pearson's correlation analysis, Principal Component Analysis (PCA), and Hierarchical Cluster Analysis (HCA) were applied to identify the sources of chemical elements present in the groundwater. This chapter also explore the impact of seasonal variability on groundwater hydrochemical processes and overall quality (SO8). Alongside investing geochemical evolution and mechanisms controlling the chemistry of groundwater in the basin, groundwater samples of wet and dry season were compared to ascertain the effect of seasonal variability in the geochemistry of the groundwater. A conceptual model for geochemical evolution and hydrogeochemical processes of groundwater in Komadugu-Yobe basin was developed (SO9).

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Paper Reference

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Authors Contribution

Conceptualization (A.S. and R.M.K.), methodology (A.S.), software (A.S., L.C.B., and I.M.L.), validation (A.S., R.M.K., and V.P.), formal analysis (A.S.), investigation (A.S.), resources (A.S.) data curation (A.S.), writing—original draft preparation (A.S.), writing—review and editing (A.S., R.M.K., V.P., L.C.B., and I.M.L.), visualization (L.C.B. and I.M.L.), supervision (R.M.K. and V.P.), project administration (A.S.), funding acquisition (R.M.K. and A.S.).

6.2 Abstract

Study region: The study is conducted in the transboundary Komadugu–Yobe Basin, Lake Chad region, a critical groundwater resource shared across national boundaries of Nigeria and Niger Republic.

Study focus: The research investigates geochemical evolution and sources of chemical constituents in groundwater through an integrated methodology that integrates geochemical modeling, molar ratios, bivariate plots, and chemometric analysis. Groundwater samples ($n = 240$) were collected during wet and dry seasons to identify seasonal variations and the impact of geogenic and anthropogenic processes on groundwater quality.

New hydrological insights: The findings revealed that Cl and NO_3 are associated with anthropogenic pollution. The Principal Component Analysis identified three main components associated with geogenic and anthropogenic processes, agricultural pollution, and mineral weathering. Hierarchical Cluster Analysis highlighted geogenic, anthropogenic, and evaporative influences. Groundwater in the basin is predominantly of Ca–HCO_3 and Na–Cl types and is significantly undersaturated with calcite, dolomite, and fluorite, though seasonal variations show saturation in some samples. Elevated partial pressures of CO_2 (pCO_2) above atmospheric pCO_2 in nearly all samples suggests active biogeochemical processes. Moreover, Gibbs plots, molar ratios, and bivariate plots, along with chloroalkaline indices (CAI-I &CAI-II) confirms influence of mineral weathering and ion exchange reactions within the aquifer system. Few locations show evaporation during the dry season. This study provides valuable insights for sustainable management of groundwater resources in semi-arid and arid regions.

Keywords

Groundwater quality, Multivariate statistical analysis, Geochemical modeling, Hydrogeochemical characteristics, Anthropogenic process.

6.3 Introduction

Geochemical modeling and chemometric analysis of groundwater quality is paramount for groundwater sustainability. The demand for potable freshwater has significantly increased worldwide due to population growth, intensive agriculture, and pollution of surface and groundwater from both geogenic and anthropogenic activities (Awaleh et al., 2024; Elumalai et al., 2020; Mohammed et al., 2022; Samtio et al., 2023; Sikakwe & Eyong, 2022; Yang et al., 2021; Zhang et al., 2020). Groundwater provides drinking water supply for over one-third of the world's population (Ismail et al., 2020; Sheng et al., 2022). As a result, groundwater is overexploited globally, exposing it to significant risk of pollution and quality/quantity degradation (Elumalai et al., 2022; Ha et al., 2022; Mohammed et al., 2023; Sarti et al., 2021; Sheng et al., 2022; Yang et al., 2021). Consequently, groundwater quality is impacted by both natural and anthropogenic processes (Jabbo et al., 2022; Mohammed et al., 2023; Samtio et al., 2023; Subba Rao & Chaudhary, 2019) including factors such as leachate from dump sites, overexploitation of wells, accidental oil spillages, effluent from industries, residential wastewater, sewage, and intensive use of synthetic fertilizer (Awaleh et al., 2024; Shuaibu et al., 2024; H. Zhang et al., 2023). Natural processes that influence groundwater chemistry include rock–water reactions, oxidation–reduction, precipitation and dissolution of aquifer materials, and groundwater recharge and discharge processes (Elumalai et al., 2022; Jehan et al., 2019; Sikakwe & Eyong, 2022; Wali et al., 2019).

Groundwater is essential in arid and semi–arid regions (Elumalai et al., 2019; Loh et al., 2020; Mohammed et al., 2022). Aquifers in Komadugu–Yobe basin (KYB) are at risk of depletion and degradation due to overexploitation, climate change impacts, and pollution from geogenic and anthropogenic activities such as urbanization, industrialization, leachate from dumpsites, and indiscriminate discharge of solid wastes and wastewaters to the environment (Goni et al., 2019; Jagaba et al., 2020; Wali et al., 2020). Groundwater overexploitation in this region for domestic and irrigation water supply makes the aquifers vulnerable to depletion and quality degradation. The primary occupation of the residents in KYB is agricultural, including rain–fed and irrigation farming, contributing significantly to the food requirements in Nigeria (Adeyeri & Arnault, 2020; Ahmed et al., 2018; Descloitres et al., 2013). It is crucial to know if groundwater in the basin meets the necessary quality standards for various uses. Several studies have recently been conducted in Komadugu–Yobe basin to evaluate groundwater quality (Abubakar et al., 2018; Bura et al., 2018; Garba et al., 2018; Goni et al., 2023; Hamidu et al., 2017; Ibrahim et al., 2021; Jagaba et al., 2020; Shuaibu et al., 2024; Suleiman et al., 2022). In contrast, geochemical modeling and chemometric analysis of groundwater at the regional scale remain challenging and had not yet been thoroughly investigated in the basin.

Geochemical modelling and chemometric analysis were employed in various studies worldwide to determine geochemical evolution and mechanisms influencing groundwater chemistry (Banda et al., 2024; Ding et al., 2024; Elumalai et al., 2019; Ha et al., 2022; Mohamed et al., 2022; Sikakwe et al., 2020; Spellman et al., 2024; Wang et al., 2024; Yang et al., 2021; Zhang et al., 2023). Chemometric analysis involves investigation of various water quality variables in a large hydrochemical data set simultaneously, compared to the univariate method, which involves evaluation of each variable in hydrochemical data set individually/using graphical methods (Liu et al., 2020; Rezaei et al., 2020; Sikakwe et al., 2020). The most effective way to examine hydrogeochemical datasets is by categorizing them into geospatial clusters with similar characteristics using chemometric analysis (Liu et al., 2020). It facilitates understanding the origin of dissolved ions in aquifer systems (Abdelaziz et al., 2020; Asomaning et al., 2023; Gautam et al., 2022; Liu et al., 2023; Sarti et al., 2021; Ullah et al., 2022). Graphical methods for assessing hydrochemical data are enhanced by employing multivariate statistical analysis (Gautam et al., 2022; Sikakwe et al., 2020; C. K. Singh et al., 2017). PCA is useful in reduction of large datasets into components and in assessing the interrelationship between different hydrochemical characteristics of analyzed water samples to understand sources and extent of pollution (Jehan et al., 2019; Wali et al., 2019). HCA is useful in identifying groups with similar characteristics in hydrochemical datasets (Elumalai et al., 2019; Kumar et al., 2018; Zhou et al., 2024). Groundwater geochemistry is usually influenced by geogenic processes and anthropogenic activities. Various factors, including aquifer lithology, travel time of groundwater, geological formations, sewage, effluent, leachates, and agrochemical applications, makes geochemical characterization of groundwater complex (Liu et al., 2020). However, the chemical reactions between water and minerals, as well as nature and characteristics of water that recharges the aquifer influences the hydrochemical characteristics of groundwater (Chen et al., 2020; Elumalai et al., 2020; Gautam et al., 2022; Kalin, 1996; Singh et al., 2017). Therefore, the interaction between water and mineral components of aquifer defines the general geochemistry of groundwater, providing valuable information on rock–water interaction process (Bradai et al., 2022; Kalin and Long, 1993).

The transboundary Komadugu-Yobe basin, located in the Lake Chad region, is characterized by intensive rainfed and irrigated agriculture, along with various industrial and domestic activities. The main source of water supply in this region is groundwater. Consequently, its significant exploitation results in a wide range of regional environmental problems, including degradation of groundwater quality/quantity. Although several studies have investigated groundwater quality in the transboundary Komadugu-Yobe basin, there has been limited research using integrated geochemical modelling and chemometric analysis on a regional scale. Previous studies in the basin focused on localized assessments of groundwater contamination, overlooking broader hydrogeochemical processes and various groundwater contamination sources. Therefore, this study has uniquely applied a combination of geochemical modelling, bivariate plots, molar ratios, and chemometric analysis to understand both geogenic and anthropogenic influences on groundwater chemistry at a basin-wide scale. It offers new insights into the impact of mineral weathering, ion exchange, and pollution from domestic and agricultural activities on groundwater quality, providing a comprehensive understanding that is critical for sustainable groundwater management. A conceptual model for groundwater evolution and distribution of geochemical processes controlling groundwater chemistry in KYB was established. The findings from this study are expected to support stakeholders and decision–makers in developing new insights into regional-scale groundwater management strategies in transboundary Komadugu–Yobe basin and the wider Lake Chad region.

6.4 The study area

6.4.1 Study Area Settings

The study area is the transboundary Komadugu–Yobe basin, a sub–basin of greater Lake Chad basin (Figure 6.1a). The basin covers approximately 150,000 km^2. The topographic elevation of the basin varies from 294 m in Yobe to 1750 m in Jos. The Komadugu Gana and Komadugu Yobe river systems flow through Yobe river and drains into Lake Chad (Adeyeri et al., 2019; Gana et al., 2018). The Hadejia Nguru wetlands and its associated river systems support different economic activities such as agriculture, fish production, pastoralism, and trading to over 20 million people residing in the basin (Adeyeri et al., 2020; Ahmed et al., 2018). KYB has national and international value due to its various internationally shared water resources and wetlands, which boosts local, national, and international economies and requires transboundary integrated water resource management among several countries in the Lake Chad region (Adeyeri et al., 2020). The climate in the basin is arid to semi–arid, characterized by frequent droughts, significant rainfall variability, and intense evaporation (Adeyeri et al., 2019; Goes, 1999). The basin has an average annual temperature of 12 ◦C in December and January and 40 ◦C in the months of March and April. The basin has a relative humidity of about 40 % per year. A mean annual precipitation of 1360 mm is estimated in Jos, whereas an estimate of 400–600 mm were recorded in Nguru and Hadejia, occurring in April to September. Mean annual evapotranspiration rate of 203 mm/year was estimated in the basin (Adeyeri et al.,2017; Shuaibu et al., 2023). The basin is characterized by arable land, and the vegetation in the basin is dominated by a variety of shrubs, dense grasses, and grasslands with scattered trees (Adeyeri et al., 2019).

6.4.2 General geology and hydrogeology

Geologically, the basin mainly consists of Precambrian basement complex rocks, sedimentary quaternary formations and Jurassic younger granites (Figure 6.1b). The Precambrian basement complex comprises crystalline rocks of Pan–African orogeny that have been exposed and overlain by younger rocks (Schuster et al., 2009). These rocks consist of migmatite–gneiss, schists, and Pan–African granites that are mostly igneous and metamorphic rocks characterized by shallow weathered basement of low permeability. The mineral composition of the Precambrian basement complex are plagioclase, quartz, and biotite. The Precambrian basement is overlain by Paleozoic to quaternary sediment deposits in the north-east (Figure 6.1c). Jurassic younger granites comprise syenites, biotite granites, gabbros, ignimbrites, and rhyolites form ring dyke structures around Ningi, Dutse, Shira, Birnin–Kudu and Riruwai. The mineralogical composition of the younger granites are pyroxene, olivine, amphibole, quartz, biotite and plagioclase. The stratigraphical sequence of sediment accumulation overlying the basement complex is the Paleozoic, lower Cretaceous, Middle Cretaceous, Continental Hamadien, upper Cretaceous, and Continental Terminal (Maduabuchi et al., 2006; Obaje et al., 2004). The sedimentary quaternary consists of a fine to coarse grained sand with an alternation of sandy Aeolian deposits. The valley consists of clayed to sandy fluvial sediments. The sedimentary basin pattern formed a complex subsurface deposit intercalated with sandy to clayey layers (Descloitres et al., 2013; Le Coz et al., 2011). The Chad formation has been continuously sedimented from the Late Miocene to the present, resulting in the deposition of Aeolian sand and clay elements (Shuaibu et al., 2022; Wali, Dankani, et al., 2020). Sand dunes and various alluvial deposits occurs in the Sedimentary Quaternary parts of the basin as a superficial deposits as parallel ridges extending several kilometers with a depth of 15 to 20 m which influence the river system around Kafin–Hausa, Miga, Jahun, and Auyo in the basin.

The primary source of groundwater in the basin is weathered basement, fracture basement and Plio–Pleistocene argillaceous sequence of Chad Formation with minor arenaceous horizons and recent Quaternary sediments (Figure 6.1c). The basin has three distinct aquifer zones in the north-eastern parts: upper aquifer, middle aquifer, and lower aquifer (Goni, 2006). The upper and middle aquifers are accessible for exploitation. However, alluvial deposits on the river floodplains along Hadejia River and Hadejia–Nguru wetlands provides groundwater at shallow depth through tube wells (Tukur et al., 2018). The upper unconfined aquifer zone consists of quaternary deposits, including sands from the lake edge and alluvial fans/deltaic sediments of varied sizes. The aquifer comprises three distinct units: an upper A unit, which is below the water table, and two other units, namely the upper B and C units, ranging from semi–confined to confined (Bura et al., 2018; Goni, 2006). The thickness of the upper aquifer varies from 15 to 100 m with depth to water table of around 20 m. This aquifer is recharged through rainfall runoff and has a transmissivity varying from 0.6 to 8.3 m^2/day (Maduabuchi et al., 2006). The middle aquifer is composed of sand beds 10 to 40 m thick interbedded with clay and diatomites, as well as sand fractions of moderately coarse to finer quartz, feldspar, mica, and feoxides. The average transmissivity of the middle aquifer is about 360 m^2/day whereas the lower aquifer has a transmissivity value ranging from 33 to 105 m^2/day.

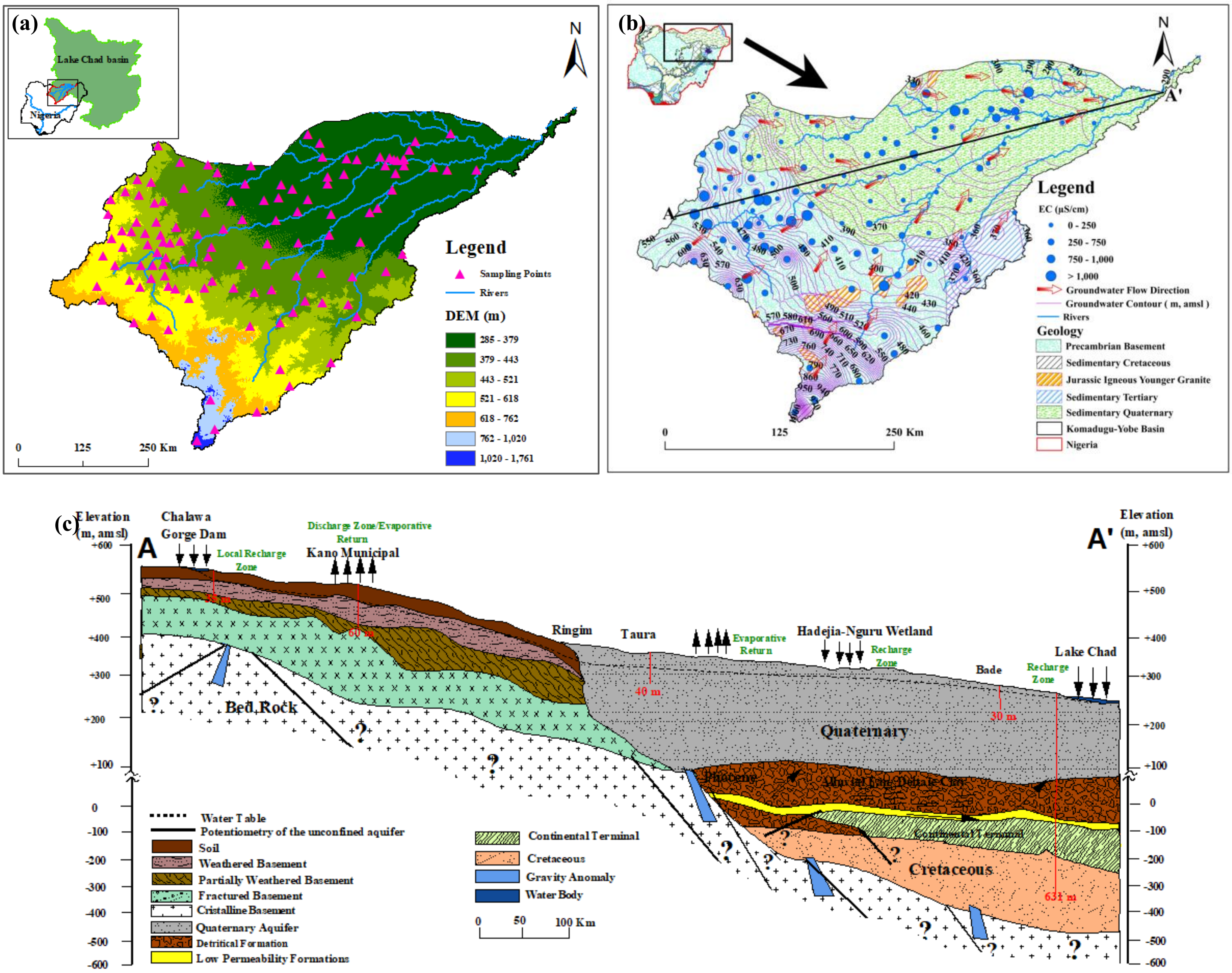


Figure 6.1 (a) Study area map showing sampling locations, various Rivers and digital elevation model. The pink triangles represent groundwater sampling points (b) Generalised geological map showing groundwater flow direction and various geologic types (c) Hydrogeological cross–section A-A′ of Komadugu–Yobe basin showing different lithologies, groundwater recharge and discharge zones and the groundwater table.

The Komadugu–Yobe River exhibits a seasonal flow pattern mainly between the months of June and December (Descloitres et al., 2013). Groundwater availability is dominant in the southern parts while the northeastern parts have some surface water resources. Groundwater flow is directed from southern parts of the basin to the northeastern parts towards the Lake

Chad (Figure 6.1b). The flow of groundwater in basement complex aquifer system is highly localized. Recharge likely occurs in the Southern part around Chalawa gorge dam while the discharge and evaporative return occur around Kano towards Ringim. Moreover, recharge in the North-eastern parts is predominant around the Hadejia-Nguru wetlands through Komadugu-Yobe valley and Lake Chad region. Groundwater recharge is focused at wetlands and Komadugu–Yobe valley and through seepage from river channels and as infiltration of floodwater and runoff along the Yobe floodplain (Carter & Alkali, 1996; Le Coz et al., 2011; Maduabuchi et al., 2006).

6.5 Materials and methods

6.5.1 Groundwater sampling and laboratory analysis

In this study, 240 groundwater samples were collected in 50 mL polyethylene bottles from 120 boreholes and hand-dug wells over two sampling campaigns in August and September 2021 (wet season) and March and April 2022 (dry season) in KYB. Wells were pumped for a minimum of 5 minutes before sampling at each location to ensure the collection of samples free from contamination by borehole pipes and stagnant water. Prior to sampling, each sample bottle was rinsed twice with groundwater from the respective well. Groundwater samples were then filtered through a 0.45 μm acetate cellulose syringe filter into two 50 mL polyethylene bottles: one bottle was acidified with 0.4 mL of nitric acid for cation analysis, while the other bottle, reserved for anion analysis, was left unacidified. Groundwater samples were sealed with watertight lids and kept below 4 ◦C in icebox coolers until laboratory analysis in Civil and Environmental Engineering Laboratory, University of Strathclyde, Glasgow, UK. Locations of each sampled well were marked using a handheld portable global positioning system (GPS) and plotted on Figure 6.1a. Prior to water samples collection, the pH, electrical conductivity (EC) were measured in–situ at each sampling location with hand–held digital electrical conductivity meter (Model 99720 pH/Conductivity meter). The equipment was calibrated using standard solutions before measurement. Total alkalinity was measured in–situ using a HACH digital alkalinity titrator (Model 16900, HACH International, Loveland, CO, USA). The major cations (Na, K, Ca, Mg and Fe) were analysed with inductively coupled plasma optical emission spectrometry (ICP–OES, iCAP 6200, Thermo Fisher Scientific), while analysis of the anions (Cl, F, SO_4, NO_3) was achieved using ion chromatography instrument (Metrohm 850 Professional IC).

6.5.2 Quality control and assurance

The quality of the fieldwork followed standard procedures to ensure the integrity of groundwater samples and in–situ measurements. The field equipment were calibrated before the start of field measurement using standard solutions and procedures. The preventive course of action and standard operating procedures (SOP) were adhered to in the field, throughout transportation, preservation, and in laboratory analysis to avoid sample aging and cross–contamination as recommended by APHA, (2012). Laboratory analysis accuracy and precision were confirmed by running standards and blanks. Finally, the reliability and accuracy of hydrochemical data were ensured by assessing ionic balance error, which was within the acceptable threshold of ± 10 % with significant percentage of wet and dry season samples below ± 5 %.

6.5.3 Multivariate statistical analysis (Chemometric methods)

Various hydrogeochemical studies conducted globally employed chemometric approaches, including correlation matrix analysis, PCA, and HCA (Kumar et al., 2018; Liu et al., 2023; Samtio et al., 2023; Singh et al., 2017; Subba Rao & Chaudhary, 2019; Ullah et al., 2022; Yang et al., 2021). These methodologies are employed to evaluate overall water quality by identifying pollution sources and to effectively disseminate water quality information (Rezaei et al., 2020). The Pearson's correlation analysis, PCA, and HCA were performed in this study using Origin Pro 2023b to determine the interrelationship of hydrochemical parameters and pollution source distribution of groundwater in Komadugu–Yobe basin.

6.5.3.1 Pearson's correlation analysis

Pearson's correlation analysis was employed to classify groundwater quality variables and ascertain their interrelationships (Ullah et al., 2022). Pearson's correlation analysis was applied to identify anthropogenic activities and underlying rock properties that affect groundwater chemistry. Major ions, such as nitrate, sulfate, sodium, and chloride, get into groundwater aquifers through municipal waste, the application of synthetic fertilizer in agricultural lands, and organic and inorganic wastes (Wali et al., 2019; Yang et al., 2021).

6.5.3.2 Principal component analysis (PCA)

PCA was used to elucidate the relationship between large number of groundwater quality parameters (Kumar et al., 2018; Liu et al., 2023). It was applied in this study to identify potential sources of pollution, and statistical independent source tracers were chosen using Varimax rotation method with Kaiser normalization (Kumar et al., 2018; Yadav et al., 2020). The PCA was carried out on 13 groundwater quality variables, namely: pH, EC, TH, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-}, NO_3^-, F^-, and Fe. The basic steps followed in the PCA are the standardization of data and extraction of principal components (PCs) (Wali et al., 2019). Principal components (PCs) with eigen value >1 were extracted from the scree plot. The variables in the respective components with higher loading were considered of greater significance regardless of sign. PCs are categorised into three classes: weak (0.30–0.50), moderate (0.50–0.750) and strong (>0.75) (Kumar et al., 2018).

6.5.3.3 Hierarchical clustering analysis (HCA)

This study adopted HCA to classify the groundwater into groups that are similar to each other (Lima et al., 2019). Moreover, the study employed the R and Q–mode HCA using Ward's approach (minimal variance) to find the best clusters (groups) and for comprehensive result interpretation. Distance between samples were measured by squared Euclidean distance (Eq. (6.1)). Dendrograms are widely used to show hierarchical clustering or grouping together with the associated linkage distances (Subba Rao & Chaudhary, 2019). The cohesiveness and correlation between the hydrochemical parameters and groundwater samples were observed by constructing a dendrogram.

$$d_{xy} = \sum_{j=1}^{p} (x_j - y_j) \qquad 6.1$$

where dxy represents squared Euclidean distance between two points, x and y, in p–dimensional space. j is used to define each individual parameter (Kumar et al., 2018).

6.5.4 Geochemical modelling

Groundwater chemistry is mainly influenced by factors including structure and composition of mineral, and rock–water equilibrium (Elumalai et al., 2022; Kumar et al., 2018). Saturation index (SI) elucidates the equilibrium between water and minerals (Eq. (6.2)). The groundwater saturation indices for KYB were determined using Geochemist's WorkBench GWB software 17.0. SI value of zero shows that mineral saturation is in equilibrium in the aquifer, whereas positive value of SI signifies over–saturation of minerals in water and negative SI value signifies under–saturation of minerals in water.

$$SI = log\left[\frac{IAP}{K_{SP}}\right] \qquad 6.2$$

IAP represents the ion activity product in the solution, while K_{SP} represents the solubility product or equilibrium constant of the reaction.

6.5.5 Chloro–alkaline indices (CAI)

The chloroalkaline indices (Eqs. (6.3) and (6.4)) were used to study ion exchange reactions occurring within aquifers of the study area. These indices were used in various studies to better understand general groundwater chemistry, ion exchange mechanisms, and rock–water interactions (Chen et al., 2020; Elumalai et al., 2022; Liu et al., 2023; Mohamed et al., 2022; Sikakwe & Eyong, 2022).

$$CAI - I = \frac{Cl^{-} - (Na^{+} + K^{+})}{Cl^{-}} \tag{6.3}$$

$$CAI - II = \frac{Cl^{-} - (Na^{+} + K^{+})}{SO_4^{2-} + HCO_3^{-} + CO_3^{2-} + NO_3^{-}} \tag{6.4}$$

Where all ions are measured in meq/L.

6.6 Results and discussion

6.6.1 Hydrochemical characteristics

The hydrochemical characteristics of the groundwater in KYB are presented in Table 6.1. The concentration of hydrochemical parameters in wet and dry seasons groundwater samples displayed a wide variation. pH values varied from 5.52 to 8.24 with a mean of 7.2 in wet season and those of dry season varied from 4.81 to 8.30 with a mean of 6.4 indicating acidic to weak alkaline water in respective seasons. EC ranges from 15 to 2746 µS/cm, with an average of 462 µS/cm and 54 to 3560 µS/cm, with a mean of 538 µS/cm in wet and dry season respectively. A significant number of samples in both seasons have EC values < 1500 µS/cm, while some samples have EC value between 1500 to 3000 µS/cm and a few of dry season samples have EC > 3000 µS/cm. Therefore, the groundwater in this region is largely fresh to brackish water in both seasons. The total hardness (TH) values of wet season samples varied from 0.8 to 704 mg/L as $CaCO_3$, with a mean of 138 mg/L as $CaCO_3$. Most of the groundwater samples in both seasons appeared to be soft. However, few samples range from hard to very hard waters in respective seasons. The major ions dominance occurs in an order of Ca > Na > K > Mg > Fe and HCO_3 > Cl > NO_3 > SO_4 > F for cation and anion and Ca > Na > Mg > K > Fe and NO_3 > HCO_3 > Cl > SO_4 > F for cation and anion in wet and dry seasons respectively. This variation in concentration is likely due to various anthropogenic and geogenic processes taking place within the study area. The hydrogeochemical analysis suggests that the wet season groundwater is mainly characterized by Ca, HCO_3^- and Na, Cl ions and those of dry season were dominantly characterized by Ca, HCO_3 and Na, NO_3 ions. This resonates with the findings of Wang et al., (2024) that the main cation and anions in the groundwater of Hutuo River alluvial-pluvial fan in China were Ca and HCO_3. Similarly, Samtio et al., (2023) identified Ca, Na, HCO_3 and Cl as the main cation and ions in the groundwater of chachro sub-district in Pakistan. The dominance of these ions in the groundwater of the study area could possibly reflects the influence of rock-water interaction and dissolution processes of plagioclase, amphibole, pyroxene, orthoclase and biotite rock minerals as well as contamination from irrigation return flows, synthetic fertilizers, potassium compost, domestic and industrial discharges, leachates and nitrification from pit latrines (Shuaibu et al., 2024; Subba Rao et al., 2022; Yu et al., 2024). It is worth noting that the high nitrate concentrations shown in Table 6.1 during the wet and dry seasons were measured in open dug wells and boreholes, where significant pollution is attributed to agricultural activities and leachate from unimproved pit latrines, particularly in the downstream areas of the basin. This corroborates with the findings of Goni et al., (2023) in parts of the Hadejia-Jama'are-Komadugu-Yobe Basin, where a high nitrate concentration of approximately 1003 mg/L was measured in a dug well affected by agricultural pollution.

Table 6.1 Descriptive statistics of hydrochemical parameters of wet and dry seasons groundwater.

Parameters	Wet Season			Dry Season		
	Range	Mean	Std Dev.	Range	Mean	Std Dev.
pH	5.52–8.24	7.2	0.6	4.81–8.30	6.41	0.5
EC	15–2,746	462	470	54–3,560	538	590
TH	0.8–704	138	125	5–1,280	139	180
Na	2–285	36	45	1.8–247	33	40
K	0.1–96	10	20	0.7–173	9	20
Ca	0.2–227	39	35	1.6–399	40	55
Mg	0.9–58	9.9	10	0.2–69	9.2	10
Cl	0.7–372	48	70	1.6–645	58	90
HCO_3	1.5–379	120	85	0–220	64	45
SO_4	0.1–133	15	20	0.1–226	16	30
NO_3	ND–314	42	55	0.1–927	65	140
F	ND–2.3	0.3	0.5	0.5–2.4	0.7	0.5
Fe	ND–19	0.98	3.0	ND–12	0.66	2.0

Note: All units are in mg/L except for dimensionless pH, TH in mg/L as $CaCO_3$, and EC in µS/cm. Std Dev.: Standard Deviation.

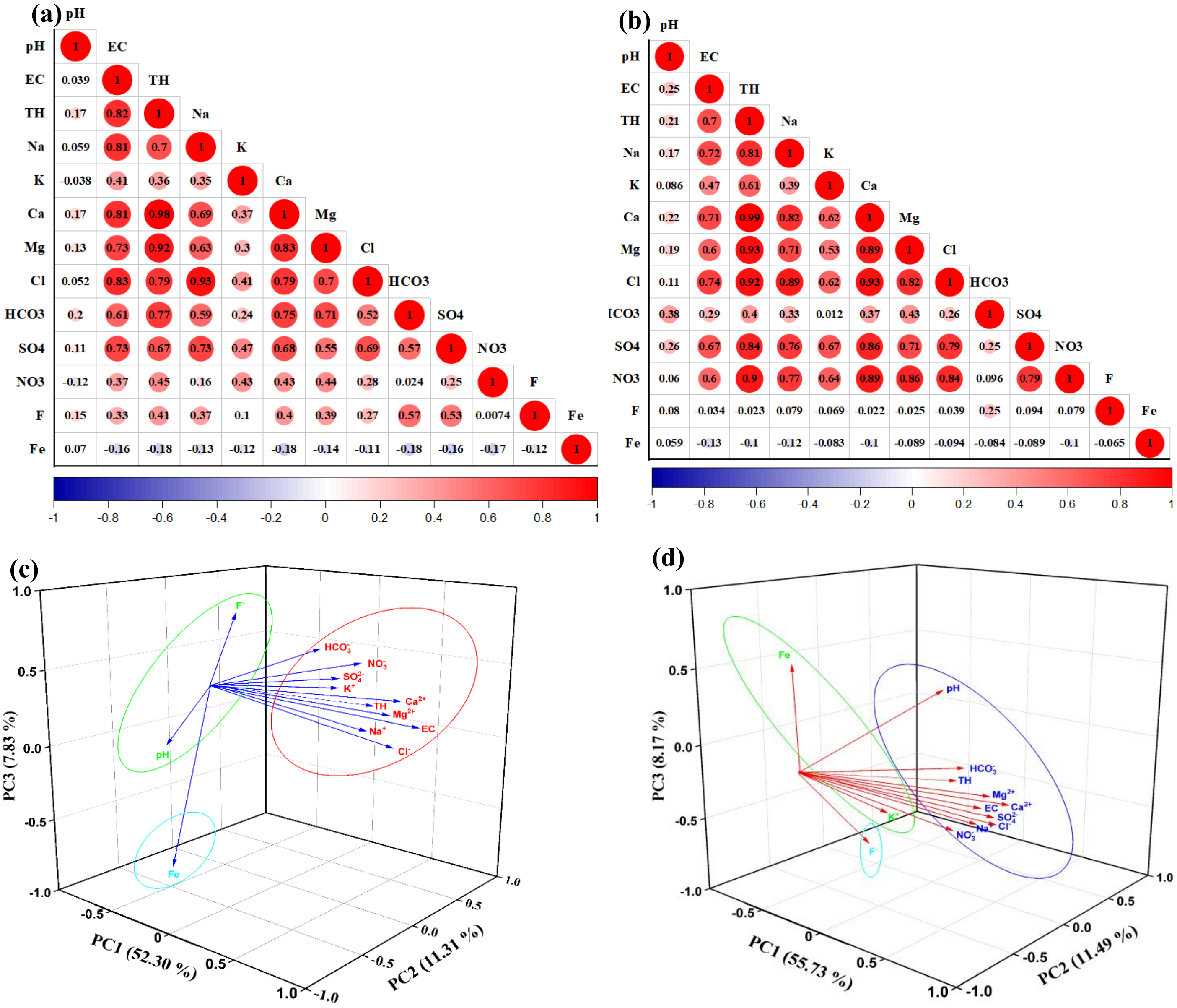
6.6.2 Chemometric analysis

6.6.2.1 Pearson's correlation analysis

Correlation analysis provides an understanding of the relationship between variables for assessing their communal origin and/or sources (Singh et al., 2017; Wali et al., 2022). Figure 6.2a and b presented the result of Pearson's correlation analysis hydrochemical parameters of wet and dry seasons. EC strongly correlated with TH ($r^2 = 0.82$), Na ($r^2 = 0.81$), Ca ($r^2 = 0.81$), Mg ($r^2 = 0.73$), Cl ($r^2 = 0.83$), and SO_4 ($r^2 = 0.73$) and is moderately correlated with HCO_3^- (r^2=0.61) in wet season samples, whereas TH ($r^2 = 0.70$), Na ($r^2 = 0.72$), Ca ($r^2 = 0.71$), Cl ($r^2 = 0.74$), and Mg ($r^2 = 0.60$), SO_4 ($r^2 = 0.67$), NO_3^- ($r^2 = 0.60$) correlates with EC in dry season groundwater samples (Table SM6.1 & 6.2, Figure 6.2a &b). There was a weak correlation between EC and K ($r^2 = 0.41$), and NO_3 ($r^2 = 0.37$) in wet season groundwaters, and K ($r^2 = 0.47$) and HCO_3 ($r^2 = 0.29$) in the dry season groundwater samples (Table SM6.2). pH does not correlate with K ($r^2 = –0.04$), and NO_3 ($r^2 = –0.12$), both of which show a very weak correlation between other variables in wet season (Table SM6.1). Fluoride shows moderate correlation with HCO_3 and SO_4 and weak correlation with all other variables in the wet season, and Fe shows no correlation with all parameters in both seasons. Cl^- significantly correlates with all parameters in wet season except pH, K^+, NO_3^-, F^- and Fe. Unlike the wet season, it is positively correlated with all water quality parameters except pH, HCO_3, F, and Fe, which implies anthropogenic sources. NO_3 and Cl displayed strong positive correlation during dry season, suggesting they were derived from both human and animal waste possibly from heavy application of chemical fertilizers, sewage and industrial effluents (Beshir et al., 2024; Dasari et al., 2024; Khan et al., 2023; Memon et al., 2023). Again, nitrate displayed a significant positive correlation with all variables in dry season except HCO_3^-, F^-, and Fe, contrary to the wet season where the association is very weak except for F^- and Fe which shows no association. This could be attributed to the intensive use of synthetic fertilizer in irrigated areas, specifically in Kano Irrigation Project (KIP), Hadejia Valley Project (HVP), and other irrigation projects along Hadejia-Nguru parts of the basin (Shuaibu et al., 2024). This is in line with the findings of Bijay-Singh & Craswell, (2021) that fertilizer N consumption in East and South Asia has adversely contributes to nitrate pollution of groundwater and surface water bodies. The correlation between Mg and Ca ($r^2 = 0.83$, wet season, and $r^2 = 0.89$, dry season) is an indication that magnesium in the groundwater is derived from either dissolution of carbonate minerals or weathering of silicate minerals such as biotite, pyroxene and amphibole in the study area. Likewise, SO_4 and Ca displayed a moderate and strong positive correlation in the wet and dry season, signifying a probable dissolution of evaporite in dry season.

6.6.2.2 Principal component analysis (PCA)

Principal Component Analysis (PCA) was conducted on 13 groundwater variables, namely pH, EC, TH, Na, K, Ca, Mg, Cl, HCO_3, SO_4, NO_3, F, and Fe in wet and dry season samples from the Komadugu–Yobe basin. This analysis aimed to understand the hydrogeochemical processes and identify sources of hydrochemical constituents within the groundwater of the basin. Three principal components (PCs) with eigenvalues greater than 1 were extracted for each season, as shown in Table 6.2. These components explain approximately 71.4 % and 75.4 % of the total variance for the wet and dry seasons, respectively. The loadings of the three PCs for the respective seasons are depicted in Figure 6.2c and d, illustrating the relationship between variables. Notably, the first component exhibits a significant correlation among variables than the subsequent components in both seasons, indicating its primary influence on hydrochemical variations. In the wet season, the first principal component (PC1) accounts for 52.3% of the variance in the groundwater dataset, with variables such as EC, TH, Na, K, Ca, Mg, Cl, HCO_3, and SO_4 displaying substantial positive loadings (Table 2). This suggests that PC1 is heavily influenced by geogenic processes, including weathering of minerals like plagioclase, biotite, amphibole, and orthoclase, as well as rock–water interactions. Additionally, anthropogenic contributions from domestic discharges and agricultural activities play a role in influencing groundwater chemistry. In this season, all variables exhibit positive loadings in PC1, except Fe, which shows a weak correlation with other variables. The second principal component (PC2), explaining 11.3% of the variance, is marked by a strong negative loading on pH and significant positive loadings on K^+ and NO_3^-. This pattern indicates non-point-source pollution from agricultural runoff and domestic waste. Elevated NO_3^- levels likely result from nitrification processes associated with the intensive use of nitrogenous fertilizers and manure in rain-fed farming. Furthermore, the widespread use of unimproved pit latrines and septic tanks in recharge areas can lead to nitrate leachate in groundwater (Chen et al., 2024; Dasari et al., 2024; Nyambar & Mohan Viswanathan, 2024). The third principal component (PC3) in the wet season, explaining 7.8 % of the variance, has significant positive loading on F and Fe, likely reflecting the influence of mineral weathering and dissolution, coupled with variations in groundwater flow and sediment transport. These results corroborates with those obtained by Ait Said et al., (2023) in South-East of Morocco.



(a)

	pH	EC	TH	Na	K	Ca	Mg	Cl	HCO3	SO4	NO3	F	Fe
pH	1												
EC	0.039	1											
TH	0.17	0.82	1										
Na	0.059	0.81	0.7	1									
K	-0.038	0.41	0.36	0.35	1								
Ca	0.17	0.81	0.98	0.69	0.37	1							
Mg	0.13	0.73	0.92	0.63	0.3	0.83	1						
Cl	0.052	0.83	0.79	0.93	0.41	0.79	0.7	1					
HCO3	0.2	0.61	0.77	0.59	0.24	0.75	0.71	0.52	1				
SO4	0.11	0.73	0.67	0.73	0.47	0.68	0.55	0.69	0.57	1			
NO3	-0.12	0.37	0.45	0.16	0.43	0.43	0.44	0.28	0.024	0.25	1		
F	0.15	0.33	0.41	0.37	0.1	0.4	0.39	0.27	0.57	0.53	0.0074	1	
Fe	0.07	-0.16	-0.18	-0.13	-0.12	-0.18	-0.14	-0.11	-0.18	-0.16	-0.17	-0.12	1

(b)

	pH	EC	TH	Na	K	Ca	Mg	Cl	HCO3	SO4	NO3	F	Fe
pH	1												
EC	0.25	1											
TH	0.21	0.7	1										
Na	0.17	0.72	0.81	1									
K	0.086	0.47	0.61	0.39	1								
Ca	0.22	0.71	0.99	0.82	0.62	1							
Mg	0.19	0.6	0.93	0.71	0.53	0.89	1						
Cl	0.11	0.74	0.92	0.89	0.62	0.93	0.82	1					
[CO3	0.38	0.29	0.4	0.33	0.012	0.37	0.43	0.26	1				
SO4	0.26	0.67	0.84	0.76	0.67	0.86	0.71	0.79	0.25	1			
NO3	0.06	0.6	0.9	0.77	0.64	0.89	0.86	0.84	0.096	0.79	1		
F	0.08	-0.034	-0.023	0.079	-0.069	-0.022	-0.025	-0.039	0.25	0.094	-0.079	1	
Fe	0.059	-0.13	-0.1	-0.12	-0.083	-0.1	-0.089	-0.094	-0.084	-0.089	-0.1	-0.065	1

Figure 6.2 Pearson's correlation analysis results (a) wet season (b) dry season. Loading plot of three PCs (PC1, PC2 and PC3) in 3D (c) wet season (d) dry season.

In the dry season, PC1 explains 55.7 % of the variance, with EC, TH, Na, Ca, Mg, Cl, SO_4, and NO_3 showing strong positive loadings. This component, like in the wet season, is influenced by mineral weathering and rock–water interactions, as well as anthropogenic inputs from agriculture and domestic sources (Bijay-Singh & Craswell, 2021; Dasari et al., 2024; Nyambar & Mohan Viswanathan, 2024). All variables, except F and Fe, exhibit positive loadings in PC1. The second component (PC2) in the dry season, accounting for 11.5 % of the variance, features significant loadings on pH, HCO_3^-, and F, indicating a carbonate buffering effect that helps regulate groundwater pH. This buffering action suggests a distinct chemical environment compared to the wet season, with less contribution from agricultural runoff. Finally, PC3 in the dry season, which explains 8.2 % of the variance, again shows strong loading on F and notable loading on Fe. This component reflects the continued influence of mineral weathering and dissolution processes, particularly from biotite, pyroxene, and amphibole minerals (Dhaoui et al., 2023; Liu et al., 2023; Zhao et al., 2024).

Table 6.2 Component matrix of groundwater quality parameters, eigenvalues, % total variance and % cumulative total variance.

Parameters	Wet Season			Dry Season		
	PC1	PC2	PC3	PC1	PC2	PC3
pH	0.21	**–0.56**	–0.15	0.12	**0.74**	0.26
EC	**0.89**	0.16	0.04	**0.76**	0.20	–0.04
TH	**0.94**	0.06	0.12	**0.96**	0.19	–0.01
Na	**0.86**	0.01	0.01	**0.84**	0.20	–0.12
K	0.45	**0.51**	0.004	**0.71**	–0.17	0.06
Ca	**0.92**	0.06	0.12	**0.96**	0.17	–0.01
Mg	**0.86**	0.06	0.10	**0.88**	0.20	–0.02
Cl	**0.89**	0.14	–0.07	**0.95**	0.06	–0.03
HCO_3	**0.76**	–0.33	0.32	0.22	**0.79**	–0.18
SO_4	**0.80**	0.01	0.17	**0.87**	0.17	–0.03
NO_3	0.35	**0.72**	0.05	**0.94**	–0.09	–0.002
F	**0.47**	–0.44	**0.45**	–0.11	**0.47**	**–0.53**
Fe	–0.06	–0.24	**–0.88**	–0.12	0.13	**0.83**
Eigenvalue	6.80	1.47	1.02	7.25	1.49	1.06
Total variance (%)	52.30	11.31	7.83	55.73	11.49	8.17
Cumulative total variance (%)	52.30	63.61	71.44	55.73	67.22	75.39

6.6.2.3 Hierarchical clustering analysis (HCA)

R–mode and Q–mode HCA were performed to 13 physicochemical parameters, to identify interrelationship between water quality parameters and samples with similar chemical composition using Ward's method for wet and season samples. The R–mode HCA produces three cluster groups for both seasons (Figure 6.3a and b, Table SM6.3). The first cluster reveals a strong association between EC, TH, Na, Ca, Mg, Cl, HCO_3, SO_4, and F for wet season samples. This suggests a mixed process of geogenic and anthropogenic inputs influence in the aquifer systems. Moreover, the dry season samples show an interrelationship between EC, TH, Na, Ca, Mg, Cl, SO_4, and NO_3 in the first cluster, suggesting geogenic processes of rock minerals and anthropogenic inputs (Dhaoui et al., 2023; Karmakar et al., 2023; Tziritis et al., 2024). However, cluster 2 in the respective seasons presented K and NO_3, and K, implying influence of anthropogenic input from synthetic fertilizers and pit latrines leading to nitrification processes in the aquifer and a probable incongruent weathering of feldspar mineral (Bijay-Singh & Craswell, 2021). It is worth noting that cluster 3 is dominated by similar variables such as pH and Fe in wet season and pH, HCO_3, F, and Fe in dry season indicating slight variation in groundwater chemistry which could be due to interactions between various geochemical processes (Karmakar et al., 2023; Liu et al., 2020).

Like R–mode HCA, Q–mode HCA performed on groundwater sampling points produced 3 cluster groups in both seasons (Figure 6.3c and d, Table SM6.4). The first cluster comprises 56 (46.7 %) groundwater samples for wet season and 67 (55.8 %) for dry season sampling points. The value of the EC in this cluster varies from 15 to 438 µS/cm with mean of 175 µS/cm and 54 to 1266 µS/cm with mean of 324 µS/cm in the respective seasons dataset, which indicates less mineralized water which is evident in the concentrations of all the groundwater quality parameters (Elumalai et al., 2022; Spellman et al., 2024; Tziritis et al., 2024). Cluster 2 contains 57 (47.5 %) and 48 (40 %) of the respective wet and dry seasons sampling points, with an EC range of 188 to 2746 μS/cm with a mean value of 593 μS/cm and 70 to 3560 μS/cm with a mean value of 635 μS/cm. This signifies moderately mineralized water influenced by anthropogenic inputs. Furthermore, cluster 3 accommodates fewer sampling points for both seasons, with only 7 (5.8 %) in wet season and 5 (4.2 %) in dry season. Groundwater in these sampling points have an EC value ranging from 960 to 2503 μS/cm with mean value of 1732 μS/cm and 1846 to 3320 μS/cm with mean value of 2465 μS/cm, signifying highly mineralized/low brackish water influenced by geogenic (plagioclase, biotite and pyroxene weathering and dissolution), salinization sources, and evaporation processes (Elumalai et al., 2022; Tziritis et al., 2024). Figure 6.4a and b present the spatial distribution of groundwater cluster groups related to geology and electrical conductivities in the study area. It is obvious that the Precambrian basement parts of the basin were dominated by moderately and highly mineralized waters. This suggests weathering and dissolution of rock forming minerals (plagioclase, biotite, amphibole and pyroxene) in this region. However, less mineralized water predominates sedimentary quaternary parts of the study area.

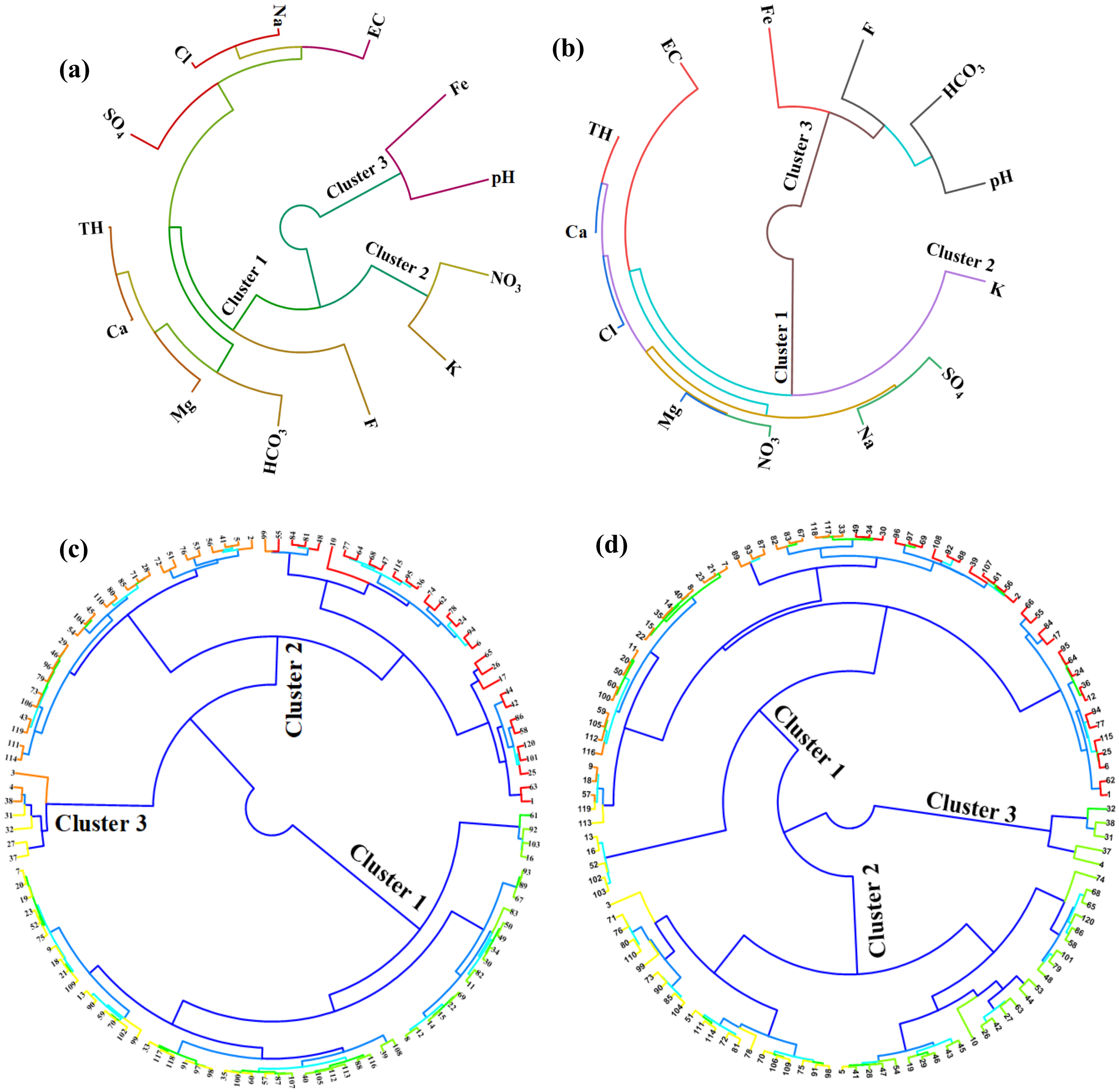


Figure 6.3 Dendrogram of groundwater quality parameters showing different clusters (a) Wet season (b) Dry season. Dendrogram of sampling locations showing different clusters (c) Wet season (d) Dry season.

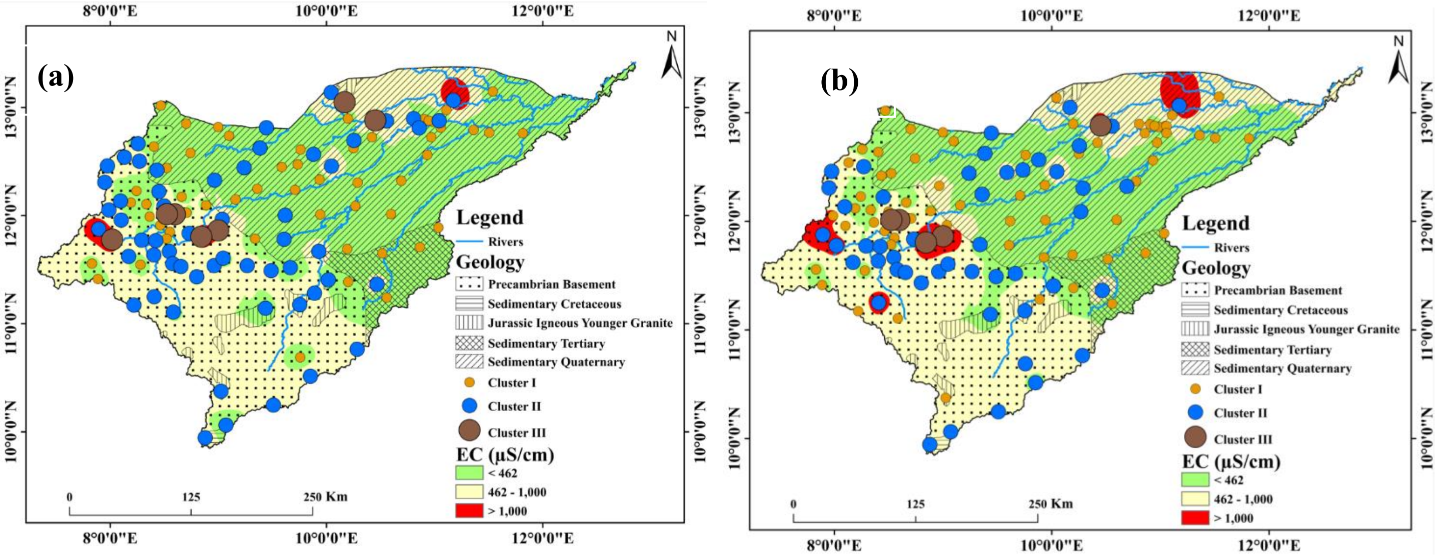


Figure 6.4 Spatial distribution of groundwater clusters related with geology and electrical conductivities (a) wet season (b) dry season.

6.6.3 Hydrochemical facies

The Piper (1944) diagram for hydrochemical classification is presented in Figure 6.5a and b. Groundwater samples of wet season were plotted mainly in A, C, and D zones of lower–left triangle. This suggests the samples are characterized by sodium–type, calcium–type, and no dominant water type for cations. Moreover, the lower right triangle shows that groundwater samples of wet season were mainly plotted in G and F zones, signifying bicarbonate and chloride dominance. It is very clear that no samples are scattered in zones B and E, suggesting that Mg^{2+} and SO_4^{2-} are not among the major ions in wet season groundwater samples. Groundwater samples of wet season were projected onto zones 1, 2, and 4 of the central diamond–shaped plot (Figure 6.5a). This suggests that wet season groundwater samples are mainly Ca – HCO_3, Na – Cl, and mixed water types. In the same vein, the dry season groundwater samples were plotted in D and C zones of lower–left triangle, and a few plotted in zone A, indicating Na^+ and Ca^{2+} as the predominant cations in dry season groundwater samples (Figure 6.5b). Furthermore, significant percentage of groundwater samples for dry season were plotted in G and F zones of lower–right triangle (Figure 6.5b) indicating the presence of HCO_3^{2-} and Cl^- anions (Hu et al., 2024; Yang et al., 2024; Zhang et al., 2024). It is obvious that dry season samples exhibited a wide range of hydrochemical compositions, and the vast majority of the samples were scattered in 1, 3, and 2 zones of central diamond–shaped plot (Figure 6.5b). This indicates that dry season groundwater samples were predominantly Ca – Na – HCO_3, Na – Cl, and mixed water types. In overall, groundwater of the study area in the respective seasons is greatly influenced by weathering of calcium and sodium feldspar minerals as well as anthropogenic contamination of surface water by irrigation return flows, drainage wastes and industrial discharges. Moreover, the dominance of Ca - HCO_3 water indicates dissolution of carbonates driven by soil CO_2 (Abu et al., 2024; Dasari et al., 2024; Elumalai et al., 2022; Liu et al., 2023; Subba Rao et al., 2022).

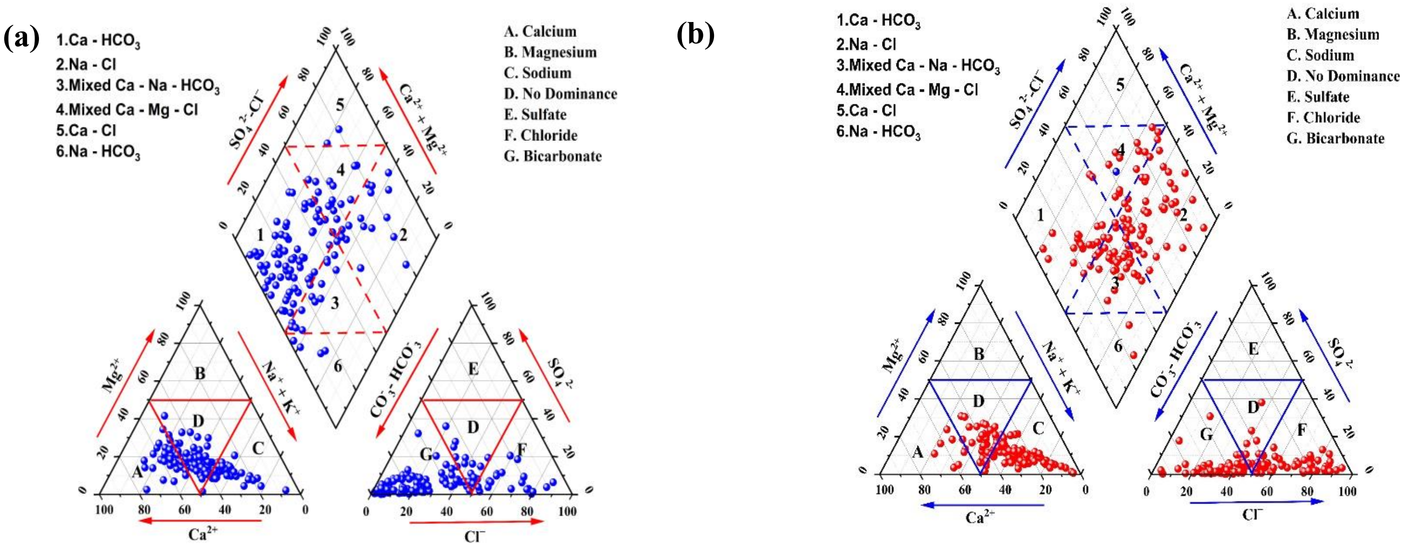


Figure 6.5 Piper diagram for groundwater samples in Komadugu–Yobe basin (a) wet season (b) dry season.

6.6.4 Geochemical Modelling

Geochemical modeling of aqueous solutions using Geochemist's WorkBench GWB software 17.0 was employed to ascertain rock–water–mineral interactions using groundwater quality datasets. These modeling techniques have been extensively used in assessing mineral weathering of silicate and carbonate minerals dissolution (Bradai et al., 2022; Elumalai et al., 2022; Ganyaglo et al., 2024; Liu et al., 2015; Trabelsi & Zouari, 2019).

6.6.4.1 Saturation indices

In this study, Geochemist's WorkBench GWB software 17.0 was employed to determine saturation indices of various minerals in wet and dry seasons groundwater samples in Komadugu–Yobe basin (Table 6.3). It was observed that a significant percentage of the samples shows undersaturation with respect to dolomite, calcite, and fluorite (Figure 6.6) with some, 41 (34.2 %) and 4 (3.3 %), 27 (22.5 %) and 1 (0.83 %), and 1 (0.83 %) of the samples indicated near saturation with respect to dolomite, calcite, and fluorite in wet and dry seasons, respectively. Figure 6.6 presents the relationship between some selected saturation indices and electrical conductivities (EC). Few samples with high EC displayed over saturation with respect to dolomite and calcite. It is noteworthy that dolomite saturation is a proxy indicating high magnesium ions in the groundwater samples. This could be due to incongruent weathering of feldspar minerals. Therefore, the occurrence of dolomite in the study area is highly unlikely. Calcite mineral may be the main source of high Ca^{2+} and HCO_3^- in the groundwater samples which results from congruent weathering and dissolution of calcite (Eq. (6.5)) (Elumalai et al., 2022; Ganyaglo et al., 2024). Moreover, carbonate minerals could be due to various rock minerals in the study area viz plagioclase, biotite, pyroxene and amphibole minerals. Fluorite saturation could be due to a common ion effect with carbonates together with weathering and dissolution of fluoride bearing minerals such as granite gneisses, fluorite and biotite minerals as a results of rock-water interaction under high alkaline condition which could be the main source of F^- in the aquifers of the study area (Abu et al., 2024; Sunkari et al., 2025). Kumar et al., (2018) posit that fluoride concentration in aquifer system results from dissolution of biotite minerals (Eq. (6.6)). Fluoride concentration in groundwater could also result from dissolution of fluorite mineral (Eq. (6.7)).

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad 6.5$$

$$KMg_3(AlSi_3O_{10})F_2 + 2OH^- \rightarrow KMg_3(AlSi_3O_{10})(OH)_2 + 2F^- \qquad 6.6$$

$$CaF_2 + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2 + 2F^- \qquad 6.7$$

Figures SM6.1 and SM6.2 shows spatial distribution of saturation indices of groundwater samples related to geology and electrical conductivities (EC) for wet and dry seasons. The figures revealed that saturation indices above the mean values are largely concentrated in Precambrian basement parts of the study area. Furthermore, most of the oversaturation in both seasons for dolomite, calcite, and fluorite dominated in Precambrian basement complex region. This could be due to the presence of plagioclase, biotite, pyroxene and amphibole rock minerals in this region. However, few samples shows oversaturation with respect to dolomite, calcite, and fluorite in the sedimentary quaternary formation and sedimentary tertiary regions of the study area in the respective seasons.

6.6.4.2 Partial pressures of carbon dioxide (pCO_2)

Geochemical processes of groundwater and reaction between groundwater and carbonate minerals are greatly influenced by partial pressure of carbon dioxide (pCO_2) which acts as a source of acid (H^+) for mineral weathering reactions (Trabelsi & Zouari, 2019). The partial pressures of CO_2 of wet and dry season groundwater samples varied from $10^{-3.86}$ to 10^{-1} atm with a mean value of $10^{-2.36}$ atm and $10^{-4.2}$ to $10^{-1.34}$ atm with an average value of $10^{-2.08}$ atm, respectively. It was observed that about 96.7% and 99.2% of groundwater samples in wet and dry seasons have pCO_2 above atmospheric pCO_2, which is about $10^{-3.5}$ atm. This indicates the presence of CO_2 in the groundwater system due to biological activity such as respiration of vegetation roots and decomposition of soil organic matters. The partial pressure of CO_2 is observed to decrease as pH of wet and dry–season groundwater samples increase (Figure SM6.3). This corresponds to the findings of Adams et al., (2001); Elumalai et al., (2022); Liu et al., (2015) and Rajmohan et al., (2021). Negative correlation of –0.61 and –0.21 were observed in groundwater samples of wet and dry seasons which might be attributed to longer residence time, rock–water interaction in aquifer systems and biogenic activities that produce CO_2. According to Liu et al., (2015), negative correlation between pCO_2 and pH signifies dissolution of feldspar along groundwater flow path, and the following reaction could be possible in the aquifer formations (Eq. (6.8)):

$$Na_2Al_2Si_6O_{16} + 2H_2O + CO_2 \rightarrow Na_2CO_3 + H_2Al_2Si_2O_8 + H2O + 4SiO_2 \qquad 6.8$$

This reaction resulted in the consumption of CO_2 and increase in concentration of Na^+ and HCO_3^- leading to pH increase and partial pressure of CO_2 decrease. It is established that the decay of organic and roots respiration releases CO_2 which is the main source of HCO_3^- in groundwater (Eqs. (6.9) and (6.10)).

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad 6.9$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad 6.10$$

Table 6.3 Descriptive statistics of mineral saturation indices.

Minerals	Wet Season				Dry Season			
	Min	Max	Mean	Std	Min	Max	Mean	Std
Calcite	–6.65	1.15	–0.88	1.24	–6.78	0.65	–2.17	1.31
Dolomite	–12.87	3.03	–1.27	2.52	–13.26	1.43	–3.85	2.66
Fluorite	–6.89	0.08	–2.64	1.38	–2.70	0.09	–1.43	0.53

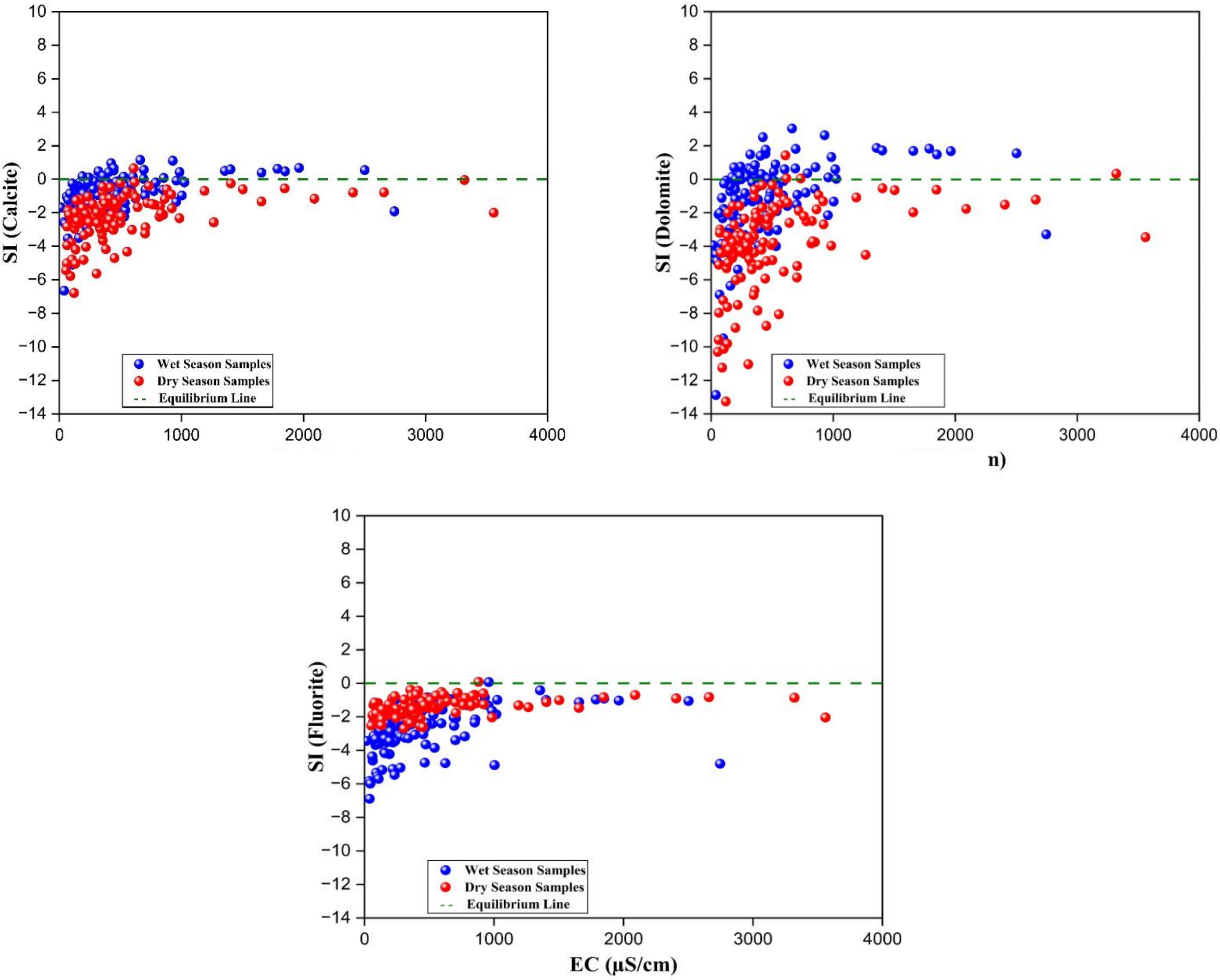


Figure 6.6 Saturation indices of some selected minerals against electrical conductivity of groundwater samples of wet and dry seasons.

6.6.5 Hydrogeochemical Processes

Gibbs plots, molar ratios, and bivariate plots were employed in this study to estimate various hydrogeochemical processes that influence groundwater chemistry in the study area.

6.6.5.1 Gibbs plots

Gibbs plots (Gibbs, 1970) was used in this study to identify the major geochemical mechanisms influencing the groundwater chemistry of the study area (Figure 6.7a and b). The figures show that majority of groundwater samples of wet and dry seasons were plotted in the region characterized by rock weathering/rock–water interaction dominance (Chen et al., 2024; Hu et al., 2024). A few samples with high TDS concentration during dry season were observed to trend towards evaporation dominance zone. Therefore, rock weathering is likely the predominant geochemical process controlling the chemistry of groundwater in the study area, except in a few areas associated with evaporation dominance during dry season.

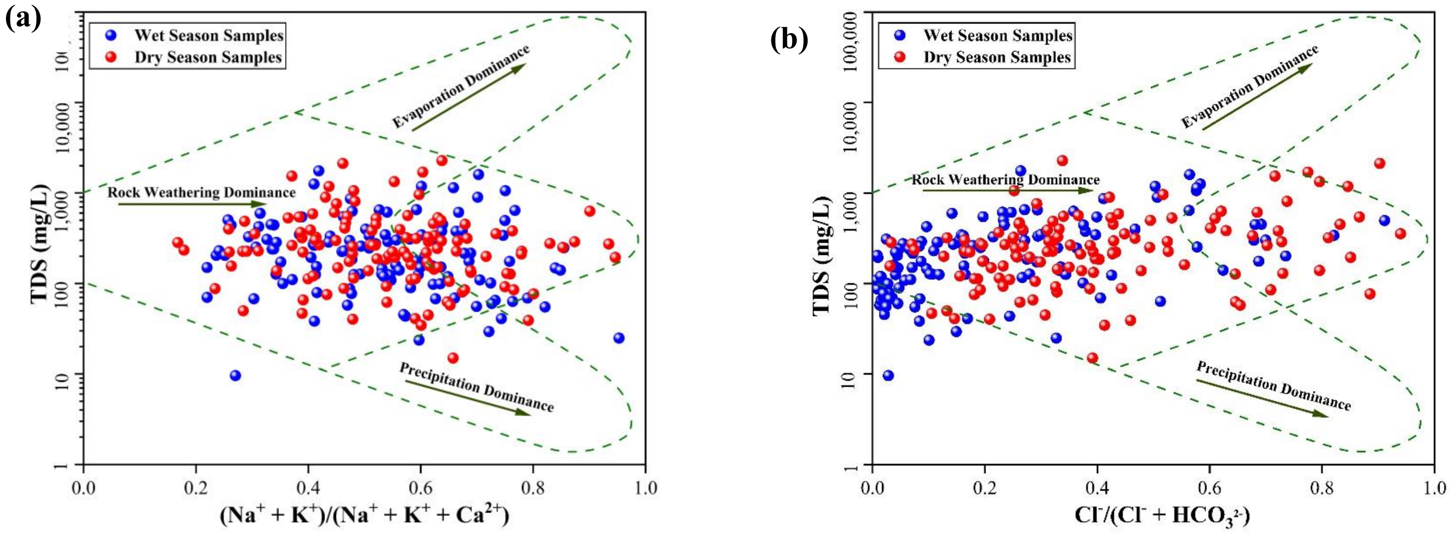


Figure 6.7 Gibbs plots of geochemical processes governing groundwater chemistry (a) cations (b) anions.

6.6.5.2 Evaporation

Evaporation process has potential to increase concentration level of all ions present in groundwater in semi–arid areas due to climate change impacts. Na^+/Cl^- vs EC plot was employed to determine the influence of evaporation processes on chemistry of groundwater in the study area (Figure 6.8a). According to Jankowski & Ian Acworth, (1997), when evaporation has significant influence on the chemistry of groundwater, Na^+/Cl^- vs EC plot will remain consistent as EC increases. Figure 6.8a reveals that only a few samples during wet season follow evaporation trend line, which suggests that evaporation does not play a vital role in influencing the groundwater chemistry during wet season. However, an appreciable number of samples during dry season follow evaporation trend line, which signifies that evaporation could be among the factors influencing the groundwater chemistry during dry season. Na^+/Cl^- ratios shows significant correlation in wet and dry seasons. Na^+/Cl^- ratios enrichment and depletion were observed, which is an indicative of the influence of ion exchange and silicate dissolution in groundwater chemistry in respective seasons. However, most of the groundwater samples in the respective seasons deviated from 1:1 section. This suggests that Ca^{2+} is being exchanged for Na^+ from clay minerals into water thereby increasing its salinity levels (Elumalai et al., 2022; Hu et al., 2024).

6.6.5.3 Carbonate Dissolution

Carbonate minerals dissolution in groundwater produces Ca, Mg, and HCO_3 ions (Elumalai et al., 2022; Rajesh et al., 2012; Rajmohan et al., 2017; Rajmohan & Elango, 2004). Molar ratio of Ca/Mg serves as a reliable indicator for calcite and dolomite dissolution processes within the groundwater system. Dissolution of dolomite will maintain Ca/Mg ratio of 1, but Ca/Mg ratio > 1 indicates dissolution of calcite, and the process of silicate weathering is associated with Ca/Mg ratios > 2 (Rajesh et al., 2012; Rajmohan et al., 2017). It is noteworthy that about 81.67n% and 73.33 % of the respective season's groundwater have Ca/Mg ratio > 2 (Figure 6.8c). This implies that the groundwater samples are dominated by silicate weathering processes. Some portions of the samples were observed to cluster between values of 1 and 2 on the Ca/Mg ratio scale, suggesting the dissolution of calcite which was described in Eq. (6.5). Moreover, the samples exhibited spatial distribution, and a few samples were closely aligned with the Ca/Mg = 1 line. This implies the occurrence of high magnesium carbonate dissolution, which is expressed by the following equation (Eq. (6.11)):

$$CaMg(CO_3)_2 + 2H_2O + 2CO_2 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \qquad 6.11$$

6.6.5.4 Silicate Weathering

High Na in groundwater could be related to silicate rock weathering. According to Jankowski & Ian Acworth, (1997), Na/Cl ratio remains constant if evaporation is the prevailing mechanism in the absence of mineral precipitation. The dissolution of halite can result in Na/Cl ratio = 1 if present, however, Na/Cl ratio > 1 increases Na concentration in groundwater system due to silicate weathering and cation exchange processes. Figure 6.8a presents Na/Cl vs EC for wet and dry seasons in Komadugu–Yobe basin. A significant increase in Na/Cl ratio is observed when electrical conductivity (EC) value is below 500, particularly in wet season groundwater samples. It was observed that 78.33 % and 71.67 % of respective wet and dry season samples exhibited Na/Cl > 1. This high Na^+ ion concentration could potentially originate from silicate weathering and/or cation exchange process (Figure 6.8a). Furthermore, Na/Cl and EC plots show significant number of samples above evaporation line, particularly in wet season. However, few dry season samples were observed in evaporation zones. Therefore, silicate weathering with ion exchange is likely the primary processes that controls the chemistry of groundwater during both seasons (Abuet al., 2024; Yang et al., 2024).

According to Rogers, (1989), if sodium is likely from silicate weathering by soil CO_2, groundwater would have bicarbonate (HCO_3) as the predominant anion. The release of HCO_3 is attributed to the reaction between feldspar crystals and carbonic acid in water. HCO_3^- is the prevailing anionic species found in groundwater of the study area (Table 6.1). Bivariate ratio plots indicate that silicate weathering is the primary geochemical process influencing groundwater chemistry in the basin, rather than carbonate and evaporite dissolution (Figure 6.8d & e). Geochemical evolution of groundwater is characterized by silicate weathering, carbonate dissolution, cation exchange, and evaporative dissolution (Adimalla & Taloor, 2020; Banda et al., 2020; Elumalai et al., 2020, 2022; Ganyaglo et al., 2024; Liu et al., 2023; Rajesh et al., 2012; Rajmohan et al., 2017; Rajmohan & Elango, 2004; Sikakwe & Eyong, 2022; Singh et al., 2017; Yang et al., 2024). The impact of evaporite dissolution appears to be limited in the basin. However, it is visible in a few locations during the dry season. This observation is indicative of prevalence of silicate source rocks and limited presence of evaporites, such as halite and gypsum. The latter are commonly related to deposits characterized by poorer permeability, inadequate flushing, and the presence of shale or marl (Banda et al., 2020; Yuan et al., 2024).The process of silicate weathering can be explained using the following weathering reaction (Eq. (6.12)):

$$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4 + 2HCO_3^- \qquad 6.12$$

6.6.5.5 Ion exchange reactions

Ion exchange and different weathering processes are best described using Na/Cl vs. EC plot (Figure 6.8a). The figure shows an increase in Na ion by ion exchange processes in water samples of both seasons. Therefore, the cation exchange process is the predominant mechanism that controls groundwater chemistry in the respective wet and dry seasons compared to reverse ion exchange. Ion exchange processes in aquifer system have been explained in several studies using chloroalkaline indices (CAI–I and CAI–II) (Eqs. (6.3) & (6.4)). Positive values of chloroalkaline indices indicate the occurrence of reverse ion exchange, whereas negative values indicate cation exchange reaction (Abu et al., 2024; Elumalai et al., 2022; Mgbenu & Egbueri, 2019). High Cl over Na and K results in positive chloroalkaline indices, suggesting reverse ion exchange reactions. Conversely, high Na and K compared to Cl result in negative values, indicating cation exchange processes (Ganyaglo et al., 2024). When the values of chloroalkaline indices are positive, Mg and Ca ions are exchanged with Na and K ions in water. Conversely, when chloroalkaline indices have negative values, it suggests that there is exchange of Mg or Ca ions in groundwater with Na or K ions in host rocks. Figure 6.8f shows positive correlation between CAI–I and CAI–II. 86.67 % of the samples had negative chloroalkaline index values during the wet season, whereas 80 % had negative values during the dry season. However, 13.33 % and 20 % have positive values during the respective seasons suggesting that cation exchange reaction is predominant in the groundwater system compared to reverse ion exchange process. Cation exchange can be explained in the following reactions (Eq. (6.13) and (6.14)):

$$2Na^+ + CaX_2 = Ca^{2+} + 2NaX \quad 6.13$$

$$Ca^{2+} + 2NaX = 2Na^+ + CaX_2 \quad 6.14$$

Where X is the cation exchange sites.

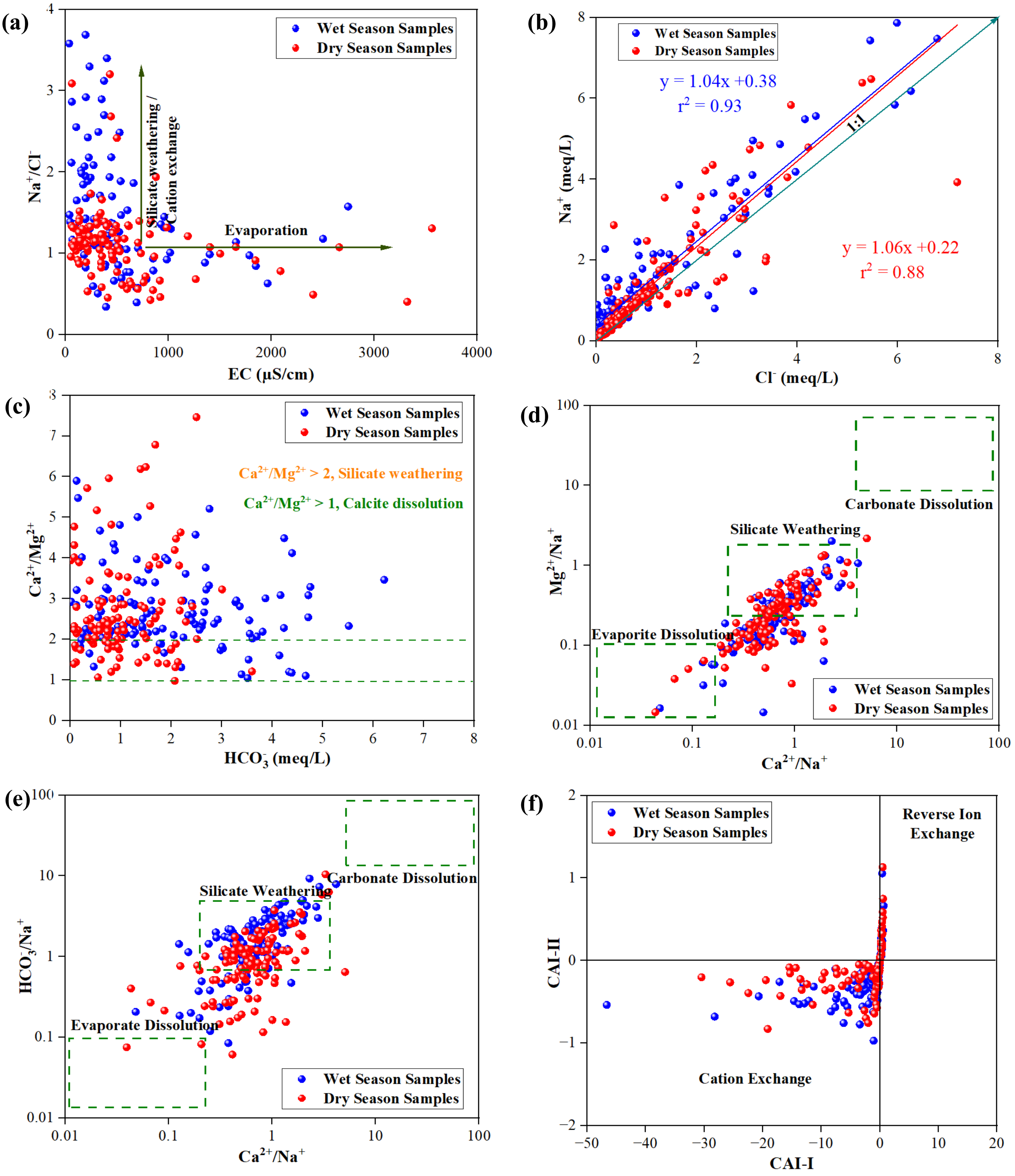


Figure 6.8 Bivariate plots of: (a) Na/Cl vs. EC; (b) Na vs. Cl (c) Ca/Mg vs. HCO_3 (d) Mg /Na vs Ca/Na (e) HCO_3/Na vs Ca/Na (f) CAI–II vs. CAI–I.

6.6.6 Conceptual model for hydrogeochemical processes controlling the groundwater chemistry of Komadugu-Yobe basin

Figure 6.9 presents a conceptual model for geochemical processes governing groundwater chemistry of Komadugu-Yobe basin. The study has established that the chemistry of groundwater in the basin is influenced by various geogenic and anthropogenic processes which indicates a subtle transformation as groundwater and surface water moves from upstream section passing through recharge zones in Hadejia Nguru wetlands to downstream parts along Komadugu Yobe River to Lake Chad. The study area is mainly characterized by local gravity driven flow due to varying topography from upstream to downstream. The aquifer in the upstream parts of the basin consists of a system of three aquifer layers resting on the Precambrian basement formation. The weathered basement which is semi-permeable in the vadose zone which hosted the water table. The partially weathered basement and the fractured basements provide groundwater in fractures, fault breccias, and joints which move from upstream to downstream direction following natural slope of the bedrock. Localized infiltration from Chalawa gorge dam, river flows, industrial discharges, irrigation return flows and domestic waste discharges as well as rock-water interaction influenced the groundwater chemistry and its evolution in upstream parts of the basin. The hydrochemical evolution shows that Ca-HCO_3 and Na-Cl water types predominated the region due to weathering/dissolution of Ca and Na bearing silicate minerals and calcite coupled with various anthropogenic inputs. Nitrate in the irrigation and residential areas may come from nitrogenous fertilizing and unimproved pit latrines respectively. However, in the downstream part of the study area, sedimentary quaternary aquifer provides groundwater mostly in unconfined aquifers. Groundwater occurs at shallow depths around Hadejia, Ringim and Guri town while it is at deeper depth in Machina town and its surroundings. Figure 6.9 shows that groundwater in this region is recharged by infiltrating water in the Hadejia-Nguru wetland (HNW), Komadugu-Yobe valley and areas around Lake Chad. However, evapotranspiration occurs around HNW and farmlands as well as evaporation losses at the verge of downstream parts towards Lake Chad. The groundwater chemistry is highly impacted by anthropogenic activities rather than geogenic processes. Nitrate infiltrates into the subsurface from irrigation return flows, domestic waste discharges and unimproved pit latrines in the region.

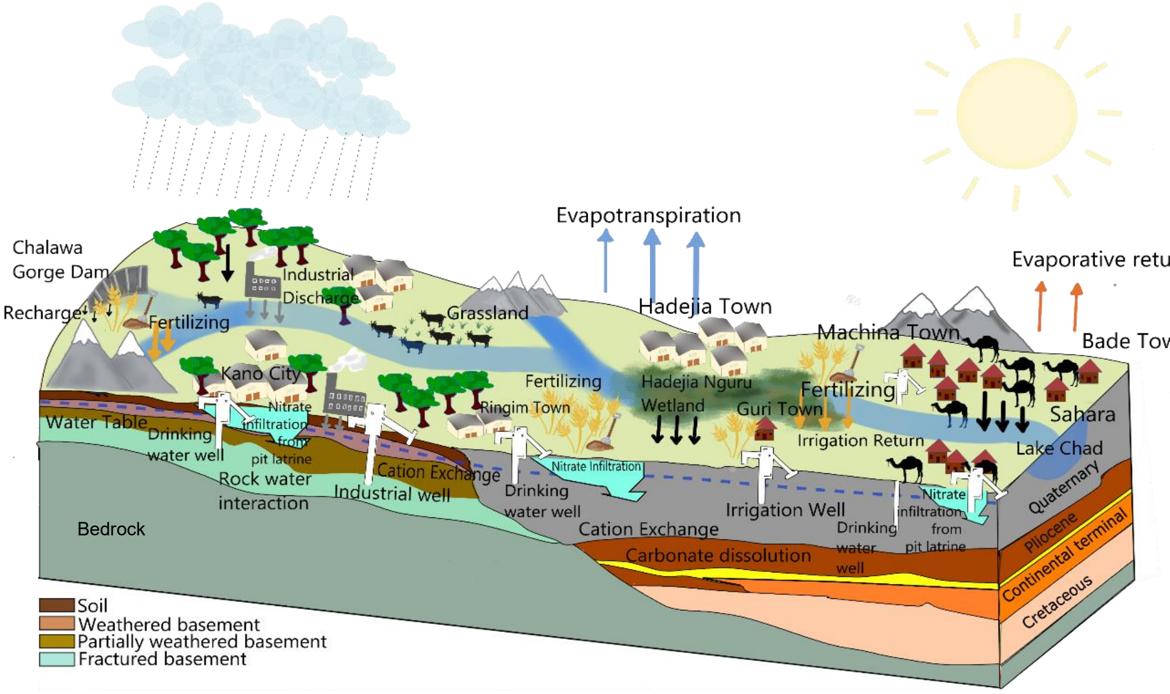


Figure 6.9 Conceptual model for geochemical evolution and hydrogeochemical processes controlling the groundwater chemistry of Komadugu-Yobe basin.

6.7 Implications to groundwater sustainability

This study has successfully used a robust approach of geochemical modeling, bivariate plots, ionic ratios, and chemometric analysis and established the sources of chemical constituent influencing the general chemistry and geochemical evolution of groundwater in transboundary Komadugu–Yobe basin, Lake Chad region. This information is crucial in developing groundwater monitoring and sustainable strategies for effective use and management of the basin's groundwater resources. Insights on the sources of chemical constituents in groundwater of the study area provides an avenue for understanding complex interplay between geogenic and anthropogenic factors influencing groundwater chemistry as well as groundwater evolution and hydrogeochemical characteristics for policy implementation as follows:

- The insights identified in this study regarding the sources of chemical constituents in groundwater are fundamental in providing strategic guides in developing and implementing effective policies for sustainable use and management of water resources. This would offer a more protective measures in ensuring healthy groundwater quality, particularly in areas prone to water contamination which is in line with SDG6 targets.
- Knowledge of various groundwater types in the study area and their distinct characteristics coupled with hydrochemical characteristics might influence decision on groundwater development projects in the region. Stringent policies should be implemented in areas at risk of contamination due to overexploitation or pollution from natural and anthropogenic sources.
- The Government of Nigeria should actively participate in the regional developmental projects being conducted by Lake Chad Basin Commission (LCBC) within Lake Chad region in restoring and safeguarding Lake Chad that provides a substantial groundwater recharge zones to the region's aquifers. These projects are essential in ensuring sustainable groundwater management and safeguarding water resources for the present population and the unborn generation.
- A significant percentage of potassium concentration due to incongruent weathering of potassium feldspar in the Precambrian basement region and nitrate contamination by irrigation return flows and pit latrines in irrigated and residential areas, as illustrated in Figure 6.9 necessitates the development of detailed irrigation master plan and pollution

model specifically addressing nitrate contamination from intensive synthetic fertilizing, pit latrines and sewerage systems. These activities would enable a more detailed analysis of nitrate-related contamination and support the establishment of stringent policies for proper land use planning to mitigate the potential health risk posed by nitrate in drinking groundwater.

- This study has undoubtedly provided an avenue for future research that would focus on PTEs contamination and their associated human health risk as well as the applications isotope hydrology to understand groundwater recharge source/origin and possibly tracing various groundwater pollution sources.

6.8 Conclusion

This study employed an integrated approach of geochemical modeling, bivariate plots, ionic ratios, and chemometric analysis to explore geochemical evolution and mechanisms controlling groundwater chemistry as well as origin/sources of chemical constituents in groundwater of the transboundary KYB. The groundwater in the basin is subjected to increased exploitation coupled with contamination from geogenic and anthropogenic inputs. The following conclusion can be drawn from the study:

- The Pearson’s correlation analysis showed a positive relationship between EC and major ions, except with pH and Fe in the wet season and pH and F^- in the dry season.
- Nitrate significantly correlated with all variables in the dry season, possibly due to excessive use of synthetic fertilizer during irrigation and nitrification from pit latrines.
- PCA results indicate that groundwater samples in PC1 were influenced by geogenic and anthropogenic sources, PC2 indicated the influence of agricultural and domestic waste inputs, while PC3 suggests fluoride enrichment due to mineral weathering and industrial activities.

- The R-mode HCA identified three cluster groups influenced by: both geogenic and anthropogenic factors (Cluster I); synthetic fertilizers and nitrification from pit latrines (Cluster II); and interactions among various geochemical processes (Cluster III).
- Q-mode HCA identified three water types with increasing mineralization levels influenced by geogenic, anthropogenic, and evaporation processes.
- Piper diagrams indicated Ca-HCO3, Na-Cl, and mixed water types, suggesting that groundwater is influenced by mineral weathering, ion exchange, and evaporation processes.
- Gibbs plots, bivariate plots, molar ratios, and chloroalkaline indices (CAI–I, CAI–II) confirm that groundwater chemistry is influenced by geochemical processes like mineral weathering, evaporation, and ion exchange processes.
- Saturation indices revealed that most samples were undersaturated with respect to dolomite, calcite, and fluorite, as a result of carbonate precipitation.
- A significant percentage of groundwater samples (96.7 % in wet and 99.2 % in dry season) had partial pressure of CO_2 above atmospheric pCO_2 levels, as a source of acid for mineral dissolution.
- The study proves that geochemical modelling and chemometric analysis are effective techniques for assessing geochemical mechanisms and various chemical constituents within aquifer systems characterized by diverse contamination sources.
- Recommendations from the study include detailed PTEs analysis and their associated health risk assessments, as well as isotope hydrology studies to identify groundwater recharge sources and contamination, supporting efficient groundwater management to mitigate significant risks to human health.

6.9 Postface

This chapter answered RQ2: 'What role can chemometric analysis and geochemical modelling play in assessing geochemical evolution and mechanisms influencing groundwater chemistry as well as origin/source of chemical constituents in groundwater of Komadugu-Yobe basin?'. An integrated approach of chemometric analysis, geochemical modelling, bivariate plots, and ionic ratios was employed to investigate various hydrochemical processes, geochemical evolution and sources of constituents in the groundwater of the Komadugu-Yobe basin. The results indicated that the groundwater chemistry is largely influenced by the rock weathering/rock-water interaction process (SO6). However, the dry season samples show evaporation dominance in a few locations in the sedimentary quaternary parts of the study area. Chemometric analysis revealed the influence of geogenic, anthropogenic, and evaporation processes on groundwater quality of wet and dry seasons (SO7 and SO8). It is worth noting that the anthropogenic contamination resulted from industrial processes, domestic discharge, agricultural activities, mining activities, and nitrification processes in pit latrines. However, both industrial processes and agricultural and mining activities contribute various PTEs contamination to groundwater systems. Thus, it is therefore imperative to comprehensively assess heavy metal pollution and their associated human health risks to have a comprehensive understanding of the groundwater resources in the basin and this will be addressed in the proceeding chapter (chapter 7). Finally, a conceptual model for geochemical evolution and hydrogeochemical processes of groundwater in the Komadugu-Yobe basin was developed (SO9).

The next chapter (chapter 7) will characterize PTEs pollution sources and their associated human health risks by using chemometric approaches and index-based models.

7 Potentially toxic elements source identification and associated health risk in groundwater of Komadugu-Yobe basin, Lake Chad region: An integrated approach using chemometric analysis and index-based techniques[3]

7.1 Preface

The previous chapter (chapter 6) answered and fulfilled RQ2: ‘What role can chemometric analysis and geochemical modelling approach play in assessing geochemical evolution and mechanisms influencing groundwater chemistry as well as origin/source of chemical constituents in groundwater of Komadugu-Yobe basin?’. Various hydrogeochemical processes and mechanisms controlling groundwater evolution and sources/origin of chemical constituents present in the groundwater of KYB were identified and discussed. A conceptual model for the hydrogeochemical processes and geochemical mechanisms influencing the chemistry of groundwater was developed.

This chapter explores a methodology which combines chemometric analysis and index-based models to identify various sources and assess the level of contamination of potentially toxic elements (PTEs) and their associated human health risks as well as the speciation of some selected PTEs in the groundwater (RQ3). Transboundary Komadugu-Yobe basin was utilized as a case study. This chapter successfully identifies the sources, evaluates the pollution status, and assesses human health risks (non-carcinogenic and carcinogenic) associated with potentially toxic elements in the basin, thus answering RQ3. The chemometric approaches helped identify both geogenic and anthropogenic sources of pollution, such as industrial processes, mining activities, and agricultural activities (SO10). Heavy metals index-based models provide a clear depiction of the contamination levels across different parts of the basin suggesting significant contamination levels in the downstream areas and a few locations upstream where human activities are more concentrated (SO10).

Chemical speciation and complexation of selected potentially toxic elements were modelled using Geochemist's WorkBench (GWB) software (SO11). This modelling helps elucidate the chemical forms and behaviour of the metals in the groundwater, providing insights into their mobility, bioavailability, and potential risks to not only human health but also the vital ecosystem. Human health risk assessment (HHRA) for non-carcinogenic and carcinogenic risks was conducted utilizing US EPA health risk assessment model (USEPA, 2014) (SO12). The assessment reveals that both adults and children are at significant risk from prolonged exposure to contaminated groundwater. Hazard indices (HI) for non-carcinogenic risks and total carcinogenic risks (TCR) values indicate the need for immediate intervention to mitigate health risks posed by PTEs like arsenic, cadmium, chromium, nickel and lead. Additionally, this chapter provides comprehensive insights into the status of PTEs pollution and probable sources in the Komadugu-Yobe Basin which would help policymakers, stakeholders and relevant government agencies to implement effective strategies for groundwater management and health risk mitigation in the region.

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Author contribution

Conceptualization (A.S.), methodology (A.S.), software (A.S.), validation (A.S., R.M.K., and V.P.), formal analysis (A.S.), investigation (A.S.) resources (A.S.) data curation (A.S.), writing—original draft preparation (A.S.), writing—review and editing (A.S., R.M.K., and V.P.), visualization (A.S., and V.P.), supervision (R.M.K., and V.P.), project administration (A.S.), funding acquisition (R.M.K., and A.S.).

7.2 Abstract

Groundwater resources in semi-arid to arid regions are threatened by potentially toxic elements (PTEs) pollution. To protect the vital ecosystem, it is critical to evaluate pollution levels, pollution sources and human health risks of potentially toxic elements in groundwater. This study employed an integrated approach using index-based models and chemometric analysis to assess the level of PTEs pollution, possible pollution sources, and human health risks and ascertain the general quality of groundwater for drinking/domestic uses and irrigation in a regional scale in transboundary Komadugu-Yobe basin. Results analysis indicates Pb, Fe, Mn, and Cd were the main contaminants in the groundwater and no significant seasonal variation between wet and dry seasons groundwater. Cdeg, HEI, HPI, and mHPI described the groundwater as less polluted in the upstream parts and highly polluted in the downstream parts of the basin. GWQI and WPI reveal a significant percentage of the groundwater is excellent and good for drinking/domestic purposes whereas IWQI grouped the groundwater into moderate to high restriction zones with few samples in low and severe restriction zones. Human health risk assessment (HHRA) reveals that both adults and children are at risk of non-carcinogenic and carcinogenic health effects from drinking contaminated groundwater in the basin (mean HI > 1 for both adults and children; mean CR > 1.0×10^{-3} for adults and > 1.0×10^{-4} for children). As, Cd, Mn and Pb are the main indicators of non-carcinogenic health risks while Arsenic, cadmium and lead are the main sources of cancer-causing health risks and CKDu for both adults and children in wet and dry seasons. Correlation analysis suggests physicochemical parameters and PTEs likely have different geochemical behaviours and originated from distinct geogenic and anthropogenic sources. PCA/FA and R-mode HCA provide evidence of mixed geogenic and anthropogenic processes from various domestic and industrial discharges, and agricultural practices as the responsible factors for PTEs pollution. The insight from this study can help policymakers, stakeholders and relevant institutions in developing effective strategies and policies to safeguard and improve groundwater quality at regional and global scales.

Keywords: Heavy metals pollution, human health risk assessment, irrigation water quality index, chemometric analysis, Komadugu-Yobe basin

7.3 Introduction

Groundwater plays crucial roles in sustaining ecosystems, drinking water supply, and supporting agricultural practices in areas characterized by semi-arid and arid climates (Abba et al., 2024; Abu Salem et al., 2023; Asmoay et al., 2024). Currently, over one-third of the world population, mainly developing economies solemnly rely on groundwater for drinking (Dippong et al., 2024; Ismail et al., 2020; Noor et al., 2024). However, groundwater quality is significantly impacted by both geogenic and anthropogenic factors (Shi et al., 2024; Shuaibu et al., 2024; Wang et al., 2024). Geogenic factors such as rock-water interaction, atmospheric precipitation, volcanism, mineral weathering and dissolution contribute to high levels of physicochemical parameters and PTEs in groundwater systems (Ha et al., 2022; Liao et al., 2022; Shi et al., 2024). Additionally, anthropogenic factors including industrial effluents, intensive fertilizing, improper solid waste disposal, municipal sewage, biomedical wastes from hospitals, metal smelting, and mining activities further contribute to elevated levels of heavy metals in groundwater above the threshold limits (Georgescu et al., 2023; Liao et al., 2022; Sheng et al., 2022). Heavy metal/PTE pollution of groundwater presents a serious concern to not only human health but also the environment (Chowdhury et al., 2016; I. Khan & Umar, 2024). PTEs are chemical elements that are non-biodegradable, persistent, bio-accumulative, and toxic which exist in the environment in very small amounts, usually less than 0.1% by weight (Abba et al., 2024; Khan & Umar, 2024; Liao et al., 2022). However, they are highly toxic and accumulate in the human body when ingested, causing serious diseases even at extremely low concentrations (Khan & Umar, 2024; Noor et al., 2024). Consequently, assessment of PTEs and groundwater quality monitoring are essential for well-being and ecosystem sustainability. Moreover, there has been increasing research interest in the issue of PTEs pollution in groundwater and its associated health risks (Aktar et al., 2023; Ayyamperumal et al., 2024; Dippong & Resz, 2024; Fang et al., 2019; Georgescu et al., 2023; Khan & Umar, 2024; Sheng et al., 2022; Shi et al., 2024; Zhang et al., 2023; Zhou et al., 2024).

In Nigeria, groundwater from shallow wells is the primary source of water for domestic use and irrigation especially in the northeastern region characterized by semi-arid to arid climate (Fatunsin et al., 2024; Shuaibu et al., 2024). Groundwater in this region is not only affected by adverse climate conditions but also by multidimensional pollution from both geogenic and anthropogenic activities. Concerns regarding PTEs pollution in groundwater, which poses a significant health threat to humans and the vital ecosystem, are increasingly becoming a prominent and pressing issue within the Komadugu-Yobe Basin (Ahmed et al., 2018a; Kwaya et al., 2017). Studies on PTEs pollution in the Northeastern region of Nigeria have specifically identified the presence of non-carcinogenic and carcinogenic PTEs in water and vegetable plants. Thus, the present study delves into a detailed assessment of PTEs pollution levels in groundwater vis-à-vis their potential sources and associated health risks within the Komadugu-Yobe basin. This was achieved by employing index-based models and multivariate statistical analysis. The water quality index (WQI) computes a single numerical value from variable water quality parameters to determine the suitability of water for different purposes and its effective dissemination of associated information (Chen et al., 2023; Shuaibu et al., 2024). Irrigation water quality index (IWQI) is useful in agricultural planning and management of soil structure and fertility as it thoroughly assesses various factors associated with irrigation. Index-based models for PTEs pollution, including the contamination degree (Cdeg), heavy metal pollution index (HPI), heavy metal evaluation index (HEI), Nemerow index (NI), metal index (MI), pollution index (PI), and modified heavy metal pollution index (mHPI), were widely employed in different regions globally to effectively characterize the fundamental geochemical behaviours and effects of PTEs pollution in groundwater (Abba et al., 2024; Abdel-Satar et al., 2017; Balakrishnan & Ramu, 2016; Gad et al., 2021; Sheng et al., 2022; Tiwari et al., 2016). Komadugu-Yobe basin is susceptible to PTEs contamination caused by industrial processes, mining operations and agricultural activities which pose a serious threat to groundwater pollution and probable health risk impacts. Therefore, it is crucial to assess PTEs in the groundwater in this basin to avert potential health risks.

Chemometric statistical analysis enables an effective understanding of the intricate relationships that exist between various PTEs in groundwater as well as their reliable sources (Dey et al., 2024; Rajkumar et al., 2020). Chemometric approaches such as principal component analysis (PCA), factor analysis (FA), and hierarchical cluster analysis (HCA) help overcome the limitations of heavy metals pollution indices in the assessment of groundwater quality (Rajkumar et al., 2020). Therefore, multivariate statistical analysis is a reliable and credible method used to analyze intricate datasets in order to elucidate various geogenic and anthropogenic sources of pollution (He et al., 2023; Ustaoğlu et al., 2020). Zhou et al., (2023) employed principal component analysis to identify the origin/sources of various PTEs in groundwater in the Southwestern region of China. Their study presented a novel approach to understanding the geochemical characteristics of PTEs in groundwater and urban surface water. However, Abba et al., (2024) integrated PCA and HCA with pollution index-based models to ascertain the geogenic and anthropogenic sources of PTEs pollution and the pollution level of PTEs in groundwaters in Saudi Arabia. Moreover, various sources of PTEs pollution in groundwater were determined using Pearson's correlation analysis, PCA and HCA by Rajmohan et al., (2023). In addition, Egbueri, (2020a) employed hierarchical cluster analysis to classify groundwater samples based on their geochemical nature with respect to PTEs and physicochemical characteristics. Their study facilitated a comprehensive understanding of the impact of geology and anthropogenic activities on groundwater quality. Egbueri, (2020b) employed an integrated approach that coupled chemometric analysis, pollution index-based models and human health risk model to study the origin of PTEs pollution and their associated probabilistic human health risk in Nigeria. The present study employed multivariate statistical analysis to examine the potential origins of PTEs pollution, to understand the underlying mechanisms responsible for the degradation of the quality of groundwater in the Komadugu-Yobe basin.

Groundwater in the Komadugu-Yobe Basin is facing significant issues of PTEs pollution from geogenic and anthropogenic impacts which requires a detailed and systematic assessment to fully understand and address. This study aims to employ reliable and credible chemometric analytical approaches and an index-based model to adequately characterize PTEs pollution sources and their potential human health risk. To date, no attempt has been made to characterize the level of PTEs contamination, pollution source identification, human health risk assessment of PTEs and general quality of groundwater for drinking and irrigation on a regional scale in the transboundary Komadugu-Yobe basin. The findings from this study are essential in protecting the vital ecosystem, enhancement of groundwater supplies, and livelihoods. This will facilitate the development of sustainable water management strategies in the Komadugu-Yobe basin and the wider Lake Chad region.

7.4 Description of the Study Area

7.4.1 Study area settings

Komadugu-Yobe basin (Figure 7.1a), is located south of the Sahara Desert in the greater Lake Chad basin, at an elevation ranging from 285 to 1,750 meters with an approximate surface area of 150,000 km^2 which contributes around 35% of the traditional flow to Lake Chad basin (Adeyeri et al., 2020). The basin has important hydrological features in northeastern Nigeria, extending into parts of the Niger Republic (Castelein, 2002). The basin is characterized by wet and dry seasons which occur between June and October and between November to May respectively. The basin has an average annual temperature of 29 °C, and an average annual precipitation between 300 mm in Yobe and 1,200 mm around Bauch and Jos Plateau. Evaporation is high in the basin, particularly towards the Lake Chad region. The basin experiences an average annual potential evaporation over a range of 1,800 mm to 2,400 mm (Bura et al., 2018; Ndehedehe et al., 2016). The climate in the basin is controlled by the northeasterly wind which blows sand and dust from the Sahara Desert towards the Gulf of Guinea during the dry season and the southerly wind typically known as the western African monsoon blows from the Atlantic Ocean which leads to higher temperatures and increased rainfall (Adeyeri & Oyekan, 2020).

The basin exhibits a wide range of geographical features, including flat floodplains and steep terrains. Two river systems Komadugu Gana and Yobe river meets to form the Komadugu-Yobe River both of which receives water from the Jama'are and Hadejia Rivers (Adeyeri et al., 2019). Rivers in the basin flow towards Lake Chad due to the typical decrease in elevation from high lands in the southern upstream to the lower lands in the north/downstream. Tiga and Chalawa Gorge dams are the two notable dams in the basin which are mostly used for irrigation and water supply to rural and urban areas. However, they tend to significantly alter the flow pattern of water and its availability accessible further downstream (M. J. Chiroma et al., 2015; Gana et al., 2018; Goes, 1999). The Komadugu Yobe Basin is strategically significant to national and international communities as its valuable wetlands support various occupations including agriculture, fishing, and forestry (Adeyeri et al., 2020; Shuaibu et al., 2024). Both subsistence and commercial farming are popular in the basin. Livestock farming, including cattle, goats, and sheep, is also an occupation among many locals in the basin. The vegetation in the basin is mostly made of savanna grasses, shrubs, trees and bushes (Goes, 2002; Goni et al., 2023). The basin is bedevilled with insurgency ranging from activities of Boko Haram in the far downstream, banditry and farmer-herders crisis around Bauch, Jigawa and Kano. Furthermore, the basin is faced with multiple environmental challenges, such as water scarcity, attenuated river flows due to upstream damming, and soil erosion. Climate change is believed to exacerbate these challenges, reducing agricultural productivity and the availability of water (Adeyeri et al., 2017; Shuaibu et al., 2022).

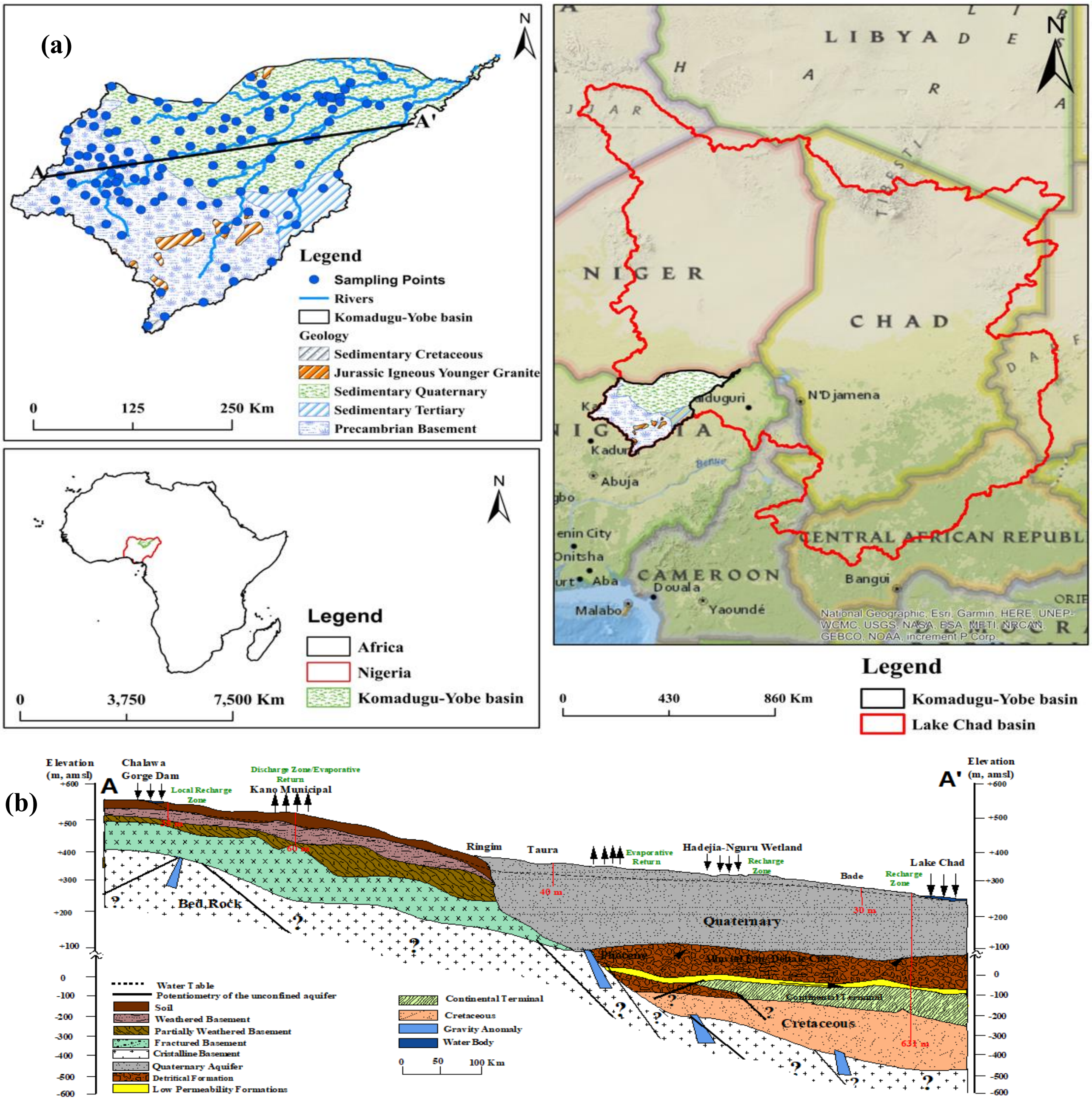


Figure 7.1 (a) The study area map showing various sampling locations, different geologies and river systems (b) Geological cross-section AA' showing stratigraphic sequence of various aquifer materials in the study area.

7.4.2 General geology and hydrogeology

Komadugu-Yobe Basin is made up of complex varying geological and hydrogeological systems. The basin is primarily underlain by Precambrian basement rock and quaternary sedimentary formation (Figure 7.1a). The latter is distributed in the eastern part of the basin towards the downstream. Sedimentary Chad formations is one of the prominent geological unit in the basin which consist of Plio-Pleistocene lacustrine deposits and sandy Aeolian deposits that is alternated in fine to coarse grained sand (Edmunds et al., 1999; Goni et al., 2023; Shuaibu et al., 2022). It also consists of sandstones, shales, alluvial fans, lake margins and conglomerates deposited over geological time from late Miocene to present by ancient river systems and lacustrine environments (Kwaya et al., 2017; Wali, Dankani, et al., 2020). The former consists of the Pan-African crystalline rocks overlain by younger granites. This formation are characterized by low permeable shallow weathered basement that are mostly igneous and metamorphic rocks of Pan-African orogeny (Schuster et al., 2009). Various rock minerals are distributed across the basin such as biotite, olivine, pyroxene, syenites, gabbros, amphibole, plagioclase, quartz, rhyolites and ignimbrites (Edmunds et al., 1999; Obaje, 2011). The stratigraphic sequence of the sedimentary quaternary includes strata such as the Keri-Keri formation, Maastrichtian Fika Shale, Gombe Sandstone, Bima Sandstone, and Gongila formation. Figure 7.1b presents a stratigraphic sequence of various aquifer materials in the basin. Faults and symmetrical folds are the main geological structures that predominate the northeast-northwest trend in the basin (Avbovbo et al., 1986; Bura et al., 2018; Goni et al., 2001; Obaje et al., 2004). The faults resulted in horsts, grabens and various other related geologic structures in the Precambrian basement sections whereas, the folds consists of simple and folded sediments which flattens with depth (Shuaibu et al., 2024). The main aquifer system in sedimentary quaternary section is Chad formation which is made up of unconsolidated sand, gravel deposits, and alluvial deposits (Ndehedehe et al., 2016). This aquifer system consists of lower, middle and upper aquifers that is separated by thick clay layers (Kwaya et al., 2017; Shuaibu et al., 2024). However, the weathered basement and fractured basements are the primary zone for groundwater supply in the Precambrian/upstream section. The primary recharge sources in the basin include rainfall infiltration, deep percolation of surface water throughout Hadejia-Nguru wetlands, Komadugu-Yobe valley, rivers, streams, Tiga dam, and Chalawa gorge dam (Goni et al., 2023). Other areas such as Yobe floodplain and Unconsolidated Lake Chad quaternary aquifer receives recharges through seepage from river channels, rainfall runoff percolation, infiltration of floodwaters and excess rainfall (Shuaibu et al., 2024).

7.5 Materials and Methods

7.5.1 Groundwater sampling and laboratory analysis

A total of 240 groundwater samples were collected in two sampling campaigns spanning from August 2021 to April 2022 covering wet and dry seasons. Multiparameter digital pH/conductivity meter (Model 99720) was used to measure the physicochemical parameters such as EC, pH, Eh and DO meter for dissolved oxygen in-situ. Groundwater sampling locations were marked using Geographic Information System (GPS) while groundwater sampling depth was measured using water level dip meter. Prior to sampling, hand pumps and borewell were pumped for about 5 - 10 min to remove any stagnant water and debris from the casing. Groundwater samples were then collected in two sets of 50 mL polyethylene centrifuge tubes labelled A and B. Samples A were filtered through 0.45 µm acetate cellulose syringe filter into 50 mL polyethylene bottle and acidified with 0.4 ml of concentrated nitric acid ($\mathrm{NHO_3}$) to maintain pH of < 2 for cations and PTEs analysis whereas samples B were filtered through 0.45 µm acetate cellulose syringe filter into a 50 mL polyethylene bottles for anions analysis. Groundwater samples were stored at ~4◦C and shipped to the Environmental Laboratory of the Department of Civil and Environmental Engineering, University of Strathclyde, United Kingdom for further analysis. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for major cations and PTEs analysis while the major ions were analysed using ion chromatography (IC) for major anions. Total alkalinity was analysed in-situ using a HACH Digital Titrator (Model: 16900, HACH International) with 0.16 N and 1.6 N H_2SO_4 cartridges and in the Laboratory using KONE equipment. The instrument's detection limits for Fe, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn were determined to be 1, 5, 1, 1, 2, 4, 0.3, 1, 4, and 0.3 µg/L. Measurement accuracy was checked by performing duplicate analysis. Additionally, ionic balance error for major ions was found to be with the recommended limits for all samples in both seasons.

7.5.2 Assessment of heavy metal pollution in groundwater

Degree of Contamination (C_{deg}), Heavy Metal Evaluation Index (HEI), Heavy Metal Pollution Index (HPI), and modified Heavy Metal Index (mHPI) were employed to ascertain the level of heavy metal pollution in this study. The methodologies for evaluating these indices were presented in Abba et al., (2024), Dash et al., (2019), Rajkumar et al., (2020) and Dey et al., (2024). Dash et al., (2019) developed modified heavy metal index that addresses the limitations of both HEI and HPI by assigning weights to each element based on their relative importance and possible health risk impacts for comprehensive assessment of the level of PTEs pollution in drinking water. The degree of contamination assesses the impacts of contaminants in drinking water by evaluating the overall deviation of concentration of PTEs from their standard value (Abba et al., 2024; Dash et al., 2019; Rajkumar et al., 2020). However, heavy metal evaluation index evaluates the risk associated with drinking contaminated water by determining the overall water quality based on concentration of heavy metal. In addition, the HPI provides the cumulative/composite effects of each heavy metal on the general quality of drinking water by evaluating the ratio of heavy metal pollution (Balakrishnan & Ramu, 2016; Rajkumar et al., 2020). The classification of C_{deg}, HEI, HPI, and mHPI are presented in Table SM7.1.

7.5.3 Groundwater quality index (GWQI)

This study employed groundwater quality index (GWQI) to elucidate the overall quality of groundwater in Komadugu-Yobe basin considering physicochemical parameters, major ions and PTEs. The basic steps and the empirical relations utilized while computing the groundwater quality index in this study were described in Shuaibu et al., (2024). Table SM7.2 presented the GWQI classification.

7.5.4 Water pollution index (WPI)

Hossain & Patra, (2020) proposed a new approach of evaluating water quality/pollution index. The approach has been applied in various research to evaluate surface water and groundwater quality and has gained widespread acceptance worldwide because of its simplicity and flexibility and gives an efficient water quality/pollution status (Abba et al., 2024; Agbasi et al., 2023; Hossain & Patra, 2020). The approach is not limited to a specific water source or quality parameter and can accommodate an unlimited number of water quality parameters (physicochemical/ PTEs) in its computation. Moreover, the method does not requires the assignment of weight to the water quality parameters which could potentially introduce bias into assessment of water quality (Agbasi et al., 2023). This study has employed the WPI to evaluate groundwater quality/pollution status following two easy steps described by Hossain & Patra, (2020). In this study, we have considered 21 parameters viz pH, EC, Na, K, Ca, Mg, Cl, HCO_3, NO_3, SO_4, F, As, Cd, Cu, Zn, Pb, Ni, Fe, Mn, Cr and Co to estimate the groundwater pollution load based on their standard permissible limits recommended by WHO, (2018) guidelines. Groundwater is classified as highly polluted when WPI > 1, moderately polluted when WPI is between 0.75 and 1, good if WPI is between 0.5 and 0.75, and excellent if WPI is < 0.5 (Abba et al., 2024; Hossain & Patra, 2020)

7.5.5. Suitability indices of irrigation water

The agricultural water quality often influences crop productivity (Samtio et al., 2023). The suitability of the groundater for agricultural purposes was assessed using water quality indices for irrigation. Various parameters employed to evaluate the quality of groundwater for irrigation together with the associated empirical relations were presented in Table 7.1.

Table 7.1 Irrigation water quality parameters.

Quality Parameter	Adopted Formular	Reference
Electrical Conductivity (EC)	-	(Ishaku et al., 2011)
Sodium adsorption ratio (SAR)	$SAR = \frac{Na^{+}}{\sqrt{\frac{1}{2}(Ca^{2+} + Mg^{2+})}}$	(Ghosh & Bera, 2023; Panaskar et al., 2016)
Sodium Percentage (Na%)	$Na^{+}\% = \left[\frac{(Na^{+} + K^{+})}{(Na^{+} + K^{+} + Ca^{2+} + Mg^{2+})}\right] \times 100$	(Eyankware et al., 2018; Rajesh et al., 2019)
Residual sodium carbon (RSC)	$RSC = (CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+})$	(Ishaku et al., 2011; Sikakwe & Eyong, 2022)
Potential salinity (PS)	$PS = Cl^{-} + \frac{SO_4^{2-}}{2}$	(Ishaku et al., 2011)
Magnesium Hazard (MH)	$MH = \left[\frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}}\right] \times 100$	(Rajesh et al., 2019)
Permeability Index (PI)	$PI = \left[\frac{Na^{+} + \sqrt{HCO_3^{-}}}{\sqrt{Na^{+} + Ca^{2+} + Mg^{2+}}}\right] \times 100$	(Panaskar et al., 2016; Rajesh et al., 2019)
Kelly Index (KI)	$KI = \frac{Na^{+}}{(Ca^{2+} + Mg^{2+})}$	(Hwang et al., 2017; Sikakwe & Eyong, 2022)

Where all ions are measured in meq/L, EC is measured in µS/cm

7.5.6 Irrigation water quality index (IWQI)

Various factors such as soil texture, crop type, climate, and irrigation methods, as well as irrigation water has a significant impact on agricultural yield and profitability (Aravinthasamy et al., 2020; Gad et al., 2021; Hussein et al., 2024). Irrigation water with higher salinity levels has a negative effect not only on soil but plants yield. Plants growth and development is disrupted by the present of mineral salt in irrigation waters which alters the soil structure and thus affecting soil permeability and aeration (Hussein et al., 2024). IWQI developed by Meireles et al., (2010) was employed to assess the quality of groundwater for irrigation. The dominant parameters that have great influence on irrigation water quality such as EC, Na, Cl, HCO_3 and SAR were used (Abbasnia et al., 2018; Batarseh et al., 2021). Irrigation water quality index computation requires three basic steps: calculation irrigation water quality limiting parameter (qi) (Eq. 7.1), Assignment of relative weight (wi) (Eq. 7.2, Table SM7.3) and finally estimation of irrigation water quality index using Eq. 7.3.

$$\boldsymbol{q_i = q_{max} - \left(\frac{(X_{ij} - X_{inf}) \times q_{amp}}{X_{amp}}\right)} \tag{7.1}$$

where, q_i parameter limiting value for irrigation water quality assessment, q_{max} is the maximum value of q_i for every class; the observed value of every parameter is represented by X_{ij}; X_{inf} refers the lower limit value of the class to which the parameter belongs; q_{amp} represents the measurement class amplitude and X_{amp} corresponds to class amplitude to which the parameter belongs. The limiting parameters of irrigation water quality (q_i) were presented in Table SM7.4.

The relative weight of each parameter was calculated using Eq. 7.2.

$$\boldsymbol{w_i = \frac{W_i}{\sum_{i=1}^{n} W_i}} \tag{7.2}$$

Finally, IWQI was calculated using Eq. 7.3.

$$\boldsymbol{IWQI = \sum_{i=1}^{n} q_i w_i} \tag{7.3}$$

Where, q_i is the irrigation water quality limiting parameter value and w_i is the unit weight of i^{th} parameter.

7.5.7. Health risk assessment of PTEs

Although several studies have recently employed various mathematical models and methods to evaluate health risks associated with PTEs all of which adhere to the same principles (Chen et al., 2023; Dey et al., 2024; Khan & Umar, 2024; Sheng et al., 2022). This study employed the human health risk assessment model proposed by the US Environmental Protection Agency (USEPA, 2014). We conducted separate human health risk evaluations encountered by children and adults owing to their physiological variations. The main pathways of exposure are widely thought to be direct ingestion and skin contact (dermal absorption) (Chen et al., 2023; Jabbo et al., 2022). Human health risks associated with PTEs are categorized as either non-carcinogenic risk (NCR) or carcinogenic risk (CR). NCR relates to health effects due to prolonged exposure to PTEs that do not cause cancer and are represented by hazard index (HI) (Eq. (7.4)). However, CR relates to probable cancer health effects an individual would develop over their lifetime due prolonged exposure to carcinogenic PTEs (Eq. (7.5)) (Barkat et al., 2023; Liang et al., 2023; Zhou et al., 2024). The chronic daily intake due to ingestion $\mathrm{CDI_i}$ and dermal absorption $\mathrm{CDI_d}$ were calculated as follows:

$$\boldsymbol{CDI_i = \frac{C_i \times IR \times EF \times ED}{BW \times AT}} \tag{7.4}$$

$$\boldsymbol{CDI_d = \frac{C_i \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT}} \tag{7.5}$$

Where, $\mathrm{CDI_i}$ and $\mathrm{CDI_d}$ are measured in (µg/kg/day), $\mathrm{C_i}$ Is the concentration of PTEs in water (µg/L), IR represents ingestion rate per day (L/day), EF refers to exposure frequency (days/year), ED is the exposure duration (Years), BW represent average weight (kg), AT represents the average exposure time (days), SA Is the exposed skin surface area ($\mathrm{cm^2}$), ET is dermal exposure time (h/day), CF is the conversion factor, and $\mathrm{K_p}$ represent the permeability coefficient of the skin in water (cm/h). Table SM7.5 presented values of all parameters required in the calculation.

NCR associated with intake and dermal absorption of PTEs was assessed by calculating the hazard quotient (HQ). Hazard index (HI) represents the overall non-carcinogenic risk of heavy metals. PTEs such as As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were considered to evaluate the non-carcinogenic health risk in both wet and dry seasons in the groundwater samples. HQ and HI were calculated as follows:

$$\boldsymbol{HQ_i = \frac{CDI_i}{RfD_i}} \tag{7.6}$$

$$\boldsymbol{HQ_d = \frac{CDI_d}{RfD_d}} \tag{7.7}$$

$$\boldsymbol{HQ = HQ_i + HQ_d} \tag{7.8}$$

$$\boldsymbol{HI = \sum HQ} \tag{7.9}$$

Where, HQ_i and HQ_d represents the hazard quotient of oral ingestion and dermal absorption of PTEs respectively, RfD_i and RfD_d represents oral ingestion and dermal absorption reference dose (µg/kg/day) respectively. RfD_i and RfD_d values for respective PTEs are detailed in Table SM7.6 in the Appendix. HI or HQ values < 1 signify no non-carcinogenic health risk, while HI or HQ values > 1 signify PTEs pollution level could cause non-carcinogenic health risks. (Fatunsin et al., 2024; Muhammad et al., 2011; Noor et al., 2024; USEPA, 2014; Wang et al., 2025).

Furthermore, the carcinogenic risk (CR) and the total carcinogenic health risk (TCR) were computed by Eqs. (7.10) – (7.13). As, Cd, Cr, Ni, and Pb were selected in the respective seasons for assessment of carcinogenic health risks as they potentially pose a cancer health risk (Dey et al., 2024; Khan & Umar, 2024; Toi Bissang et al., 2024).

$$\boldsymbol{CR_i = CDI_i \times SF} \tag{7.10}$$

$$\boldsymbol{CR_d = CDI_d \times SF} \tag{7.11}$$

$$\boldsymbol{CR = CR_i + CR_d} \tag{7.12}$$

$$\boldsymbol{TCR = \sum CR} \tag{7.13}$$

Where, $\mathrm{CR_i}$ and $\mathrm{CR_d}$ represents the carcinogenic health risk from oral ingestion and dermal absorption of PTEs respectively, SF Is the cancer slope factor (µg/kg/day). Table SM7.5 presented values of the respective PTEs required for the calculation. The cancer risk ranking criteria are presented in Table SM7.1.

7.5.8 Tracing the source of PTEs using multivariate statistical analysis

This study employed key methodologies such as principal component analysis (PCA), factor analysis (FA), hierarchical cluster analysis (HCA), and correlation analysis to identify different sources of heavy metal pollution and their interrelationships. Pearson’s correlation coefficient assesses the relationship between various PTEs in groundwater (Sheng et al., 2022). It is widely used in various disciplines, including engineering, statistics, economics, psychology, and biology. PCA is a statistical method that extracts information from a set of original, correlated variables by converting them into linearly independent variables known as principle components (PCs). (Rajkumar et al., 2020; Sheng et al., 2022; Yu et al., 2022; Zhang et al., 2021). Factor Analysis (FA) is closely linked to PCA and reduces the influence of less important Principal Components (PCs) by applying varimax rotation to the axis determined by PCA (Sheng et al., 2022). PCA/FA is a statistical technique that transforms original variables into uncorrelated variables called principal components, enabling dimensionality reduction while maintaining the significant information in the dataset (Varol, 2020). Sheng et al., (2022) demonstrated the effectiveness of PCA/FA-based analysis for investigating the potential origins of PTE pollution in water. Therefore, this study employed PCA/FA using varimax rotation to identify the source of PTEs in the groundwater. It is established by several studies that PTEs with elevated loading in the same PC generally originate from similar sources (Barkat et al., 2023; Rajkumar et al., 2020; Rajmohan et al., 2023; Sheng et al., 2022; Varol, 2020; Yu et al., 2022; Zhang et al., 2020). Hierarchical cluster analysis is used to group parameters that exhibit similar attributes together in large datasets (Papazotos et al., 2023). The hierarchical clustering analysis (HCA) was employed to classify the datasets based on their similarity (Jabbo et al., 2022). This study employed the R-mode HCA using the ward's linkage method which groups water quality parameters in the same cluster based on their similarity or dissimilarity. The variation of PTEs and cluster similarities were estimated using the squared Euclidean distances. Moreover, the Z-score data standardization technique was adopted to minimize statistical biases in the groundwater datasets (Abba et al., 2024).

7.6 Results and Discussion

7.6.1 Hydrochemical Characteristics of Physicochemical Parameters and PTEs

Figure 7.2 shows box plots of the physicochemical parameters and various trace elements in wet and dry season groundwater of the Komadugu-Yobe basin. Mean concentrations of pH, EC, Eh, DO, Na, K, Ca, Mg, Cl, HCO_3,SO_4, NO_3, and F were 7.2, 462 µS/cm, 62.5 mV, 6.2 mg/L, 36 mg/L, 10 mg/L, 39 mg/L, 9.9 mg/L, 48 mg/L, 120 mg/L, 15 mg/L, 42 mg/L, and 0.3 mg/L for wet season and 6.41, 538 µS/cm, 76.3 mV, 6.2 mg/L, 33mg/L, 9 mg/L, 40 mg/L, 9.2 mg/L, 58 mg/L, 64 mg/L, 16 mg/L, 65 mg/L, and 0.7 mg/L for dry season. The groundwater is mostly alkalescent and oxidized in both seasons based on the mean concentration of pH and Eh. However, mean values of physicochemical parameters fell within the permissible limits of drinking water prescribed by WHO, (2018) except for nitrate during the dry season and mean values of nitrate are very close to the maximum acceptable limit in the wet season. This could be due to various anthropogenic inputs into groundwater systems from irrigation returns, synthetic fertilizers, domestic sewage, leachate and nitrification from pit latrines. However, high mean values of EC, Ca, K, SO_4, and Cl relative to their maximum concentrations may be ascribed to the process of weathering and dissolution of geological minerals as well as various other anthropogenic activities. No significant variations were observed with respect to physicochemical parameters between wet and dry season groundwater samples (Figure 7.2a and b). However, the groundwater chemistry is evolving primarily due to overexploitation, anthropogenic inputs, rock-weathering and mineralization (Shuaibu et al., 2024).

PTEs groundwater contamination necessitates comprehensive groundwater research due to its toxicity and life-threatening challenges. Though, PTEs , like Cu, Se, and Zn are essential at very low concentrations for human physiological processes, while their presence at higher concentrations can be harmful (Toi Bissang et al., 2024; Wickramarathna et al., 2017). Results of the descriptive statistics of the PTEs are presented in Figure 7.2c. It is worth noting that As, Cd, Co, Cr and Ni particularly in the upstream parts of the basin have concentrations below the detection limits during the respective wet and dry seasons. For instance, As, Cd, Co, Cr, and Ni have concentrations above the detection limit in only 4, 23, 8, 5 and 29 samples out of 120 collected in the wet season respectively while 4, 21, 8, 5 and 16 samples out of the 120 collected recorded As, Cd, Co, Cr, and Ni concentration above the detection limits during dry season respectively. However, Pb, Cu, Fe, Mn and Zn have concentrations above the detection limits in almost all the samples collected during respective seasons. As concentration varied from 5 to 46.5 µg/L (mean of 5.6 µg/L) and from 5 to 18.8 µg/L (mean of 5.3 µg/L) in the wet season and dry season respectively, (Figure 7.2c); 2.5 % and 1.67 % of the groundwater in the respective seasons had concentrations exceeding the permissible limits for As of 10 µg/L (WHO, 2018). Moreover, Pb varied considerably in concentrations (4–32.1, 28.8 µg/L, average of 7.9 and 7.1 µg/L in the respective seasons. Fe had varied from 1 to 19430, and 11780 µg/L with an average of 979.9 and 659.4 µg/L in the respective seasons. Cd, Co, Cu and Cr varied from below detection limits (bdl) to 22.6, 13.5, 53.4 and 5.5 µg/L with mean concentrations of 2.1, 1.2, 7.9 and 2.1 µg/L in the wet season and from bdl to 19.2, 19.0, 56.3 and 6.4 µg/L with mean concentrations of 1.9, 1.4, 6.9 and 2.1 µg/L in the dry season. 0.8 % and 2.5 % of the groundwater in the respective seasons had concentrations exceeding the drinking water limits for Co of 4 µg/L ((WHO, 2018)). Similarly, Mn, and Ni were observed to have a maximum value of 2305 and 25.7µg/L, and 1846 and 9.3 µg/L in the respective seasons. Their mean concentrations in the respective wet and dry seasons were 134.7 and 1.6 µg/L, and 118.2 and 1.3 µg/L. Finally, Zn varied from 1.3 to 264.9 µg/L (mean of 36.6 µg/L) and from 4.9 to 684.5 µg/L (mean of 41.2 µg/L) in the respective seasons.

Mean concentration of the PTEs decreased in the following order: Fe > Mn > Zn > Cu > Pb > As > Cr > Cd > Ni > Co in the wet season and Fe > Mn > Zn > Pb > Cu > As > Cr > Cd > Co > Ni in the dry season. Mean value of all trace elements fell below the maximum acceptable limits recommended by WHO, (2018) in the respective seasons except for Fe, Mn, Pb and Cd. Accordingly, 37.5 % and 27.5 %, 25 % and 23.3 %, 21.67 % and 15 %, and 12.5 % and 14.2 % of the respective wet and dry season samples exceeded the WHO, (2018) maximum permissible limits for Fe (300 µg/L), Mn (80 µg/L), Pb (10 µg/L), and Cd (3 µg/L). Thus, Fe, Mn, Pb and Cd were the main contaminants in terms of PTE pollution in the basin. Long-term exposure to Cd, Pb, Ni, Cr and As are the main aetiological factors for chronic kidney disease of unknown aetiologies (CKDu) (Ahmed et al., 2018; Diyabalanage et al., 2017; Fiseha et al., 2024; Nanayakkara et al., 2019). Moreover, elevated Cd and As in the groundwater can cause tubular cell necrosis, newborn deaths, myocardial infarction, diabetes mellitus and keratoderma (Abba et al., 2024; Toi Bissang et al., 2024). As gets enriched in the groundwater system through the application of pesticides and synthetic fertilizers. Therefore, Cd, Pb and As could be influencing factors for CKDu and cancer-causing PTEs in the basin. Long exposure to Cu and Zn could lead to health issues associated with gastrointestinal disorders and stomach pain, nausea and diarrhoea respectively (Abba et al., 2024). However, high concentrations Fe, Mn, and Co present in groundwater are associated with "red-hot diseases", neurological deficits, and polycythaemia and artery complications (Egbueri, 2020b; Fatunsin et al., 2024). Fe and various other PTEs enter groundwater through the process of weathering of ferromanganese minerals, such as biotite, pyroxene and amphiboles, which are commonly found in gneissic and charnockitic rocks (Wickramarathna et al., 2017). In a nutshell, the results of the trace elements indicated some concentrations exceeding the recommended limits of WHO, (2018). Co, Mn and Fe displayed concentrations exceeding the recommended limits in a few samples whereas Cr, Cu, Ni and Zn in all samples had concentrations below the maximum permissible limits recommended by (WHO, 2018) in both seasons.

Figure 7.3a and b present Pourbaix diagrams of Fe and As in groundwater. Dissolved Fe species plot showed most of the groundwater samples during both seasons belong to the hematite field with the remaining samples in both seasons categorized in reduced ferrous Fe^{2+} field (Figure 7.3a). This suggests that the groundwater is generally in an oxidizing environment with sufficient Eh enough to favour hematite formation. However, some of the groundwater samples that occurred under reducing conditions could favour conditions for metals and various other contaminants to be mobile. The Eh-pH plot for dissolved As species shows that most of the groundwater samples in respective seasons belong to $H_2AsO_4^-$ and $HAsO_4^{2-}$ while the remaining samples falls into $As(OH)_3$ and Orpiment (As_2S_3) field (Fig. 7.3b). $H_2AsO_4^-$ and $HAsO_4^{2-}$ field indicated that the As is in oxidized form (As^{5+}) which is mobile in shallow groundwaters. However, the $As(OH)_3$ field correspond to As in reduced form (As^{3+}) arsenite which is mobile and very toxic under anoxic conditions mostly in deep or stagnant groundwater systems while the orpiment field indicated the precipitation of arsenic as As_2S_3 in the present of sulfide under very reducing conditions (Khan & Umar, 2024). In a nutshell, arsenic in oxidized form As^{5+} predominates over As^{3+}which is in reduced form in the aquifers. Furthermore, the Eh-pH plots for dissolved NO_3^- species and that of As in the presence of Pb and sulfide are presented in Figures 7.3c and d. Most of the groundwater samples in both seasons fall into the N_2 field which indicates less reducing conditions leading to the denitrification process while the remaining samples are projected into the NH_4^+ region suggesting strong reducing conditions (Figure 7.3c). This indicates the presence of biogeochemical processes occurring in the groundwater system. Moreover, the Eh−pH plot for dissolved As species in the presence of Pb and sulphide indicates that most of the groundwater projected onto $Pb_3(AsO_4)_2$ field which indicates that arsenic oxidized to arsenate in the presence of Pb and S_2 to form lead arsenate whereas the remaining are projected in $As(OH)_3$ and realgar (As_4S_4) region with the latter indicating reducing condition that converted arsenic to arsenite which is more toxic and mobile and the former indicated arsenic in form of sulfide mineral under very reducing conditions.

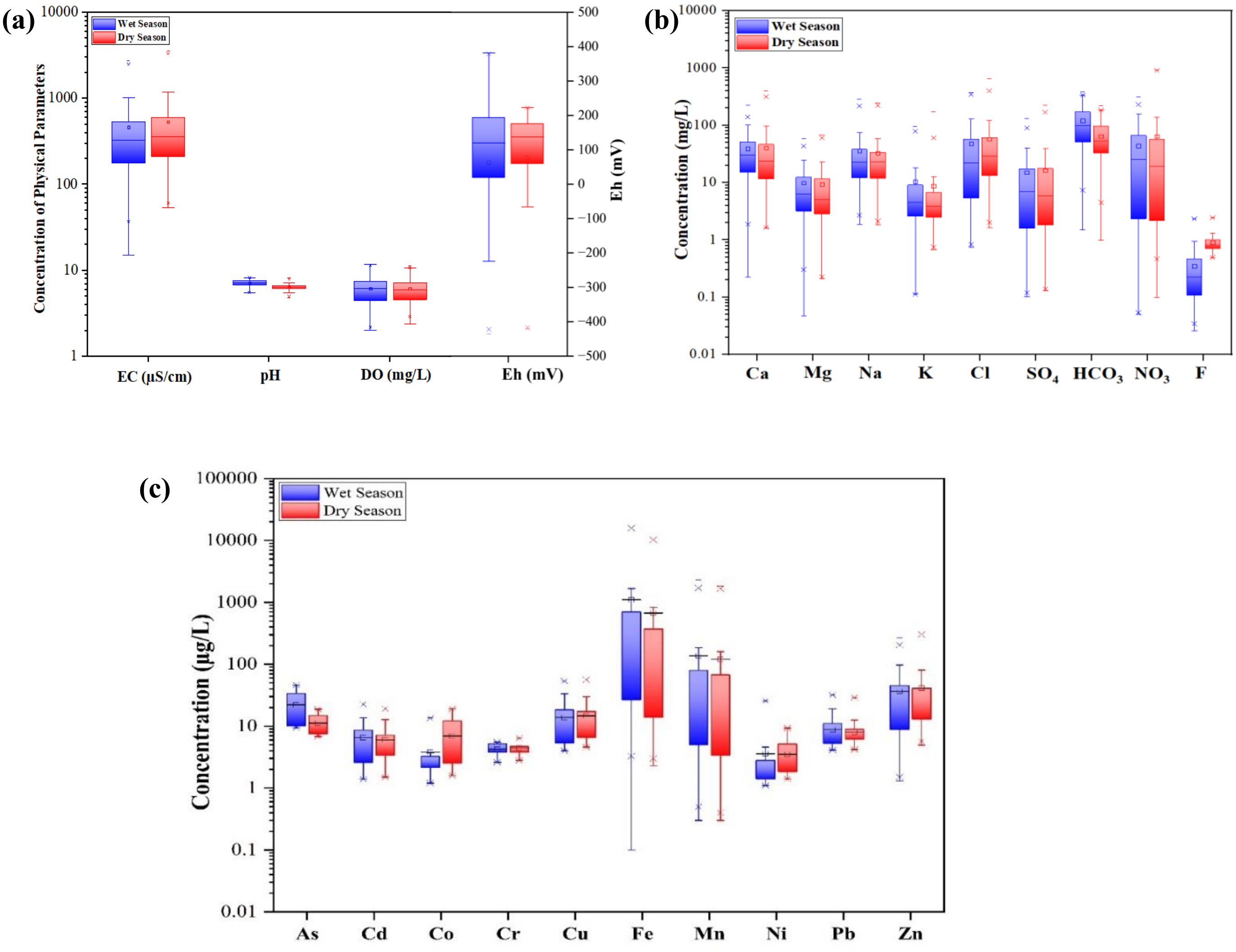


Figure 7.2 Box plot of (a) physicochemical parameters (b) major ions (c) PTEs.

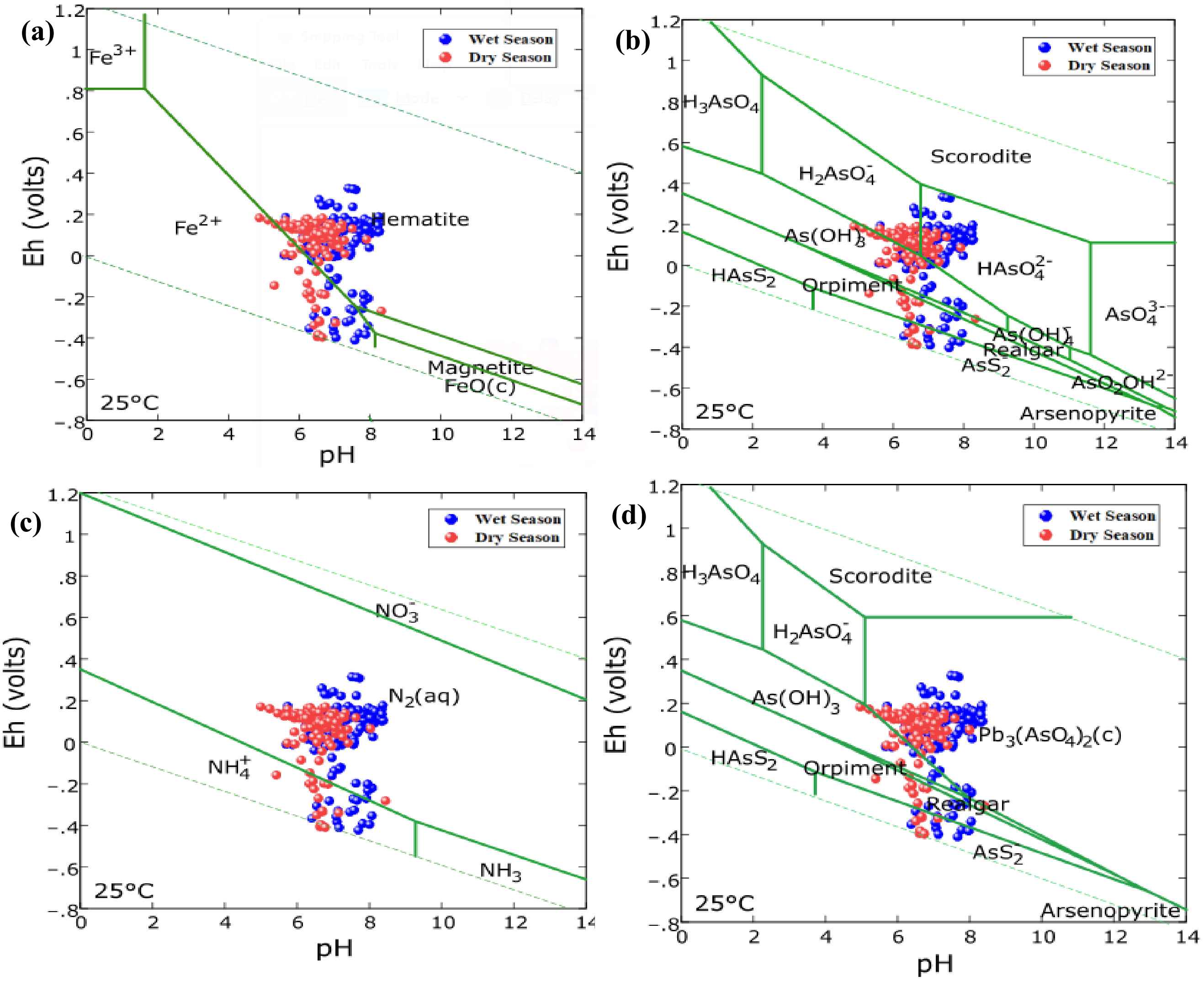


Figure 7.3 Pourbaix diagram of (a) Fe species (b) As species (c) NO_3^- species (d) As species in the presence of Pb and S_2.

7.6.2 Pollution status of PTEs in groundwater

A thorough understanding of contamination levels caused by PTEs in groundwater is crucial for environmental sustainability. Four indexical models namely Cdeg, HEI, HPI and mHPI were employed to assess the level of pollution of specific PTEs in groundwater for an effective understanding of their geogenic and anthropogenic sources in the groundwater of the Komadugu-Yobe basin. The value of Cdeg varied from -8.4 to 58.8, with a mean value of -2.6 in the wet season and from -8.4 to 32.9 with a mean value of -4.0 in the dry season (Table 7.2).

The classification criterion for Cdeg is presented in Table SM1. Accordingly, about 89.2 %, 4.2 %, 3.3 %, and 3.3 % of the groundwater revealed low, moderate, considerable and very high contamination with respect to Cdeg values during the wet season while the dry season groundwater samples revealed about 91.7 %, 1.67 %, 3.3 % and 3.3 % in low, moderate, considerable and very high/significant contamination categories. This is corroborated with the findings of Hamidu et al., (2021) in the Chalawa and Sharada industrial areas of Kano city, Nigeria. Furthermore, the spatial distribution map of Cdeg indicates that upstream parts of the basin had the lowest level of contamination whereas some locations in the sedimentary quaternary (downstream) parts exhibited significant contamination levels in both seasons (Figure SM7.1). HEI of the groundwater samples varied from 1.6 to 88.8 (mean of 7.4) and from 1.6 to 42.9 (mean of 6.0) in the wet and dry seasons respectively. HEI value below 10 signifies low contamination, values between 10 and 20 show moderate contamination, and values greater than 20 signify high contamination level (Asmoay et al., 2024; Dippong & Resz, 2024). Approximately 83.3 %, 9.2 %, and 7.5 % of the groundwater revealed low, moderate, and high contamination levels with respect to HEI values during the wet season. In the same vein, the dry season groundwater samples revealed about 87.5 %, 5.8 %, and 6.7 % were categorized in low, moderate, and high contamination classes. The spatial distribution map of HEI shows the dominance of low pollution classes in the Precambrian basement parts of the basin during both seasons (Figure SM7.1). This resonated with the results of Cdeg above. The study conducted by Abba et al., (2024) in Saudi Arabia on PTE pollution displayed very close results between Cdeg and HEI. Additionally, HPI ranged from 31.4 to 338.3 (mean of 55.7) and from 31.4 to 286.6 (mean of 52.9) in the respective seasons (Table 7.2). Table SM7.1 presents the ranking criterion for HPI. Accordingly, about 90 % and 10 % of the wet season groundwater samples showed low and high pollution classes while the dry season groundwater samples revealed approximately 88.3 % and 11.7 % were in low and heavy pollution classes.

It was observed that most of the low pollution classes were mainly situated in the upstream parts in both seasons (Fig. SM1). As per mHPI, the basin is dominated mostly by excellent and good groundwater categories in both seasons (Fig. SM1). mHPI varied from 17.4 to 624.6 (mean 68.1) and from 17.6 to 390.6 (mean 55.6) in the respective seasons (Table 2). The ranking criterion for the mHPI is presented in Table SM7.1. According to the mHPI ranking, approximately 66.7 %, 18.3 %, 8.3 %, 3.3 % and 3.3 % of groundwater in the wet season were in the respective excellent, good, poor, very poor and unsuitable groundwater classes while dry season groundwater samples showed about 75.8 %, 13.3 %, 6.7 %, 0.8 and 3.3 % were in excellent, good, poor, very poor and unsuitable classes respectively. In conclusion, most of the groundwater samples were found to be less contaminated with respect to PTEs. However, some samples, mostly in the downstream parts, were highly contaminated by various PTEs (Figure SM7.1).

Table 2 Descriptive statistics of heavy metals indices.

Indices	Wet Season				Dry Season			
	Cdeg	HEI	HPI	mHPI	Cdeg	HEI	HPI	mHPI
Min	-8.4	1.6	31.4	17.4	-8.4	1.6	31.4	17.6
Max	58.8	68.8	338.3	624.6	32.9	42.9	286.6	390.6
Mean	-2.6	7.4	55.7	68.1	-4.0	6.0	52.9	55.6
Std Dv.	10.7	10.7	44.2	93.1	8.4	8.4	39.5	71.7

7.6.3 Drinking and irrigation water quality assessment

7.6.3.1 Groundwater quality index (GWQI) and water pollution index (WPI)

GWQI for wet and dry season samples was estimated based on 21 parameters namely: pH, EC, Na, K, Ca, Mg, Cl, HCO_3, SO_4, NO_3, F, Fe, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn. GWQI varied from 15.4 to 351.9 (mean 55.5) during the wet season and from 15.0 to 242.1 (mean 50.4) during the dry season (Table 7.3). According to the classification criterion presented in Table SM 2. Approximately 65.8 %, 23.3 %, 7.5 %, 2.5 %, and 0.8 % of groundwater in the wet season and 70.8 %, 18.3 %, 6.7 %, 4.2 %, and 0 % of groundwater in the dry season were classified as excellent, good, poor, very poor, and unsuitable for drinking purposes respectively. Most of the very poor to unsuitable GWQI values were situated in the sedimentary quaternary section in both seasons (Figure 7.4a and b). This is concordant with the findings of Shuaibu et al., (2024) who investigated the GWQI during the wet season in the KYB considering only physicochemical parameters. High values of GWQI could be linked to elevated levels of PTEs, nitrate and EC (Figure 7.2a). Moreover, the study employed WPI to ascertain the level of pollution in groundwater for drinking purposes. WPI ranged from 0.12 to 3.4 (mean 0.56) and from 0.15 to 2.4 (mean 0.54) in the respective seasons (Table 7.3). Based on the classification criterion of WPI, 10.8% of the groundwater samples were classified as highly polluted, 7.5% as moderately polluted, 17.5% as good, and 64.2% as excellent water quality class during the wet season. During the dry season, 69.2%, 15%, 4.2%, and 11.7% of the groundwater samples were classified as excellent, good, moderately polluted, and highly polluted, respectively. Therefore, the groundwater is mainly good to excellent. Furthermore, most of the good and excellent groundwaters were situated in the Precambrian basement section during respective seasons (Figure 7.4b and c). However, some portions of the Precambrian basement and sedimentary quaternary had highly polluted groundwaters. Demineralization of rock minerals, rock-water interaction and intensive irrigation activities could be the main source of ions and PTEs in the basin (Jabbo et al., 2022; Shuaibu et al., 2024). In general, the results of GWQI and WPI were similar highlighting a significant percentage of the groundwater samples as good to excellent water types.

Table 3 Descriptive statistics of the water quality indices.

Water Quality Indices	Wet Season			Dry Season		
	GWQI	IWQI	WPI	GWQI	IWQI	WPI
Min	15.4	0.33	0.12	15.0	4.85	0.15
Max	351.9	74.13	3.4	242.1	89.68	2.4
Mean	55.6	52.62	0.56	50.4	52.74	0.54
Std Dv.	50.6	9.76	0.52	46.8	11.74	0.48

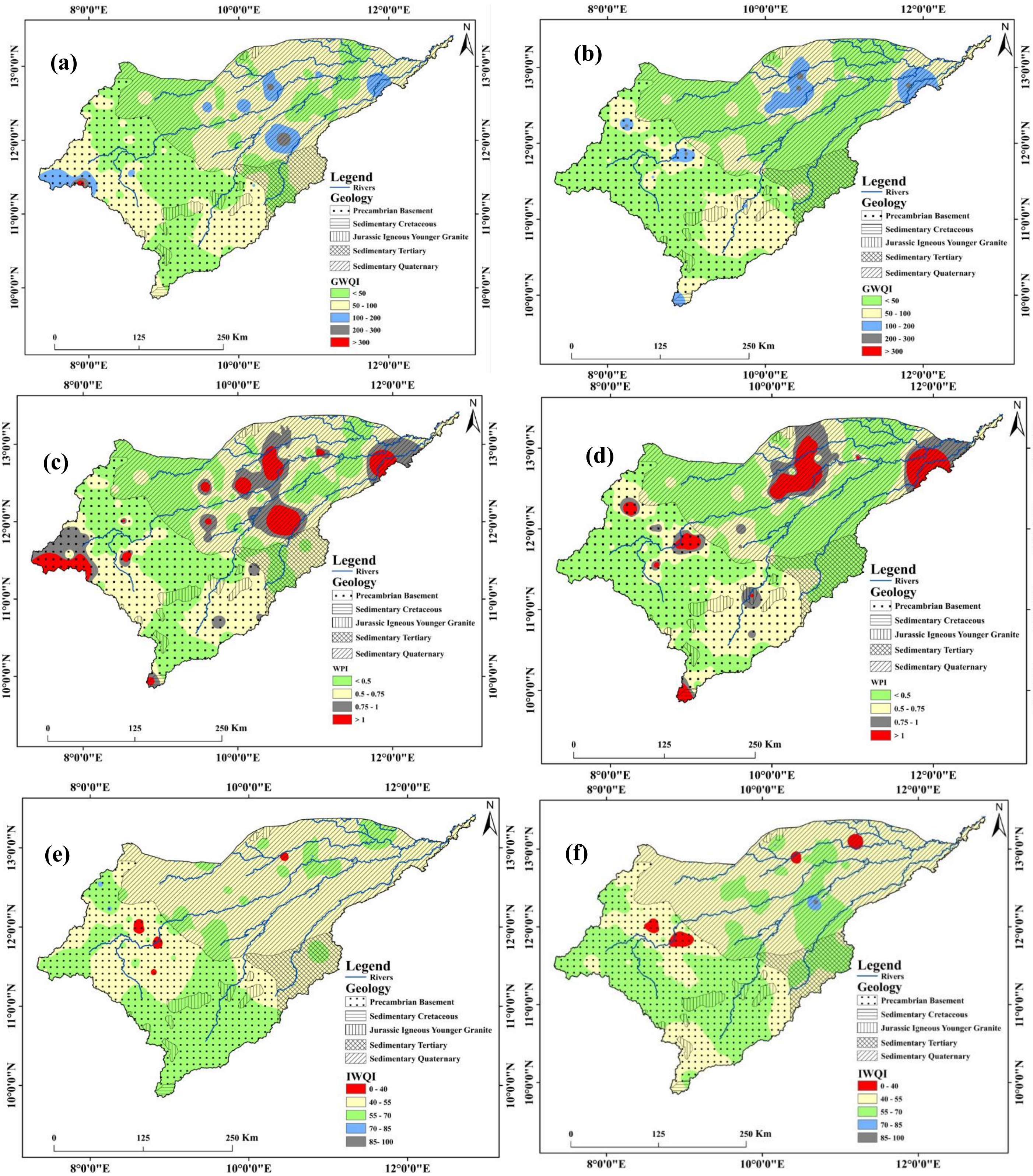


Figure 7.4 Groundwater quality index (a) wet season (b) dry season. Water pollution index (a) wet season (b) dry season. Irrigation water quality index (a) wet season (b) dry season.

7.6.3.2 Suitability of irrigation water

7.6.3.2.1 Hydrochemical indices

Various hydrochemical indices of irrigation water quality such as electrical EC, Na%, SAR, RSC, PS, MH, PI, and KI were employed to evaluate the irrigation suitability of groundwater in wet and dry seasons (Figure SM7.2 & SM7.3). The groundwater is largely good to excellent in terms of salinity hazards in both wet (42.5 – 41.7 %) and dry (50 – 31.7 %) seasons (Table 7.4). This suggests that using this water for irrigation in both seasons may not be significantly detrimental to plants and soils. However, ~ 14.2 % and 1.7% of the wet season groundwater and 15 % and 3.3 % of the dry season groundwater were in respective medium and poor classes with respect to salinity. This water can be applied to salt-tolerant crops on highly permeable soils. High salinity in groundwater may result from the geogenic process of rock-water interaction, recharge of salt-enriched waters and evaporation processes (Mukherjee et al., 2022). SAR ranged from 0.1 to 6.1 (mean 1.3) and from 0.1 to 5.8 (mean 1.3) during wet and dry seasons respectively. SAR values < 10 were classified as excellent water types (Table SM7). Therefore, the quality of all groundwater samples (100%) during the respective seasons was excellent with respect to SAR (Figure SM7.2). This implies that the groundwater may be used for irrigation without any restrictions. The plot of SAR against EC shows most of the wet and dry season groundwater was projected in slight to moderate infiltration problem zones (Figure 7.5a). Therefore, it is recommended that gypsum or magnesium should be applied in the soil coupled with good drainage to avert the harmful effect of sodium ions. Na% had ranged from 11. 7 % to 91.6 % and 12.1 % to 92.2 % in wet and dry season respectively. According to the ranking criterion for Na %, approximately 7.5 %, 38.3 % 8.3 % and 0.8 % of the wet season groundwater were excellent, good, permissible, doubtful and unsuitable. In the same vein, 6.7 %, 43.3 %, 39.2 %, 8.3 % and 2.5 % of groundwater in the dry season were classified as excellent to unsuitable (Table SM7.7). Na % greater than 60% can lead to the deterioration of soil structure and physical properties (Chen et al., 2019; Jahin et al., 2020; Öztürk et al., 2023). Approximately, 9.1 % and 10.8 % of the respective wet and dry seasons had Na % above 60 %. An elevated sodium concentration in the groundwater can be ascribed to the process of mineral dissolution and the interaction between rocks and water, as well as the extensive application of synthetic fertilizers. Therefore, excessive usage of this water for irrigation could lead to slight increases in soil salinity which can be toxic to plants and may destroy soil structure (Batarseh et al., 2021).

According to RSC, groundwater during wet and dry seasons was generally safe for irrigation except 1.7 % of wet season groundwater exhibiting RSC values between 1.25 to 2.5 rendering it marginally suitable for irrigation purposes. High RSC values increase soil pH which hinders crops from up-take of soil water (Batarseh et al., 2021). Potential salinity ranged from 0.1 to 11.4 meq/L, (mean of 1.5 meq/L) and 0.1 to 20.6 (mean of 1.8 meq/L) in the respective seasons. PS results showed that 95 % and 93.3 % of wet and dry season groundwater were classified as excellent to good for irrigation, 3.3 % and 2.5 % were classified as good to injurious, and 1.7 % and 4.2 % were classified as injurious to unsatisfactory for irrigation (Table SM7.7). MH ranged from 2.9 % to 48.8 % (mean 27.8) and from 3.4 % to 50.5 % (mean 28.4 %) in the respective seasons. All of the groundwater exhibited MH values < 50 % making them suitable for irrigation except 1 sample during the dry season which is unsuitable for irrigation as elevated Mg content in irrigation water leads to stunted crop growth and damages soil structure (Jahin et al., 2020; Sreedevi et al., 2019). PI values varied from 31.2 to 206.3 meq/L (mean 85.2 meq/L) and from 21.3 to 163.5 meq/L (mean 79.0 meq/L). According to the ranking criterion for PI, all of the groundwater samples in the respective seasons were categorized as moderately suitable to highly suitable except 1 sample in the dry season which had a PI value < 25 making it unsuitable (Table SM7.7; (Aravinthasamy et al., 2020; Doneen, 1964; Hosni et al., 2024)). Doneen's diagram (Doneen, 1964) indicates that the majority of groundwater in both seasons was located in class II, suggesting that the groundwater samples are moderately suitable for low permeability soil (Figure 7.5b). Therefore, prolonged use of such water for irrigation might lead to decreased soil aeration and stunted crop growth. On the other hand, KI showed a significant percentage of groundwater during wet (84.2 %) and dry (81.7%) seasons were within the acceptable limits for irrigation water. KI > 1 is believed that the groundwater contains excessive sodium thereby generally not recommended for irrigation. ~ 15.8 % and 18.3 % of groundwater of the respective seasons were above the acceptable limits, hence unacceptable for irrigation. High KI in water may be due to high evaporation and cation exchange reactions that produce high Na in water (Chen et al., 2019; Ghosh & Bera, 2023; Mukherjee et al., 2022).

Table 4 Hydrochemical indices of irrigation water.

Parameters	Wet season			Dry season		
	Min	Max	Mean	Min	Max	Mean
EC	15	2746	462.5	54	3560	537.7
SAR	0.1	6.1	1.3	0.1	5.8	1.3
Na %	11.7	91.6	40.6	12.1	92.2	41.6
RSC	-8.5	1.7	-0.7	-24.3	0.9	-1.7
PS	0.1	11.4	1.5	0.1	20.6	1.8
MH	2.9	48.8	27.8	3.4	50.5	28.4
PI	31.2	206.3	85.2	21.3	163.5	79.0
KI	0.1	7.8	0.7	0.1	10.5	0.9

7.6.3.2.2 Wilcox diagram

The Wilcox diagram (Wilcox, 1955) shows the relationship between EC (salinity hazard) and Na % (Sodium concentration) (Batarseh et al., 2021). The diagram enabled the classification of irrigation water into; “excellent to good”, ”good to permissible“, “permissible to doubtful”, “doubtful to unsuitable”, and “unsuitable”. ~ 84. 2 % and 80 % of groundwater samples in the respective seasons are largely *excellent to good* as shown in the Wilcox diagram (Figure 7.5c). This indicates that the application of these waters for irrigation may not cause any detrimental damage to crops and soils. However, approximately 10.8 % and 12.5 % of groundwaters in the respective season were classified into *good to permissible* categories. Groundwater in this category can be utilized for irrigating salt and semi-salt tolerant crops under good drainage conditions. Moreover, ~ 3.3 % of both wet and dry season samples belonged to *permissible to doubtful* class and usage of such water for irrigation would cause detrimental damages to both crop and soil structure. A small percentage of wet and dry season samples 1.7 % and 2.5 % respectively were categorised as *doubtful to unsuitable* for irrigation and usage of such water for irrigation without prior special treatment would cause detrimental effects to plant growth and soil profile (Ghosh & Bera, 2023; Mukherjee et al., 2022). None of the wet season groundwater fell under *unsuitable* class while ~ 1.7 % of the dry season groundwater was categorized as *an unsuitable* class and such water should not be used for irrigation.

7.6.3.2.3 USSL diagram

US Salinity (USSL) diagram (USSL-Staff, 1954) shows the relationship between sodium content (SAR) and salinity hazard (EC) (Figure 7.5d). Approximately 41.7 % and 42.5 5 of the wet season groundwater samples belonged to C1S1 and C2S1 classes while a few groundwater samples were categorized in C3S1 (10%), C3S2 (4.2 %), C4S1 (0.8 %), and C4S2 (0.8 %) classes during wet season. Similarly, most of the groundwater during the dry season belonged to C1S1 (31.7 %) and C2S1 (49.2 %) classes. However, a few samples during the wet season; 0.8 %, 11.7 %, 3.3 %, 2.5 % and 0.8 % belonged to C2S2, C3S1, C3S2, C4S1, and C4S2 zones respectively (Figure 7.5d). It was observed that most of the groundwater samples in the respective seasons are situated in the C1S1 and C2S1 zones which represent the low salinity class (C1), medium salinity class (C2) and the lowest SAR class (S1) and usage of such groundwaters for irrigation on almost all soil types and crops is encouraged. However, there could be some detrimental effects on soil structure and sodium-sensitive crops when it is applied to the soils for quite a long time. Therefore, it is recommended to inculcate a small to moderate leaching process under normal irrigation practice on low-permeable soil. Samples that belonged to C2 or S2 classes can be applied to moderate salt-tolerant crops without any adequate drainage while usage of such water on other crops requires special salinity control practice. It is noteworthy that samples categorized in S2 should not be used on low permeable soil with high cation exchange capacity and fine texture (Aravinthasamy et al., 2020; Hosni et al., 2024; Mukherjee et al., 2022). However, all other samples that were categorised in C3 and C4 are unsuitable for irrigation usage except for high salt-tolerant crops on very high permeable soil.

7.6.3.2.4 Irrigation water quality index (IWQI)

IWQI was employed to assess the overall quality of the groundwater for irrigation. IWQI provides effective information required by policymakers and stakeholders in developing sustainable water management strategies (Aravinthasamy et al., 2020; Batarseh et al., 2021; Hosni et al., 2024). IWQI classification is related to the impact irrigation water would pose on soil and resulting toxicity to plants and the ranking criterion is presented in Table SM7.7. Accordingly, all groundwater samples in the wet and dry seasons presented lower to severe restrictions on soils and crops except one sample in the dry season which shows no restriction (Table SM7.7). Approximately, 3.3 % and 5.8 % of the wet and dry season groundwater samples were situated in severe restriction for irrigation category which renders them suitable for exclusively high salt tolerant crops and should be avoided under normal conditions. It is crucial to use specific salinity management practices, particularly for irrigation waters with high sodium, chloride, and bicarbonate content. Application of gypsum is highly recommended in soil with high permeability to avoid salt accumulation (Aravinthasamy et al., 2020; Dey et al., 2024; Mukherjee et al., 2022). However, a significant percentage of the groundwater samples 56.7 % and 50.8 % during the wet and dry seasons respectively belong to the high restriction zone (satisfactory). These waters can be applied to moderate to high salt-tolerant crops on high-permeable soils with no compact layers (Hosni et al., 2024; Mukherjee et al., 2022). ~ 37.5 % and 40 % of the respective wet and dry season samples exhibited moderate restriction which rendered the groundwaters to be used on moderate salt tolerant crops on soil with moderate to high permeability and moderate leaching process to avoid degradation of soil structure (Abbasnia et al., 2018; Öztürk et al., 2023). However, ~ 2.5 % of groundwater in the respective seasons was situated in the low restriction category and the groundwater should not be used for salt-sensitive plants in light texture soil with moderate permeability to prevent sodicity problems. Figures 7.4e and f presented the spatial distribution of the irrigation water quality index.

Figure 7.5 (a) Infiltration problem diagram (b) Doneen's diagram (c) Wilcox diagram (d) USSL diagram.

7.6.4 Health risk assessment of PTEs

(c)

In this study, NCRs and CRs for adults and children were estimated using the US EPA human health risk assessment model. Total non-carcinogenic health risk (NCRs) expressed as hazard index (HI) for adults varied from 0.8 to 4.9 (mean 1.4) and from 0.91 to 5.3 (mean 1.4) during respective seasons whereas HI values for children had ranged from 0.8 to 4.9 (mean 1.3) and from 0.8 to 4.8 (mean 1.2) in the respective wet and dry seasons (Table SM7.8). HI < 1 signifies no non-carcinogenic health risk (acceptable) while HI > 1 indicates non-carcinogenic health risks. Accordingly, HI values for adults showed that about 46.7% and 30.8 % of the respective season's groundwater was within acceptable limits. However, ~ 53.3 % and 69.2 % of the respective wet and dry season samples were above the acceptable limits and, hence may pose non-carcinogenic health risks to adults. As per non-carcinogenic health risks to children, about 52.5 % and 64.2 % of groundwater in the respective seasons were within the acceptable limits (HI >1) signifying no non-carcinogenic health risks. However, ~47.5 % and 35.8 % of groundwater in the respective seasons have HI values greater than 1 which could probably pose non-carcinogenic health risks to children. The results confirm that adults are more susceptible to non-carcinogenic health risks compared to children. It was observed that As, Cd, Mn and Pb provided the highest contribution to non-carcinogenic health risks (Figure 7.6a and b). Therefore, these PTEs might serve as indicators for non-cancer health risks in the Komadugu-Yobe basin.

The cancer health risks expressed as TCRs varied from 6.1×10^{-4} to 3.8×10^{-3} with a mean value of 1.1×10^{-3} and from 6.1×10^{-4} to 3.4×10^{-3} with a mean value of 1.0×10^{-3} for adults in the respective seasons. Moreover, the TCR ranged from 1.2×10^{-4} to 7.6×10^{-4} (mean of 2.2×10^{-4}) and from 1.2×10^{-4} to 6.8×10^{-4} (mean of 2.0×10^{-4}) for children in wet and dry seasons respectively. TCR for adults is situated in the range of 1×10^{-4} - 1×10^{-2} signifying moderate to high cancer risks. However, TCR for children falls within the range of 1×10^{-4} - 1×10^{-3} signifying moderate cancer risks (Table SM7.8). Accordingly, 50.8 % and 55.8 % of the respective wet and dry season groundwater samples displayed moderate carcinogenic health risks to adults. However, 49.2 % and 44.2 % of groundwater in the respective seasons showed high cancer risk in adults. As per carcinogenic health risk to children, all (100%) groundwater samples were within the moderate carcinogenic health risk range. Furthermore, As, Cd, and Pb were observed as the primary source of cancer-causing health risks for both adults and children in the respective seasons with mean CR values ranging from 1×10^{-4} to 1.0×10^{-3}. However, Ni and Cr contribution to cancer-causing health risk is not pronounced as their mean CR values ranged from 1.0×10^{-6} to 1.0×10^{-4} (Figure 7.6c and d, Table SM7.8). The results are in consonant with the findings of Sheng et al., (2022), Jabbo et al., (2022), Raja et al., (2021), Muhammad et al., (2011) and Jibrin et al., (2024). In conclusion, groundwater in some sections of the basin particularly the downstream section is not safe for drinking and domestic uses as it presents a non-carcinogenic health risk and moderate to high cancer risk in both seasons (Figure SM7.4).

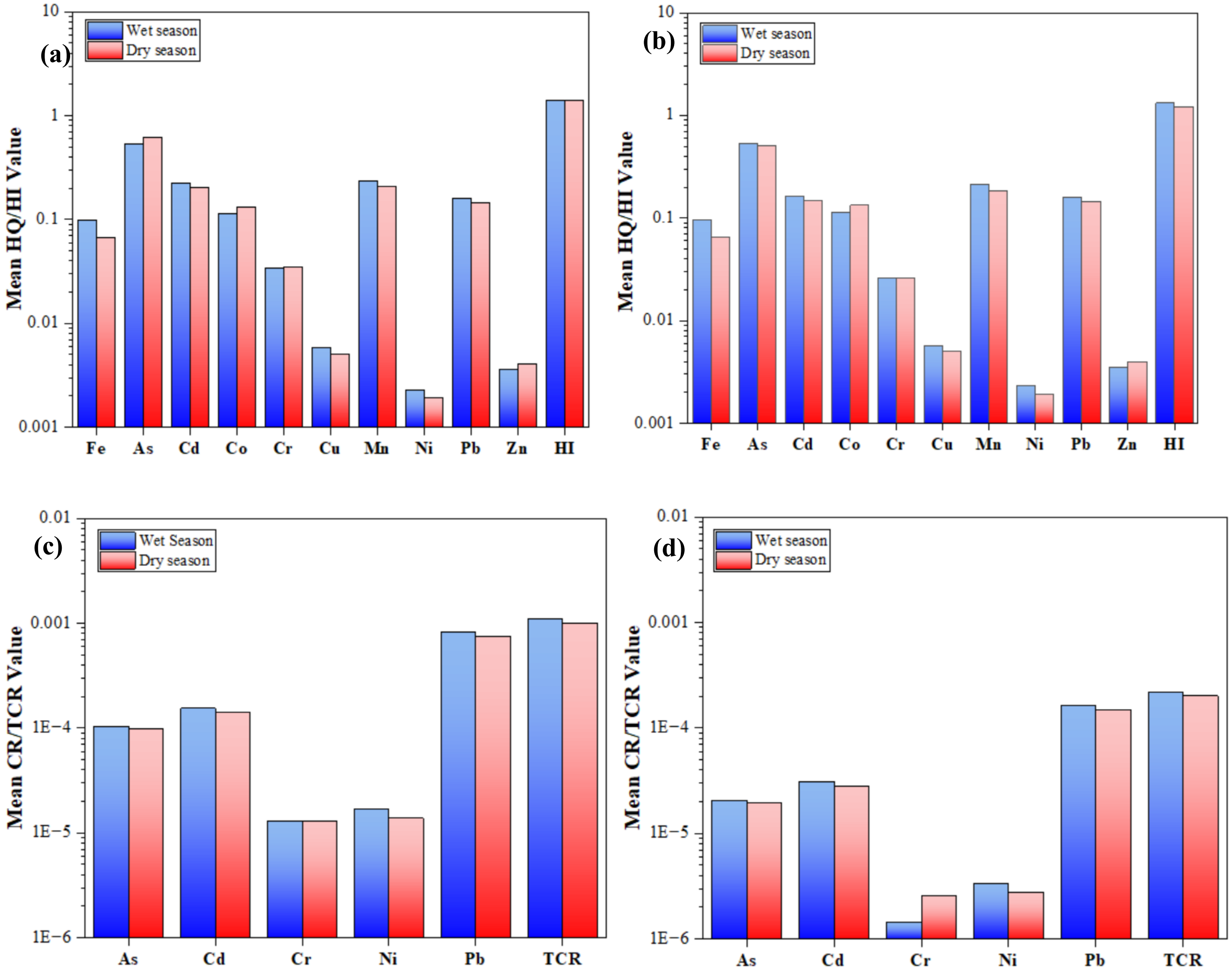


Figure 7.6 Mean values of (a) HQ/HI for adults (b) HQ/HI for children (c) CR/TCR for adults (d) CR/TCR for children.

7.6.5 Tracing PTEs pollution sources using chemometric analysis

7.6.5.1 Pearson's correlation analysis

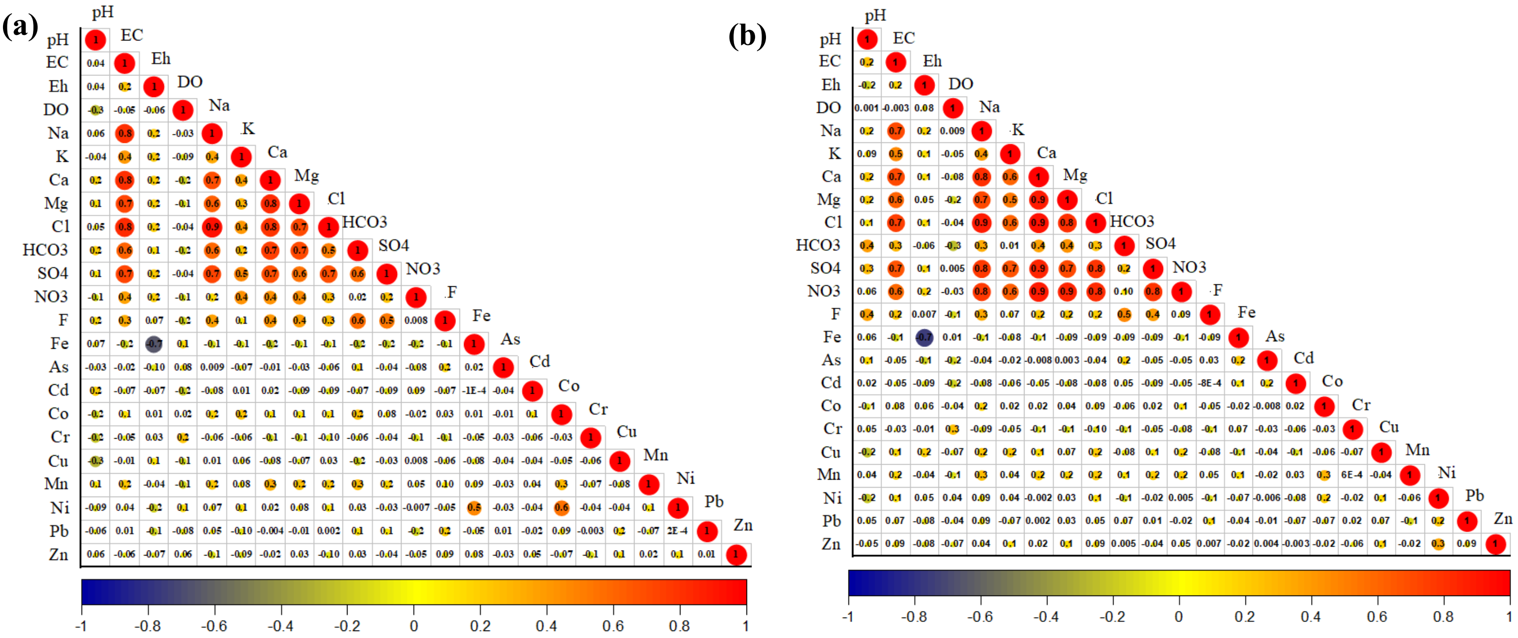
Although, sources of groundwater pollution can vary significantly due to their complexity. This study employed Pearson's correlation analysis to identify the sources of groundwater pollution in the Komadugu-Yobe basin (Figure 7.7a and b and Table SM7.9 and SM7.10). Both positive and negative correlations were observed among various water quality parameters. This suggests that these parameters likely have different geochemical behaviours and originated from distinct geogenic and anthropogenic sources (Mukherjee & Singh, 2022; Sheng et al., 2022; Zhang et al., 2023). For instance, a positive correlation was observed between pH, EC, Eh, Na, Ca, Mg, Cl, HCO_3, SO_4, F, Fe, Cd, Mn and Zn during respective seasons. In addition, there was a negative correlation between EC and Fe, As, Cd, Cr, Cu, and Zn during the wet season indicating that they originated from different sources. Furthermore, Cd correlated positively with pH, K, Ca, NO_3, Co, Mn, and Zn during the wet season. This indicates that they might have originated from common geogenic and anthropogenic sources. However, a negative correlation between Cd and EC, Eh, DO, Na, K, Ca, Mg, Cl, SO4, NO3, F, Cr, Cu, Ni, Pb and

Zn in the dry season suggests that the elements from distinct geogenic and anthropogenic sources (Figure 7.7b, Table SM7.10).

Figure 7.7 Pearson's correlation matrix (a) wet season (b) dry season.

7.6.5.2 Principal component analysis/factor analysis

PCA/FA was employed to identify factors that govern the distribution of PTEs in the groundwater. Eight and six factors with eigenvalues> 1 that explained 71.4 % and 64.3 % of overall variance were extracted from respective wet and dry seasons (Figure 7.8a and b, Table SM7.11). In the wet season, Factor 1 (F1) explained about 26.74 % of the overall variance and displayed a significant positive loading on EC, Na, K, Ca, Mg, Cl, HCO_3, SO_4, and F. This indicates that these parameters shared common sources of contamination which may be geogenic and/or anthropogenic. F2 consists mostly of Eh, Fe, Co and Ni, and explains about 9.3 % of the overall variance. A strong positive correlation between Fe and Ni was observed and a moderately negative and weak correlation between Eh and Co respectively. This factor



is influenced by geogenic inputs. The third factor (F3) had a moderate correlation on pH and a weak correlation on DO and F explaining about 7.9 % of the overall variance. This factor can be related to natural hydrogeochemical evolution. F4 explained about 7.0 % of the overall variance with weak loading on DO, NO_3, Cd and Pb indicating that F4 is greatly influenced by domestic and industrial discharges and agricultural practices. F5 had a moderate positive correlation with Cu and Pb accounting for about 5.97 % of the overall variance. This factor is influenced by the impact of local geogenic processes. Factors 6, 7 and 8 had moderate positive loadings on Co, Zn, and As explaining about 5.4 %, 4.6 % and 4.5 % of the total variance respectively indicating that they are greatly influenced by geogenic process mineralization processes and the impact of rock-water interaction. In the dry season, Factor 1 consists of EC, Na, K, Ca, Mg, Cl, SO_4, and NO_3 which explains about 28.42 % of the total variance. This indicates that it is greatly influenced by a mixed process of geogenic and anthropogenic activities from domestic sewage and agricultural practices. F2 explained 9.86 % of the overall variance and consists of pH, Eh, HCO_3, Fe, and Cu. Fe and Cu are crustal elements which form an important component of soil that gets into groundwater systems by mineral weathering and rock water interaction (Nordstrom, 2011; Raja et al., 2021; Wickramarathna et al., 2017). This factor is greatly influences the natural processes of rock weathering mainly from carbonate weathering. F3 consists of Eh, F and Fe explaining about 7.39 % of the overall variance. This factor is influenced by geogenic inputs. F4 explained about 6.87 % of the overall variance with weak negative loading on DO and moderate loadings on Ni, Pb and Zn indicating that F4 is greatly influenced by geogenic inputs. F5 had moderate positive loading DO and weak negative loading on Co and Mn explaining about 6.22 % of the total variance. This factor indicates the influence of geogenic impacts from geochemical evolution. F6 accounted for about 5.53% of the overall variance, displaying weak positive loadings on Mn and moderate positive loadings on Co. This suggests that it is significantly affected by the geogenic process of rock-water interaction.

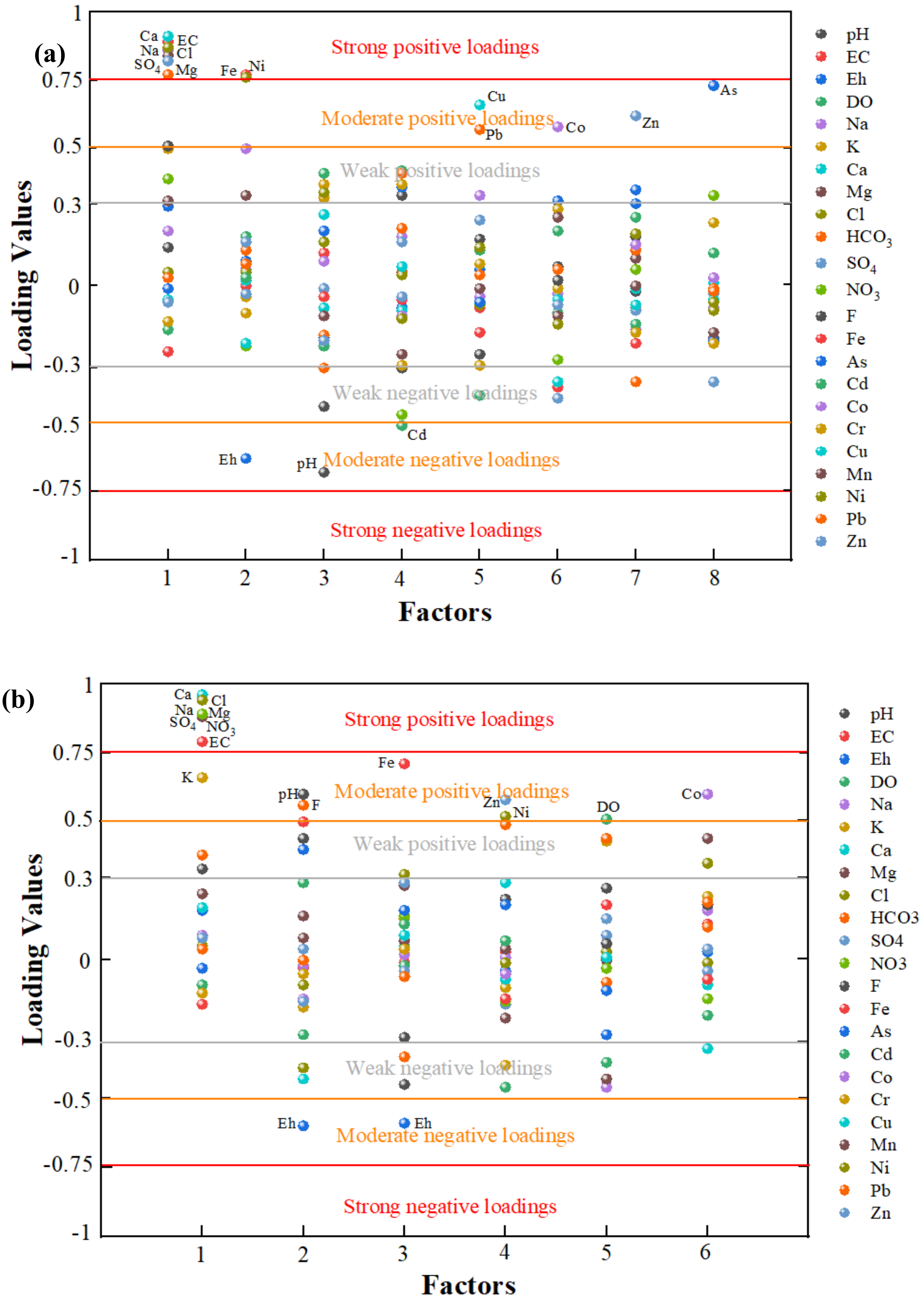


Figure 7.8 Factor loading diagram (a) wet season (b) dry season.

7.6.5.3 R-type Hierarchical Cluster Analysis

This study employed R-mode HCA to identify the source/origin of various PTEs in the groundwater of the Komadugu-Yobe basin. Figures 7.9a and b presented dendrogram which grouped the groundwater quality parameters into two distinct clusters in both wet and dry seasons. During the wet season, Cluster I grouped 12 parameters, namely pH, DO, Fe, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn. This cluster consists of all PTEs analysed together with pH and DO in the groundwater samples which indicates these elements originated from mixed geogenic and anthropogenic processes. Various human activities which release untreated effluent into the environment such as tanning, textile, and plastic processing around the vicinity of the Kano metropolis, Dutse, Bauchi and Hadejia are amongst the potential sources of these elements in the groundwater system. Moreover, intensive agricultural practices that involve the use of synthetic fertilizers, animal dung, and agro-allied chemicals in various parts of the study area unleash PTEs into the soils and groundwater systems. (Hamidu et al., 2021). The geochemical process of mineral weathering and rock-water interaction may also be among the sources of PTEs in the groundwater. The second cluster (Cluster II) consists of primarily major ions (Na, K, Mg, Ca, Cl, HCO_3, SO_4), Eh, EC, F, and NO_3. This cluster indicated that these parameters originated from both geogenic and anthropogenic processes possibly the geochemical process of mineral weathering and dissolution and intensive agricultural activities in the basin. Similar to the wet season, cluster I during the dry season consists of all PTE together with pH, DO and Eh indicating geogenic and anthropogenic sources. The second cluster in the dry season consists of EC, Na, Ca, K, Mg, Cl, SO_4 and NO_3 indicating shared origin and contribution to EC. Their presence in the groundwater is likely from combined human activities and natural processes of rock weathering.

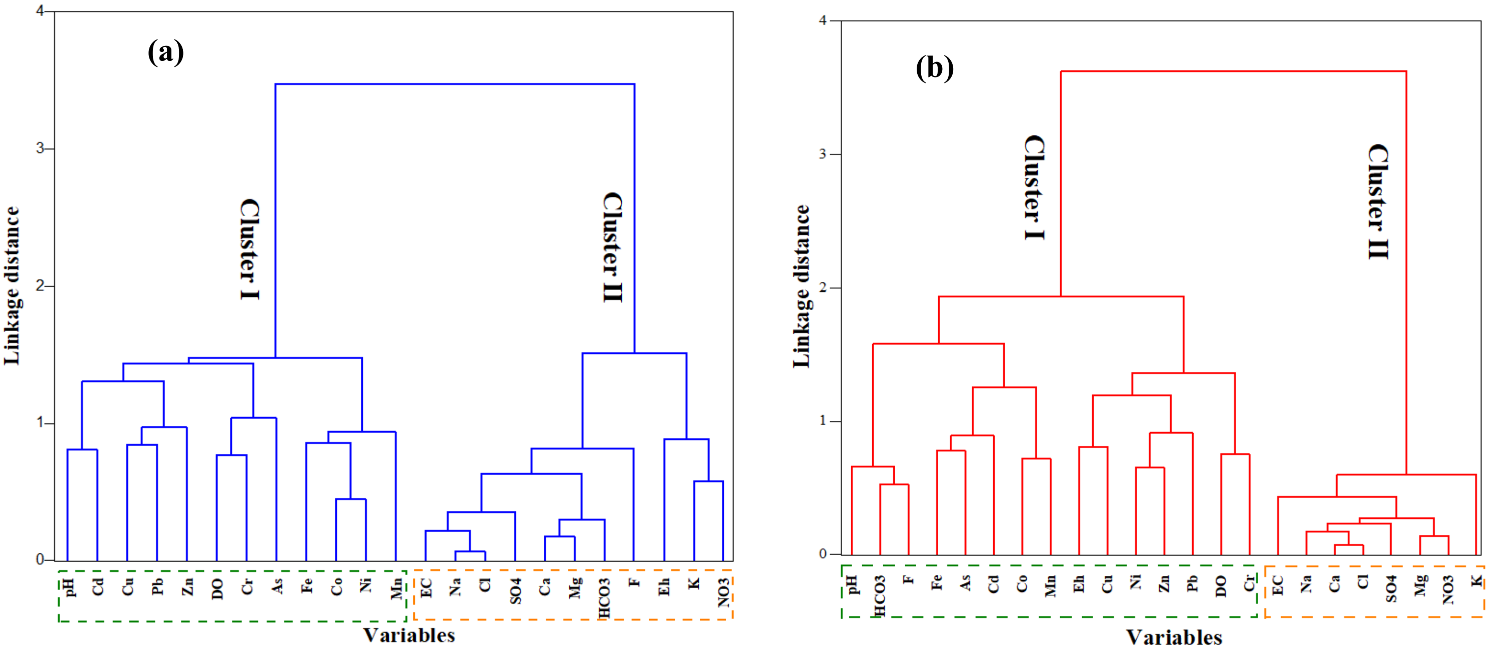


Figure 7.9 Dendrogram of (a) wet season groundwater (b) dry season groundwater.

7.7 Conclusion

In this study, index-based models and chemometric analysis were employed to ascertain PTE pollution status, various pollution sources, and human health risk assessment and evaluate general groundwater quality on a regional scale in the transboundary Komadugu-Yobe basin. The results displayed no significant variation between wet and dry season groundwater concerning physicochemical parameters and PTEs with Fe, Mn, Pb and Cd as the main contaminants. Cd, Pb and As could be influencing factors for CKDu and cancer-causing PTEs. Indexical-based models: Cdeg, HEI, HPI, and mHPI all together described the groundwater as less polluted in the Precambrian basement parts (upstream) and highly polluted in the quaternary sedimentary sections (downstream) of the basin. GWQI and WPI revealed a significant number of the wet and dry seasons groundwater samples were grouped into excellent classes dominated mostly in the Precambrian basement. However, some samples were categorized as highly polluted mostly in the downstream parts. Furthermore, IWQI indicated significant percentage of the groundwater samples were grouped into moderate to high restriction zones with few samples in low and severe restriction zones related to irrigation. The groundwater in the study area could pose non-carcinogenic health risks as the mean hazard index for both adults and children is above the threshold limits (>1). As, Cd, Mn and Pb could serve as the main indicators of non-carcinogenic health risks for both adults and children in the basin. Adults are more susceptible to non-carcinogenic and carcinogenic health risks compared to children in the basin. Arsenic, cadmium and lead were the primary sources of cancer-causing health risks. The groundwater in the downstream part may cause carcinogenic health risks and hence should be given increased attention. Therefore, government agencies, policymakers and stakeholders should take decisive and timely action to address PTE contamination in the eastern region of the basin. Correlation analysis suggests physicochemical parameters and PTEs likely have different geochemical behaviours and originated from distinct geogenic and anthropogenic sources. Moreover, PCA/FA and R-mode HCA highlighted the influence of mixed geogenic and anthropogenic processes from various domestic and industrial discharges, and agricultural practices. Insights from this study are essential for the protection and management of groundwater resources in semi-arid to arid basins affected by PTE contamination. Future research should focus on the application of isotope hydrology to accurately trace the origin/sources of PTE pollution in the Komadugu-Yobe basin and the wider Lake Chad region.

7.8 Postface

This chapter fulfilled and answered RQ3 'What are the sources and status of PTEs pollution and their associated health risk in Komadugu-Yobe basin and how does these metal form speciation and complexation reactions in aqueous solution? PTE pollution source, their contamination levels and associated human health risks were identified and discussed (SO10 and SO12). This was achieved by employing reliable and credible chemometric approaches and heavy metals index-based models to the wet and dry season groundwater datasets. The results indicated that the sources of PTEs in the groundwater were mainly mixed geogenic and anthropogenic processes from various domestic and industrial discharges, and agricultural activities (SO10). Fe and NO_3 are specific to both free and toxic species in the groundwater (SO11). Chemical constituents like nitrate and heavy metals such as lead, nickel and Fe were identified as the main contaminants affecting the groundwater chemistry, contributing to various non-carcinogenic and carcinogenic health risks in the basin. Tracing the origin of nitrate and lead requires the application of nitrogen and lead isotope analysis. The application of stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ is a prerequisite for conducting nitrogen and lead isotope studies. Moreover, these pollutants get into the groundwater system through direct infiltration and deep percolation of surface and rain waters. Understanding the origins and recharge mechanisms of groundwater in the basin, as well as the sources of these harmful contaminants, is essential for developing an effective Integrated Water Resources Management (IWRM) strategy for the basin and the broader Sahel region of West Africa. This will be addressed through the application of stable isotope tracers in the next chapter.

The next chapter (final chapter) will continue to use the Komadugu-Yobe basin as a case study to explore the role stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ offer in investigating groundwater recharge origin and mechanisms. Moreover, spatial distribution and seasonal variability of stable isotopic signatures will be presented and discussed in the next chapter.

8 Investigation of groundwater recharge mechanisms in the transboundary Komadugu–Yobe basin Nigeria using stable isotopes of ^{18}O and ^{2}H and comparison with the wider Sahel, Africa[4]

8.1 Preface

The previous chapter (chapter 7) answered and fulfilled RQ3: **'**What are the sources and status of PTEs pollution and their associated health risk in the Komadugu-Yobe basin and how do these metals form speciation and complexation reactions in aqueous solution?'. The level of PTE pollution and sources/origin of various PTEs present in the groundwater of KYB were identified and discussed.

This final chapter addresses RQ4: 'What role can stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ offer in identifying the origin of groundwater recharge and its mechanisms in the transboundary Komadugu-Yobe basin?'. This research question was answered via two specific objectives (SO13 and SO14). 240 groundwater samples were collected in two sampling campaigns from the Komadugu-Yobe basin and analysed for stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ to understand the origin and mechanisms of groundwater recharge in the basin (SO13). The stable isotopic results highlighted the groundwater is recharged by meteoric water along the Hadejia River valley, Hadejia-Nguru wetland and other local recharges around the vicinity of Chalawa gorge dam, Tiga dam, Kano River irrigation project KRIP and Hadejia Valley Project HVP. The spatial distribution and seasonal variability of stable isotopic signatures of groundwater were analyzed and discussed (SO14). Finally, stable isotope datasets across major basins in the Sahel region of West Africa were incorporated with this isotopic result to develop integrated water resources management (IWRM) strategies in the basin and the wider Sahel region.

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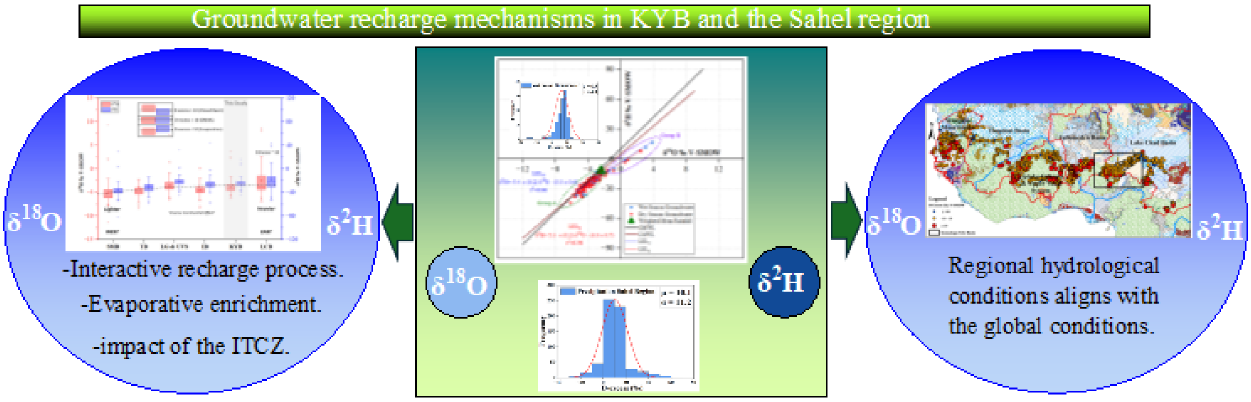
Author Contribution:

Conceptualization (A.S.), methodology (A.S.), software (A.S.), validation (A.S., R.M.K., and V.P.), formal analysis (A.S.), investigation (A.S.) resources (A.S.) data curation (A.S.), writing—original draft preparation (A.S.), writing—review and editing (A.S., R.M.K., V.P., and L.C.B. R.G.K.H), visualization (A.S., V.P., and L.C.B., R.G.K.H), supervision (R.M.K., and V.P.), project administration (A.S.), funding acquisition (A.S.).

Highlights

- ITCZ influenced rainfall-recharge processes in the Lake Chad region.
- The primary source of moisture in the Sahel region is the Atlantic Ocean.
- The regional hydrological and climatic conditions are consistent with global averages.
- Groundwater recharge in Precambrian and Sedimentary aquifers is from rainfall.
- Groundwater in the lowlands of the Komadugu-Yobe basin shows signs of evaporative isotopic enrichment.

GRAPHICAL ABSTRACT



8.2 Abstract

The transboundary Komadugu–Yobe basin is critical for food security in northern Nigeria and southern Niger Republic. Groundwater and surface water resources in the basin are prone to pollution and are becoming scarce due to the arid to semi-arid climate and overexploitation. Stable isotopes of ^{18}O and ^{2}H were used to determine the source of groundwater recharge to inform integrated water resource management in the basin compared with the wider Sahel region. The local meteoric water line (LMWL) for the Komadugu–Yobe basin was defined as δ^{2}H = 6.7 (± 0.1) δ^{18}O + 4.1 (±0.4) using stable isotope datasets from 3 local and 4 regional isotopes in precipitation stations. The regional meteoric water line for the Sahel region was found to be δ^{2}H= 6.2 (± 0.1) δ^{18}O + 2.9 (±0.6). The variability in isotopic composition of the local and regional precipitation in the transboundary Komadugu-Yobe basin was attributed to the impact of the inter-tropical convergence zone (ITCZ) and changes in regional orography. The isotopic analysis of wet and dry season groundwater samples indicated that the groundwater undergoes evaporative enrichment before infiltration. Deuterium excess results showed a complex recharge process in the Precambrian basement and sedimentary Quaternary formation aquifers of the basin in connection with rainfall. Moreover, groundwater recharge in the Sahel occurs during the months of heavy rainfall when precipitation isotopic signatures are more depleted. D-excess analysis suggests that average precipitation in the entire Sahel region exhibits a general continental effect until the ITCZ meets the Congo Basin. Results provide valuable information for integrated water resources management in the context of climate change, an ever-growing population, over-exploitation of groundwater, and pollution from geogenic and anthropogenic sources.

***Keywords*:** Transboundary Komadugu–Yobe basin; groundwater recharge; isotope hydrology; integrated water resources management (IWRM); Sahel region

8.3 Introduction

Assessment of groundwater recharge processes is crucial for sustainable groundwater management in arid and semi-arid regions. Groundwater recharge processes can be estimated using electromagnetic and modelling methods, geochemical tracers, isotopes, changing water levels, temperature profiles, and water balance data (Ahmed, Chen, and Khalil 2022; Banda et al. 2021; Fang et al. 2024; Ju et al. 2024; Swetha et al., 2020; Tewolde et al. 2019; Zhou et al. 2024). Sustainable water resource management strategies in the context of climate variability and anthropogenic activities require a thorough understanding of groundwater recharge processes (Bello et al., 2019). Groundwater levels in the Komadugu-Yobe basin have drastically decreased due to excessive withdrawal of groundwater during the past decades, triggered by industrialization, a fast-growing population, and intensive agricultural practices (Ansari et al., 2022; Shamsuddin et al., 2018; Zhu et al., 2019). Thus, it is imperative to assess groundwater recharge mechanisms to develop comprehensive management strategies for valuable groundwater resources. One tool is isotope tracers (Eissa et al., 2019; Reda et al. 2022; Roy et al., 2024; Zhu et al., 2019). The use of isotope tracers in recharge evaluation is expanding, providing more knowledge and versatility (Banda et al., 2019; Banks et al., 2021; Liberoff and Poca 2023; Xu et al., 2019).

Presently, arid and semi-arid areas of the African continent depend on groundwater for domestic, agricultural, and industrial applications (Eissa et al., 2019; Hirwa et al., 2022; Nyantakyi–Frimpong & Bezner–Kerr, 2015). The exploitation of groundwater has increased dramatically across the globe due to rising water demands for economic development, drinking, agriculture, and energy (Ansari et al., 2018). Due to increased surface water contamination and pollution from anthropogenic activities, particularly along the Gashua axis, Hadejia–Nguru wetland, and Kano River irrigation project (KRIP), residents of the Komadugu–Yobe basin (KYB) have primarily focused on using groundwater for domestic and agricultural purposes. (Abubakar et al., 2018; Ahmed et al., 2018; Kwari & Angyu–petinrin, 2015; Umar et al., 2019). Hence, the quality of groundwater may eventually be impacted due to increased surface water pollution. (Salifu et al., 2017; Sophocleous 2002). The Komadugu–Yobe Basin is experiencing domestic and irrigation water shortages, particularly during the dry season. There is no comprehensive study on the source of groundwater recharge in the basin. Moreover, despite flooding and high seasonal rainfall upstream, the scarcity of freshwater during the dry season is a serious concern with groundwater as the only available water resource in the basin.

The isotopic signatures of $\delta^{18}O$ and $\delta^{2}H$ in water, modified by meteoric processes, provide an efficient and practical tracer for determining the source and pathway of groundwater (Azzaz et al., 2008; Bello et al., 2019; Liberoff and Poca 2023; Salifu et al., 2017; Swetha et al., 2020). These isotopes are part of the water molecule and are unaffected by hydrochemical processes in the aquifer systems (Ansari et al., 2022; Salifu et al., 2017; Shuaibu et al., 2024; Valdivielso et al., 2024). Isotope hydrology can be used to identify the source of water, the processes of recharge and mixing, the flow pattern, the residence time, and variations in climatic conditions (Ansari et al., 2018; Goni 2006; Hssaisoune et al., 2017; Kamtchueng et al., 2015; Tian et al., 2023; Xu et al., 2024; Zhou et al., 2024). Moreover, it can support the conceptual modelling of recharge processes, essential for developing effective strategies for sustainable management of groundwater resources in the context of climatic variability and anthropogenic pollution (Bello et al., 2019; Tian et al., 2023; Tsujino et al., 2024). The unique heavy–to–light isotopic ratios that atmospheric moisture and precipitation acquire as a result of isotopic fractionation processes, make their isotopic ratio effective water tracers (Gibrilla et al., 2017; Jasechko, 2019; Ju et al., 2024; Valdivielso et al., 2024).

There is a significant body of research on management of groundwater resources using stable isotopes (Ayuba et al., 2019; Banda et al., 2019; Bouchez et al., 2016; Fang et al., 2024; Fantong et al., 2020; Heydarizad et al., 2021; Li et al., 2022; Liberoff and Poca 2023; Loh et al., 2022; Salifu et al., 2017; Solder and Beisner 2020; Tian et al. 2023; Zakaria et al. 2013; Zhu et al., 2019). Previous research in the Sahel region, such as Goni, (2006), suggests that water from Middle and Lower aquifers may contain palaeowater recharged during wetter and cooler periods than present. A study conducted by Gibrilla et al., (2017) demonstrated groundwater recharge dynamics using $\delta^{18}O$ and $\delta^{2}H$ characteristics in groundwater, rainwater and spring in the Amedzofe area of Ghana. The result of their investigation reveals that groundwater recharges in the study area occur in the months of March, June, and August. Zouari et al., (2023) employed hydrochemical analysis and isotope tracers for groundwater quality monitoring and evaluation of recharge processes for the Ilullemeden aquifer system, Sahel region. A study within the Sahel region of the Taoudeni aquifer system using stable ($\delta^{2}H$, $\delta^{13}C$, $\delta^{18}O$) and radioactive (^{3}H, ^{14}C) isotopes (Trabelsi et al., 2023) assessed geochemical mechanisms and groundwater recharge processes. Goni et al., (2021) used stable isotope composition from groundwater and rainfall in the southwest Lake Chad Basin of Nigeria to assess groundwater recharge processes and their relationship with rainfall intensity. Maduabuchi et al., (2006) analysed $\delta^{18}O$, $\delta^{2}H$ and ^{3}H signatures in the upper aquifer of Chad basin. The analysis indicated that the groundwater is replenished with modern meteoric water. However, the middle and lower aquifers show no mixing with contemporary waters. Their results are in line with earlier studies conducted at the same period in the Sahel region.

Groundwater is a fragile resource, thus assessing its recharge processes will help in developing an effective strategy for integrated water resources management of the river basin. (Ben-Daoud et al., 2021; Chen et al., 2024; Emvoutou et al., 2024; Gao et al., 2023; Ngene et al., 2021; Swetha et al. 2020). The main aim of this study was to identify the source/origin of groundwater recharge in the Komadugu–Yobe basin using stable isotopes of $\delta^{18}O$ and $\delta^{2}H$. The specific contribution of this research was to characterize the $\delta^{18}O$ and $\delta^{2}H$ signatures of groundwater, assess their seasonal variations, and explore their relationship with geological formations to enhance the understanding of recharge mechanisms in the transboundary Komadugu–Yobe Basin. This study was then compared with the results of previous work to inform the rainfall-recharge relationship within the Nigerian Lake Chad basin and the wider Sahel region for sustainable management of groundwater resources.

8.4 Materials and Methods

8.4.1 Study area setting

The transboundary Komadugu–Yobe basin covers the northwestern and north-eastern part of Nigeria, which lies within latitude 10°N and 13°N, and longitude 9.45°E and 12.30°E, across the Sahel region in West Africa (Figure 8.1a and c). The basin has an approximate area of 150,000 km^2, with an elevation between 294 and 1750 m a.s.l. The Komadugu–Yobe basin contributes about 35% of water to the greater Lake Chad basin. The basin is drained by two subsystems: the Komadugu Gana River and the Yobe River, originating from the Jama'are and Hadejia River tributaries. The basin supports over 20 million people, providing resources for farming, fishing, livestock, and water supply (Adeyeri et al., 2019; Shuaibu et al., 2025).

Rainfall occurs from the month of May to October, with an annual rainfall range of 300 to 1200 mm across the basin area (Adeyeri et al., 2020; Goni et al., 2023). High seasonal variation in rainfall results from the influence of the Inter–Tropical Convergence Zone (ITCZ) on the regional climate (Adeyeri et al., 2017). The highest rainfall occurs in August, and stream flow ends in late September (Adeyeri et al., 2020). The average maximum temperature in the basin is 40°C while the mean minimum temperature is 12°C. The basin has an annual potential evaporation of 1,800 to 2,400 mm, with the lowest rate recorded at Jos (Adeyeri et al., 2017; Bura et al., 2018). An annual evaporation rate of about 203 mm was measured in the basin, with a relative humidity of 40 % per annum (Adeyeri et al., 2019). Severe drought episodes and high climate variability occur in some parts of the basin (Adeyeri et al., 2017). The vegetation in the basin consists of dense grasslands, Shrubs, and a few trees. Agriculture in the basin is supported by the Kano River irrigation project, Trimming Project and Hadejia Valley irrigation project (Chiroma et al., 2015; Gana et al., 2018).

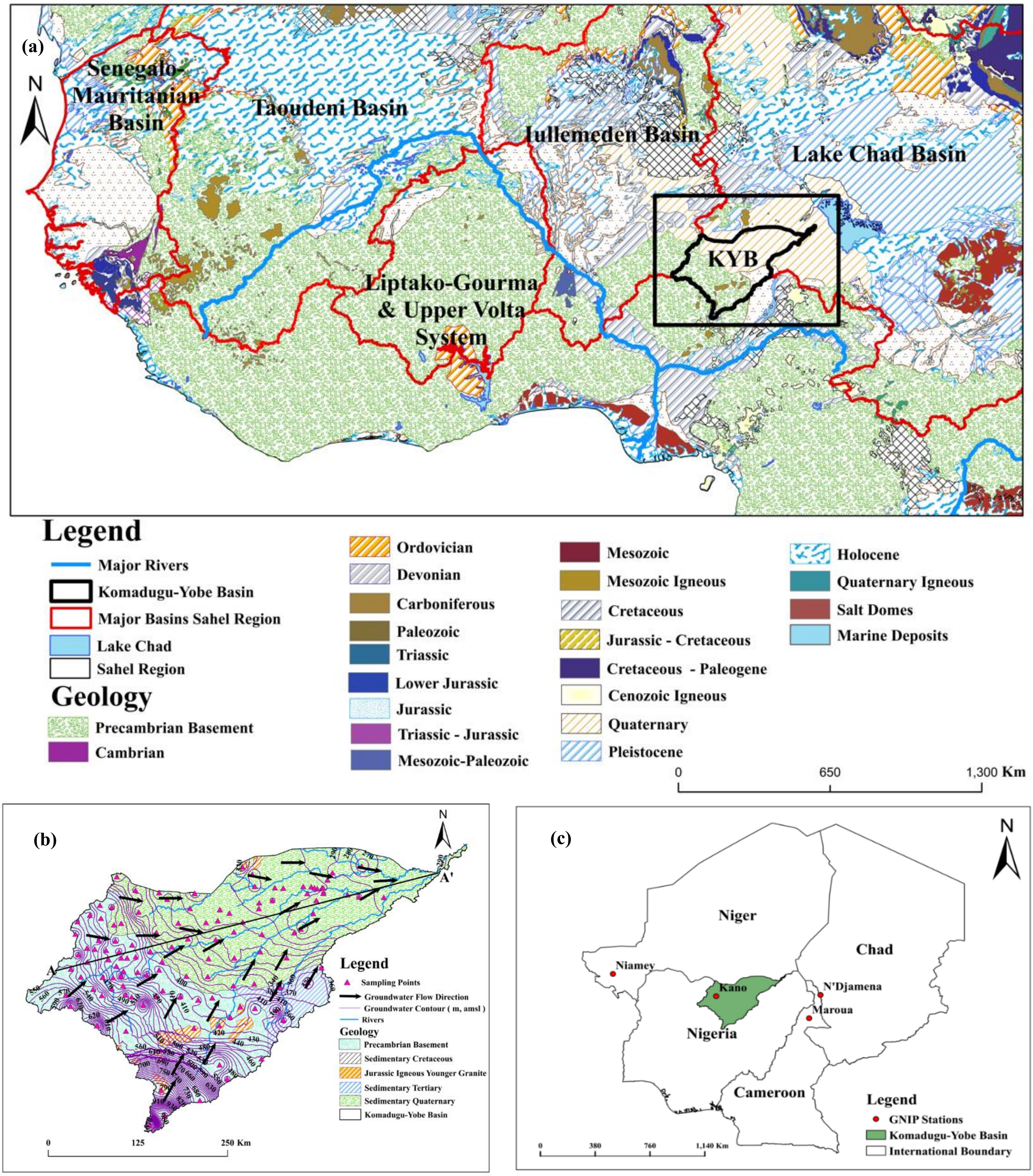


Figure 8.1 (a) The black rectangle shows the Komadugu-Yobe basin extent within the Sahel with different geologic formations represented by various coloured areas. Major Rivers are presented by the blue lines and major basins in the Sahel region demarcated by red coloured lines. (b) Generalized geological map of the study area showing groundwater sampling points, groundwater flow control, groundwater contour lines and various geologic types. (c) Location map of regional GNIP stations in Lake Chad region. GNIP: Global Network of Isotopes in Precipitation.

8.4.2 Regional Geology and Hydrogeology

The study area is mainly underlain by the Precambrian basement complex and Jurassic younger granite in the upstream part, and the sedimentary Quaternary formations in the eastern part (Figure 8.1b). The Precambrian basement complex consists of crystalline rocks formed during the Pan-African orogeny, which have been exposed and subsequently covered by younger rock formations. The crystalline rocks comprise migmatite-gneiss, schists, and Pan-African granites, that are predominantly igneous and metamorphic in nature and characterized by shallow weathered basement. (Schuster et al., 2009; Shuaibu et al., 2025). The granites and migmatites are formed during the Pan-African orogeny and the metasedimentary rocks such as schists, quartzites, and amphibolites have undergone metamorphism, while some intrusive rocks such as pegmatites, dolerites, and diorites, reflect magmatic activity in the Precambrian basement complex region (Le Coz et al., 2011; Descloitres et al., 2013). The mineralogical composition of the Precambrian basement complex includes biotite, quartz and plagioclase. Rocks of the Jurassic younger granites include syenites, biotite granites, gabbros, ignimbrites, and rhyolites, which formed ring dyke structures around the southwestern part of the basin. These granites are composed of amphibole, biotite, pyroxene, olivine, quartz, and plagioclase minerals (Shuaibu et al., 2024, 2025).

The sedimentary Quaternary formations are primarily Plio–Pleistocene lacustrine, fluvial and deltaic deposits with varying lithologies in both lateral and vertical orientation which consist of fine to coarse-grained sandy Aeolian deposits (Edmunds et al., 1999; Mohammed et al., 2017; Shuaibu et al., 2025). The valley in the Sedimentary Quaternary consists of fluvial sediments ranging from clay to sand. The Chad formation in the sedimentary quaternary formed a complex subsurface deposit which has been sedimented continuously from the Late Miocene to the present (Shuaibu et al., 2025; Wali, Dankani, et al., 2020). Dunes and various alluvial deposits are present as superficial layers in the sedimentary Quaternary sections of the basin forming parallel ridges of several kilometres, with depths ranging from 15 to 20 meters which significantly affected the river systems towards the downstream parts of the basin. The clays are primarily lake deposits formed in non–turbulent settings; the origin of the sands is attributed to alluvial fans, lake margins, or deltas (Edmunds et al., 1999). Various researchers have described the stratigraphic sequence of the sediments in the basin such as; (Le Coz et al., 2011; Goni 2006; Lopez et al., 2016).

The hydrogeology of the Komadugu-Yobe basin has a complex groundwater system controlled by geology, lithology, and hydrological processes. The younger overlying Quaternary sediment and Plio–Pleistocene argillaceous Chad formation with minor arenaceous horizons, weathered basement, partially weathered basement and fractured basement are the primary sources of groundwater in the basin (Figure 8.2) (Edmunds et al., 1999; Shuaibu et al., 2025). Groundwater is generally derived from three main aquifer units of arenaceous Chad formation in the upper, middle, and lower aquifer zones in the northeastern parts. These aquifers evolve in the basin as unconsolidated alluvium aquifers along river valleys and around the wetland areas. The sandstone aquifers are either confined, semi-confined, or unconfined within the Quaternary Chad formation. The upper and middle aquifers are readily available for exploitation. Additionally, alluvial deposits along the river floodplains of the Hadejia-Nguru wetlands and Hadejia River provide groundwater at depths. The upper unconfined aquifer zone has a depth to the water table of about 20 m with thickness varying from 15 to 100 m which is made up of Quaternary deposits of varying grain sizes which is subdivided into 3 distinct units of upper A, B and C units, located below the water table (Shuaibu et al., 2025; Tukur et al., 2018). This aquifer has a transmissivity ranging from 0.6 to 8.3 m^2/day. The middle aquifer has a thickness ranging from 10 to 40 meters and consists of sand beds interlayered with clay and diatomites of moderately coarse to fine grains with an average transmissivity of approximately 360 m^2/day. However, the transmissivity of the lower aquifer ranges between 33 and 105 m²/day (Maduabuchi et al., 2006; Shuaibu et al., 2025). Groundwater in the basin is derived from the Precambrian basement section of the basin from the weathered basement, partially weathered basement, and fractured basement (Figure 8.2). The fractured basement supplies groundwater through fractures, fissures, and joints at depths below 45 and 60 meters, particularly around Kano Municipal. In contrast, groundwater is more readily accessible in the weathered and partially weathered basement at shallower depths, ranging between 30 and 45 meters.

The source of the Komadugu–Yobe River is the highlands of Jos and Kano and exhibits seasonal flow patterns between the months of June and December (Descloitres et al., 2013). The Hadejia–Katagum, Kaffi–Kefin Hausa, and Burum Gana river systems are the principal sources of surface water in the Komadugu–Yobe basin (Ovie and Raji 2006; Shuaibu et al., 2022). The hydrology of the basin is largely controlled by dams constructed along the river systems within the basin. Each year, the Komadugu–Yobe basin provides more than 1.12 billion cubic meters of surface water. (Mohammed et al., 2017). Groundwater is available in both the southern and northeastern parts of the basin with the northeastern areas having more surface water resources. Groundwater flows from the southern and southwestern parts of the basin toward the northeast, which eventually discharges into Lake Chad (Figure 8.2). In the basement complex aquifer system, groundwater flow is highly localized. Groundwater recharges are likely to occur in the southern region around the vicinity of Challawa Gorge Dam, with discharge and evaporative return concentrated around Kano Municipal, extending toward Ringim. However, in the northeastern parts, groundwater recharges take place around the Hadejia-Nguru wetlands, the Komadugu-Yobe valley and the Lake Chad region through processes such as seepage from river channels, infiltration of floodwaters, and runoff along the Yobe floodplain (Carter and Alkali 1996; Le Coz et al., 2011; Maduabuchi et al., 2006; Shuaibu et al., 2025).

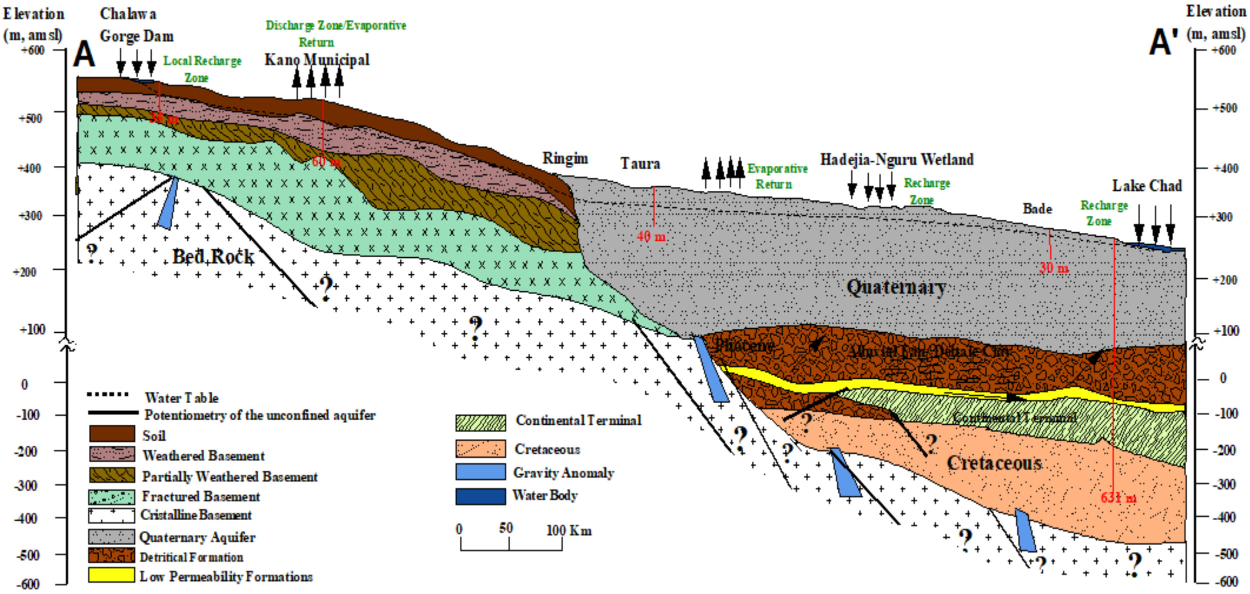


Figure 8.2 Hydrogeological cross-section AA' of Komadugu-Yobe basin showing groundwater from direction, various lithological units, aquifer zones, groundwater table and recharge and discharge zones (after Shuaibu et al., (2025)).

8.4.3 Sampling and laboratory analysis

Two sampling campaigns collected groundwater samples from the Komadugu–Yobe basin between August to September 2021 (Wet season) and between March and April 2022 (Dry season) in 50 ml pre-cleaned polypropylene bottles without headspace for stable isotope analysis. A total of 240 groundwater samples were collected from hand–dug wells, hand–pumps and motorized boreholes using composite sampling approaches of selective, ease of access, grid, and random methods to collect representative samples across the study area due to security concerns of banditry and Boko haram activities along Yunusari and Gaidam axis of Yobe state. Water was discharged from each sampling point for 5–10 min before sampling to flush out any debris and the standing water column to collect representative samples. Hand-dug wells were properly examined and checked to make sure they were in constant use before sampling. The groundwater sampling depth ranges from 21.8 to 75 m, which does not adequately represent deeper aquifers. The groundwater samples were labelled as (IS) and packed in cooler boxes at ~ 4°C.

Stable isotope analysis of δ^2H and $\delta^{18}O$ was conducted at the IAEA Isotope Laboratory, Vienna and the Isotope Laboratory for the Ministry of Water in Lilongwe, Malawi. The International Standard Procedures (ISP) described in Banda et al., (2019) were adopted in the isotopic analysis of the groundwater samples. The isotopic ratios were expressed as δ (‰) relative to Vienna–Standard Mean Oceanic Water (V–SMOW) (Eq. (8.1)).

$$\boldsymbol{\delta = \frac{R_{Sample} - R_{Standard}}{R_{Standard}} \times 1000\ ‰} \qquad 8.1$$

where δ is a deviation in isotopic ratio from reference material (standard) expressed in ‰, R_{Sample} is the ratio of oxygen ($^{18}O/^{16}O$) or hydrogen ($^2H/^1H$) of the groundwater sample, and $R_{Standard}$ is the Vienna Standard Mean Ocean Water (Craig, 1961). The analytical precision of the analysis process was 0.01 ‰ for $\delta^{18}O$ and 0.2 ‰ for δ^2H.

The deuterium excess (D–excess) is a deviation from the meteoric water and is defined by Equation (2) (Dansgaard, 1964). It was employed in this study to analyse evaporation and recirculation of atmospheric air masses.

$$\boldsymbol{D - excess = \delta^2H - 8\delta^{18}O} \qquad 8.2$$

8.4.4 Local and Regional Precipitation Dataset

There is only one GNIP (Global Network for Isotope in Precipitation) station at the study area located in Kano at an altitude of 476 masl with 33 stable isotope data for rainfall between 1964 and 1973. Other study area stations are at Grain Alkali with daily rainfall data for 2001, Jos with daily rainfall data from 1988 to 1989, and Maiduguri with daily rainfall data for 2001 and 2018 only (Table 8.1). These datasets are not enough to give a current and representative local meteoric water line for the Komadugu–Yobe basin. Moreover, the GNIP station at Kano is currently non-functional and the datasets from local stations at Garin Alkali, Maiduguri Airport and Jos are obsolete and scarce. Therefore, datasets from these local stations were augmented with those of regional GNIP stations in Chad (Ndjamena) located at an altitude of 294 masl, Niger Republic (Niamey) located at an altitude of 220 masl and Cameroon (Maroua) located at an altitude of 396 masl extracted from IAEA Global Network for Isotope in Precipitations (GNIP) database (https://www.iaea.org/services/networks/gnip) to better describe the local and regional meteoric conditions (Banda et al., 2021). This was achieved by assessing any possible deviation from the Global Meteoric Water Line (GMWL). These stations share somewhat similar climatic conditions in certain respects with the transboundary Komadugu–Yobe basin, hence relevant for the current study. The location of the local and the surrounding GNIP stations in the Lake Chad region are presented in Figure 8.1c. The daily rainfall datasets from Jos and Maiduguri local stations were converted to the monthly weighted average amount of $\delta^{18}O$ and δ^2H in rainfall using Eq. (8.3)

$$\text{Monthly weighted average isotope value, } \boldsymbol{\delta}_{‰} = \frac{\sum_{i=1}^{n} P_i\delta_i}{\sum_{i=1}^{n} P_i} \qquad 8.3$$

Where Pi is the precipitation amount in the i^th^ month, and δ_i is the isotopic composition in the i^th^ month.

8.4.5 Isotopic groundwater database

This study combined groundwater stable isotopic datasets obtained from field surveys in Komadugu-Yobe basin between 2021 and 2022 covering wet and dry seasons and stable isotopic datasets of 5 major basins across the Sahel region obtained from isotopic surveys carried out between 2011 to 2023 under the framework of RAF 7011 and 7021 projects (framework of IAEA technical Co-operation project) (Huneau 2017; Laurence 2017; Taupin 2017; Travi 2017; Zouari 2017). Only δ^2H and $\delta^{18}O$ groundwater datasets were considered in this study for the analysis from the Komadugu-Yobe basin and 5 major basins across the Sahel region. The Lake Chad Basin (Central African Republic, Cameroon, Chad and Niger), Iullemeden basin (only in Nigeria, Niger and Benin), Liptako–Gourma and Upper Volta system

(Niger, Burkina Faso, Mali, Benin, Togo, and Ghana), Taoudeni basin (Mauritania, Mali, and Burkina Faso), and Senegalo–Mauritanian basin (Mauritania and Senegal).

8.4.6 Software analysis

ArcGIS software (10.8) was used for the development of different geospatial maps of stable isotopes and mapping sampling locations. Origin Pro software (2023b) was used in plotting various graphs of isotopic compositions while Microsoft Excel and Minitab were used for statistical analysis.

Table 8.1 Statistical summary of stable isotopic signatures of rainfall from local stations.

Local Stations	Period	Variables	Count (n)	Min	Max	Average	Range
Garin Alkali	1992–1997	δ^2H	15	–36.0	36.0	–3.8	72.4
		δ^{18}O	15	–6.8	4.2	–2.2	11.0
		D–excess	15	2.8	21.5	13.6	18.7
Maiduguri Airport	2001	δ^2H	6	–31.8	10.1	–16.9	41.9
		δ^{18}O	6	–5.1	0.6	–3.1	5.7
		D–excess	6	5.1	11.2	8.3	6.0
	2018	δ^2H	6	–38.3	16.5	–16.2	54.8
		δ^{18}O	6	–6.3	0.9	–3.4	7.2
		D–excess	6	6.0	14.6	11.2	8.6
Jos	1988–1989	δ^2H	11	65.5	1.3	–20.2	66.8
		δ^{18}O	11	–8.1	0.1	–3.7	8.2
		D–excess	11	–0.9	16.5	9.4	17.4

8.5 Results

8.5.1 Oxygen and hydrogen isotopic composition of local and regional precipitation

The δ^{18}O and δ^2H for rainfall from the local stations at the Komadugu–Yobe basin were highly variable (Table 8.1). The rainfall samples collected at Garin Alkali between 1992 and 1997 by

Goni et al., (2001) ranged from –6.8 ‰ to 4.2 ‰ for $\delta^{18}O$ and –36 ‰ to 36 ‰ for $\delta^{2}H$. Rainfall samples collected at Maiduguri Airport in 2001 and 2018 by Goni, (2006) and Goni et al., (2023) varied between –8.1 and 3.8 ‰ for $\delta^{18}O$ and –58.8 and 31.6 ‰ for $\delta^{2}H$ in 2001, whereas $\delta^{18}O$ values ranges from –10.44 to 3.3 ‰ and $\delta^{2}H$ from –74.4 and 27.4 ‰ in 2018. Rainfall samples collected at Jos between 1988 and 1989 by Mbonu and Travi, (1994) varied from –8.1 ‰ to 0.1 ‰ for $\delta^{18}O$ and –65.5 ‰ to 1.3 ‰ for $\delta^{2}H$. The only GNIP station (Kano) within the study area has rainfall isotope signatures ranging from –7.7 ‰ and 2.4 ‰ for $\delta^{18}O$ and –58.3 ‰ and 22.3 ‰ for $\delta^{2}H$. The statistical summary of isotopic signatures for $\delta^{18}O$ and $\delta^{2}H$ from the Kano GNIP station and the three selected surrounding regional GNIP stations (N'djamena, Niamey and Maroua) are presented in Table 8.2.

Table 8.2 Statistical summary of stable isotopic signatures of precipitation from selected GNIP stations.

GNIP Stations	Period	Variables	Count (n)	Min	Max	Average	Range
Kano	1961–1973	$\delta^{2}H$	33	–58.3	22.3	–16.3	80.6
		$\delta^{18}O$	33	–7.7	2.4	–2.9	10.1
		D–excess	33	–13.4	21.0	7.1	34.4
N'djamena	1964–1995	$\delta^{2}H$	73	–53.4	56.4	–4.0	109.8
		$\delta^{18}O$	73	–9.4	9.2	–1.3	18.6
		D–excess	73	–25.1	26.4	6.5	51.5
	2015–2021	$\delta^{2}H$	35	–56.4	38.7	–16.3	95.1
		$\delta^{18}O$	35	–8.7	3.9	–3.0	12.5
		D–excess	35	–6.1	15.8	8.0	21.8
Niamey	1992–1999	$\delta^{2}H$	34	–59.0	17.0	–19.7	76.0
		δ18O	34	–8.4	1.9	–3.1	10.3
		D–excess	34	–5.2	11.8	5.0	17.0
	2009–2020	$\delta^{2}H$	74	–56.8	28.8	–11.0	85.6
		$\delta^{18}O$	74	–8.3	3.7	–2.4	12.0
		D–excess	74	–16.2	18.2	8.1	34.5
Maroua	2020–2021	$\delta^{2}H$	12	–58.7	34.2	–17.9	92.9
		$\delta^{18}O$	12	–8.5	6.5	–3.0	15.0
		D–excess	12	–17.8	13.0	6.4	30.8

8.5.2 Variability of the isotopic composition of local and regional precipitation

The rainfall $\delta^{18}O$ and $\delta^{2}H$ in the study area are predominantly enriched at lower elevation stations (Garin Alkali and Maiduguri station) due to arid to semi-aid climatic conditions, which influence rainfall frequency, atmospheric air masses and rainfall amount relative to higher elevation stations at Kano and Jos Plateau. Moreover, the movement of air masses and the significant effect of the intertropical convergence zone (ITCZ) influences rain-bearing moisture (Banda et al., 2024; Wotany et al., 2021). The ITCZ moves north and south of the equator throughout the year. During the wet season, when the ITCZ is overhead, rainfall is often associated with more depleted $\delta^{18}O$ and $\delta^{2}H$ isotopic signatures due to intense rainfall which enhances the "amount effect," where heavier isotopes preferentially condense and fall out earlier, leaving lighter isotopes in the remaining moisture (Kern et al., 2016; Panarello and Dapeña 2009; Stoll et al., 2007). ITCZ is also associated with strong convection processes which lift moist air to high altitudes leading to depletion of heavier isotopes during condensation. Additionally, rainfall during this season often originates from distant moisture sources such as the Atlantic Ocean in the case of the study area, leading to progressive isotopic depletion as the air mass loses moisture along its path (Rincón-Martínez et al., 2010; Sánchez-Murillo et al., 2016; Wellington and Dunbar, 1995). Conversely, the dry season is characterized by less or no rainfall, typically from local sources or re-evaporation, which results in isotopically enriched signatures (Stoll et al., 2007; Vargas et al., 2022). The variation in isotopic values of $\delta^{18}O$ and $\delta^{2}H$ in the surrounding GNIP stations dataset is more pronounced when compared to the datasets of the local stations. This may be attributed to the spatial and temporal variability of the isotopic signatures influenced by geographical location and regional orography (Bowen, 2008; Moreno et al., 2021), and the “continental effect”, that occurs when moist air and clouds move inland from the Atlantic Ocean and become gradually isotopically depleted due to progressive rainout effect (Dansgaard, 1964). Elevation and/or amount effect may also be a factor as results from isotopic stations located at the higher altitude show less variation in $\delta^{18}O$ when compared to stations at lower elevations in Niamey, and N'djamena.

8.5.3 Local meteoric water line

The stable isotope datasets obtained from the local stations including (GNIP in Kano) and regional GNIP stations provided comprehensive information on the local meteoric system for the Komadugu–Yobe basin. The isotopic datasets collected from the local stations at the Komadugu–Yobe basin were used to define the local meteoric characteristics of the basin (Figure 8.3a). The local meteoric water line (LMWL) for the local stations is described in (Eq. (8.4)). A mean intercept of 6.2 (±1.3) ‰, below the global meteoric water line (GMWL) intercept (Eq. (8.5)) signifies local rainfall receives moisture contribution from the various sources with distinctive isotopic signatures or attributed to variation in local climatic conditions such as temperature due to reduced evaporation and isotopic fractionation resulting in heavier isotopic signatures. A significant portion of the local rainfall samples were plotted below the GMWL, suggesting raindrop evaporation during rainfall events (Banda et al., 2021).

$$\delta^2H = 7.4\ (\pm 0.3)\ \delta^{18}O + 6.2\ (\pm 1.3);\ (r^2=0.91) \tag{8.4}$$

$$\delta^2H = 8\delta^{18}O + 10\ \text{(Craig, 1961)} \tag{8.5}$$

Figure 8.3b and Eq. (8.6) show the regional meteoric water line (RMWL) obtained by augmenting the dataset from local stations and surrounding GNIP stations. The regional meteoric water line has a lower slope than the Global Meteoric Water Lines (GMWL) see Eq. (8.6);

$$\delta^2H = 6.7\ (\pm 0.1)\ \delta^{18}O + 4.1\ (\pm 0.4);\ (r^2=0.95) \tag{8.6}$$

The slope of the RMWL is attributed to evaporative fractionation of rainfall (Ansari et al., 2022). Figures 8.3c and d present the distribution of D-excess for rainfall in local and regional stations, respectively. Mean d-excess values of 8.1 and 7.2 ‰ for local rainfall and regional precipitation suggest the influence of evaporation. Large-scale evaporation process in Lake Chad, repeated recycling of air masses as they travel from the ocean and hot and dry climates in the Lake Chad region may result in isotopic enrichment. The paucity of data underscores the need for the collection of long–term stable isotope data for rainfall from Kano GNIP station and other local stations in Nigeria to improve the local representativeness of the country to regional global stable isotope characterization and underpin integrated water resources management (IWRM) in a regional context.

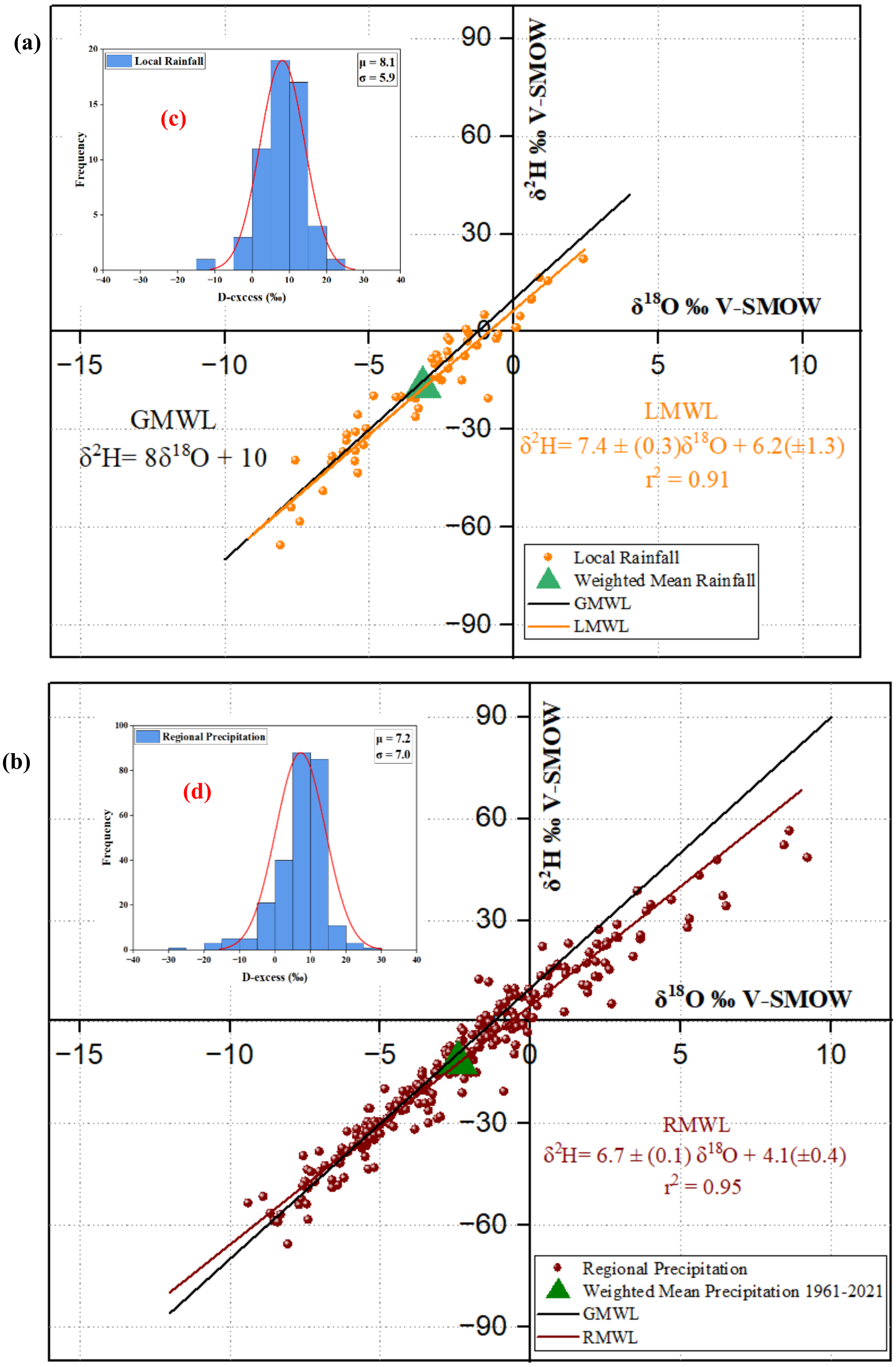


Figure 8.3 (a) Plot of local meteoric water line in KYB based on monthly rainfall stable–isotope dataset from local stations (n =71). LMWL: the weighted local meteoric water line for local stations. The green triangle is the weighted average rainfall. (b) Plot of δ^2H and δ^{18}O signatures for Rainfall stable–isotopic dataset from Local stations and Surrounding Regional GNIP stations (n =299). RMWL: Regional Meteoric Water Line. GMWL: Global Meteoric Water Line. The green triangle is the weighed mean regional precipitation including the local rainfall. (c) Histogram showing the distribution of d-excess for local rainfall (d) Histogram showing the distribution of d-excess for regional precipitation.

8.5.4 Groundwater Isotopic Composition

The isotopic signatures for groundwater samples from the KYB (n = 240) varied from –5.4 ‰ to 3.9 ‰ for oxygen and –36.9 ‰ to 16.5 ‰ for hydrogen in the wet season and from –6.2 ‰ to 2.4 ‰ for oxygen and –44.1 ‰ to 8.4 ‰ for hydrogen in the dry season, respectively. The groundwater regression lines for the study area for wet and dry seasons are found in Figure 8.4a, and Eqs. 8.7 & 8.8.

$$\delta^2H = 5.4\ (\pm\ 0.2)\ \delta^{18}O - (3.3\ \pm 0.6);\ (r^2=0.96) \qquad 8.7$$

$$\delta^2H = 5.3\ (\pm\ 0.2)\ \delta^{18}O - (4.0\ \pm\ 0.7);\ (r^2=0.94) \qquad 8.8$$

The mechanisms controlling groundwater (GW) recharge processes in the Komadugu–Yobe basin during the wet and dry seasons were assessed by plotting the $\delta^{18}O$ and δ^2H signature of the groundwater samples for both the wet and dry seasons concerning the LMWL (Eq. (8.6)) and GMWL (Figure 8.4a). A large subset of the GW samples plotted along the LMWL and GMWL (Group–A), indicating that it is recharged directly by modern local rainfall. However, a group of the GW samples were observed to deviate from the LMWL and GMWL (Group–B) indicating evaporation during or after infiltration (Ansari et al., 2018).

The lower slopes and negative intercepts of the evaporation line LEL (Eqs. (8.7) & (8.8)) compared to that of the LMWL (Eq. 8.6)) suggests evaporative enrichment effects on groundwater (McConville et al., 2001, Ansari et al., 2018). Moreover, the evaporation lines have slopes that indicate GW has undergone evaporative enrichment (Ansari et al., 2018; Ju et al., 2024). Furthermore, the dry season groundwater samples show higher evaporative effects as their slope and intercepts; 5.3 and –4.0 are lower than those of the wet season samples; 5.4 and –3.3 respectively (Figure 8.4a). Again, Figure 8.4 d and e show the distribution of d-excess of wet and dry seasons groundwaters with a mean value of 6.5 ‰ and 6.3 ‰ respectively. These collectively indicate the influence of significant changes in source characteristics due to local climatic (Semi-arid to arid) and or physiographic conditions. Suffice to say that the wet and dry season GW both are recharged by water that has undergone evaporation before or during infiltration.

Segregation into uplands and lowlands GW (Figure 8.4 b & c) for the wet and dry seasons reveals a significant percentage of the Group–A data (more enriched) were sampled from the lowlands water points. Mean d-excess values of 8.4 ‰ and 3.4 ‰ for the uplands, and 8.3 ‰ and 3.5 ‰ for the lowlands, were recorded in groundwater samples collected during the wet and dry seasons, respectively (Figure 8.4 f & g, and h & i). Low mean d-parameter values were observed in the lowland areas, predominantly along the Komadugu–Yobe Valley, the Bade Axis, and the Hadejia–Nguru Wetlands. The uplands correspond to the basement complex region, characterized by weathered, partially weathered, and fractured basement rocks that receive localized recharge. However, the lowlands correspond with sedimentary Quaternary regions, which experience significant recharge due to the highly permeable formations prevalent in the area. This distinction in geological settings significantly influences the observed isotopic signatures and d-excess values in both the lowlands and uplands, reflecting their distinct recharge dynamics.

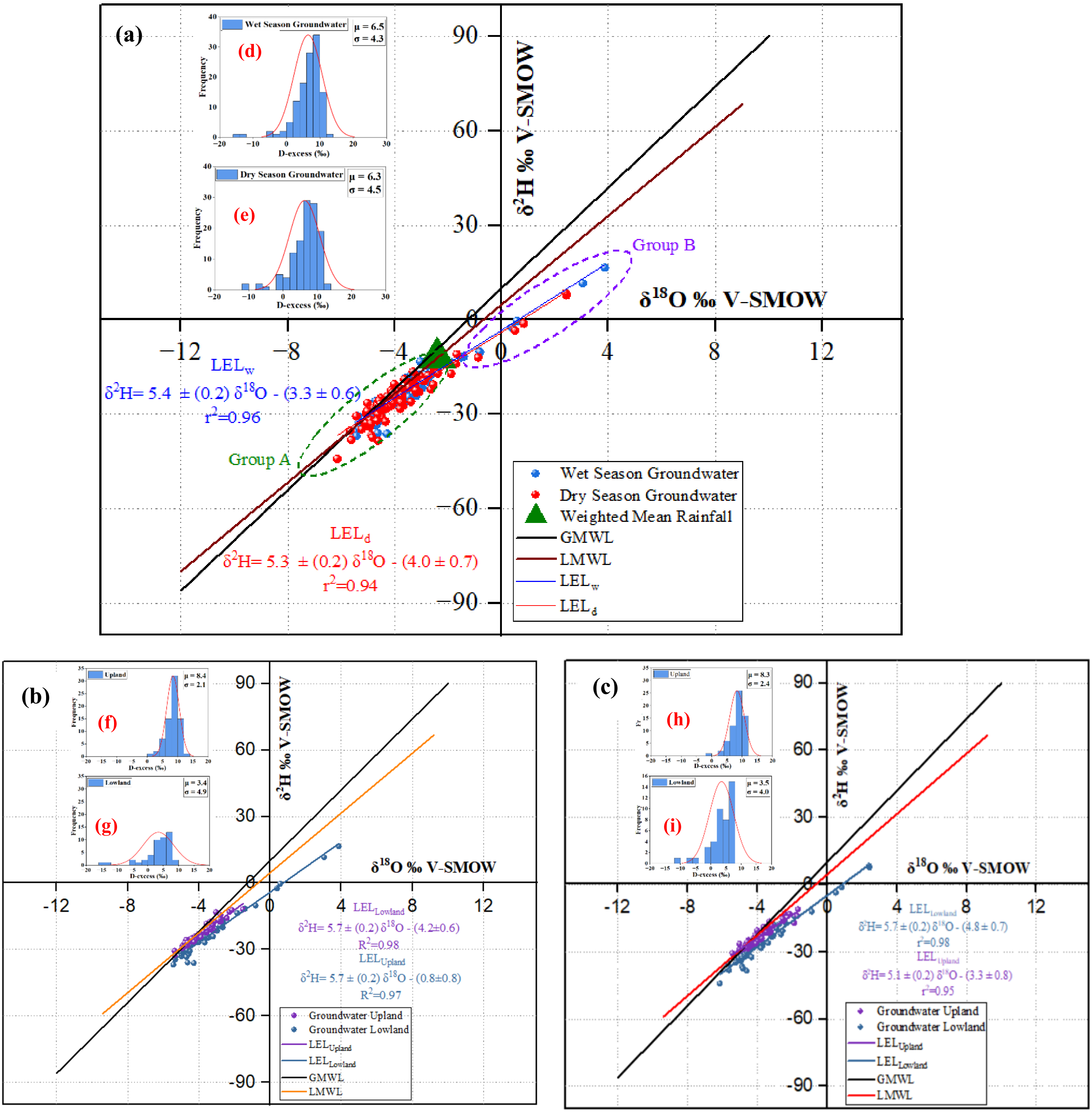


Figure 8.4 (a) Plot of δ^2H and δ^{18}O signatures for the wet and dry seasons groundwater samples (n = 240). Local meteoric water line (LMWL) represents the weighted local meteoric water line. GMWL: Global meteoric water line. GMWL. LEL: Local evaporation line. The subscript w and d refer to wet and dry season respectively. (b) Plot of δ^2H and δ^{18}O signatures for groundwater samples of Komadugu–Yobe basin segregated to upland and lowland sampling points for wet season. (c) Plot of δ^2H and δ^{18}O signatures for groundwater samples of Komadugu–Yobe basin segregated to upland and lowland sampling points for dry season. Histogram show in distribution of groundwater (d) wet season (e) dry season (f) wet season upland (g) wet season lowland (h) dry season upland (i) dry season lowland.

8.5.5 Deuterium Excess of Groundwater

Dansgaard, (1964) defined deuterium excess (Eq. 8.2), a measure used for understanding the origin of vapour masses. The relative humidity, air temperature, ocean surface temperature and wind speed are factors that affect deuterium excess. (Ansari et al., 2018; Feher et al., 2024). It can be used to estimate how evaporation affects groundwater recharge and to understand its recharge conditions. (Ansari et al., 2018; Chen et al., 2024; Zhu et al., 2019). The deuterium excess of GW samples in the Komadugu–Yobe basin varies from –14.4 ‰ to 12.2 ‰ with an average value of 6.5 ‰ for the wet season and –11.6 ‰ to 13.8 ‰ with an average value of 6.3 ‰ for the dry season, respectively (Figure 8.4d and e). The deuterium excess values of GW samples in the dry season are slightly higher than those of wet season samples. This may be due to the increased evaporation rate in the dry season particularly in the northeastern region of the basin around Bade, Karasuwa and close to the verge of Lake Chad which is characterized by semi-arid to arid climate. Variation in deuterium excess could be related to the change in the mixing proportion of different water sources (precipitation, surface water and deeper groundwaters) as well (Krishan et al., 2020; Masiol et al., 2021; Sreedevi et al., 2021).

8.5.6 Spatial distribution of isotopic composition in groundwater

The isotopic signatures of $\delta^{18}O$ and $\delta^{2}H$ in groundwater samples of the Komadugu–Yobe basin for respective wet and dry seasons show spatial variation (Figure 8.5 a & b and c & d). The $\delta^{18}O$ and $\delta^{2}H$ isotopic compositions for the groundwater were subdivided based on altitude: lowlands (altitude < 400 m) and uplands (altitude > 400 m). In the upland sites of the basin, more depleted isotopic values were observed compared to the lowland sites (Figure 8.5). This is indicative of higher rainfall amounts, and lower evaporation rates in the uplands. In contrast, the lowlands have semi-arid to arid climates characterized by low precipitation, higher air temperature and elevated evaporation, particularly during the dry season. GW samples that indicate groundwater recharge during the wet season include the areas of Hadejia, Lamisu, and

Garin Alkali (Northeastern part of the basin) with elevation below 400 m (amsl) and mean annual rainfall of about 850 mm displayed depleted $\delta^{18}O$ and $\delta^{2}H$ signatures of −3.9 ‰ and −25.4 ‰, −4.3 ‰ and −36.2 ‰, and −4.7‰ and −33.4 ‰, respectively. Interestingly, wet season samples from uplands areas of Fagge and Gumau with elevations above 400 m (asl) and mean annual rainfall of 1200 mm amount show enriched $\delta^{18}O$ and $\delta^{2}H$ signatures of −2.3 ‰ and −13.1 ‰, and −3.4 ‰ and −17.7 ‰, respectively. It is worth noting that the dry season data shows a similar trend.

The most effective way to characterize the isotopic composition of groundwater is to observe how it interacts with the various geological formations (Birks et al., 2019; Jasechko, 2019). The exchange of ions with minerals when groundwater flows through geological formations influences the isotopic values of groundwater (Chen et al., 2021; Jasechko, 2019; Li et al., 2019). The more enriched $\delta^{18}O$ and $\delta^{2}H$ signatures in the groundwater samples were predominantly observed in the sedimentary Quaternary formation region whereas the highly depleted $\delta^{18}O$ and $\delta^{2}H$ signatures correspond to the region underlain by the Precambrian basement complex in the study area (Figure 8.2). The more enriched isotopic signatures in the sedimentary Quaternary formation region suggest recharge from local precipitation with minimal isotopic fractionation, possibly due to the permeable nature of the sedimentary formation which facilitates rapid infiltration, particularly around Hadejia-Nguru wetland and the verge of Lake Chad as shown in Figure 8.2. However, the highly depleted isotopic signatures in the Precambrian basement complex indicate the recharge could be from higher altitudes or older water sources, with significant isotopic fractionation during the recharge process, possibly due to preferential evaporation. Additionally, rock-water interaction within the weathered and fractured basement in the groundwater system in the region could also influence the isotopic signatures (Figure 8.2).

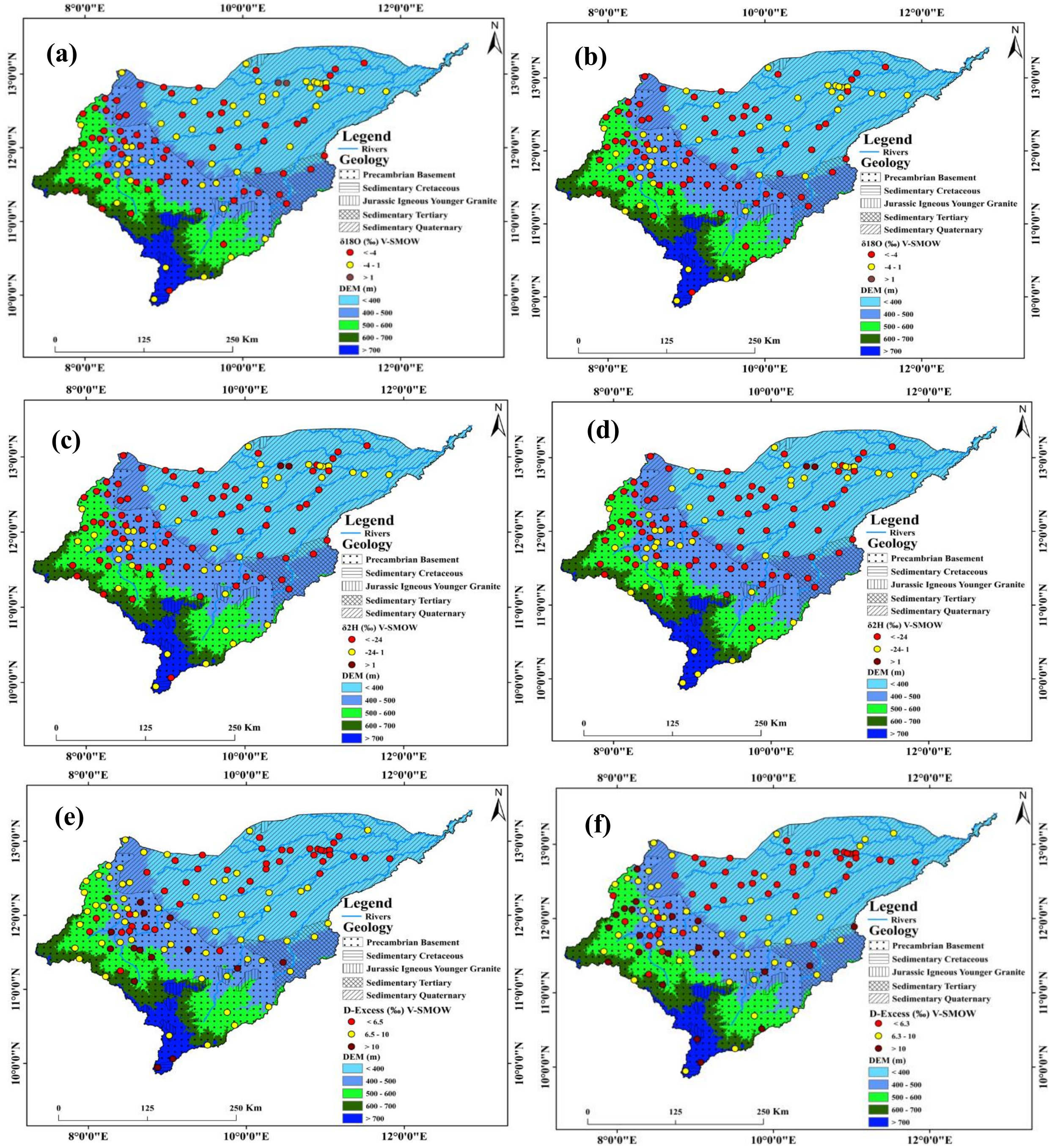


Figure 8.5 Spatial distribution of $\delta^{18}O$ isotope in groundwater of KYB related to geology and altitude (a) wet season (b) dry season. Spatial distribution of $\delta^{2}H$ isotope in groundwater of KYB related to geology and altitude (c) wet season (d) dry season. Spatial distribution of D–Excess in groundwater of KYB related to geology and altitude (e) wet season (f) dry season.

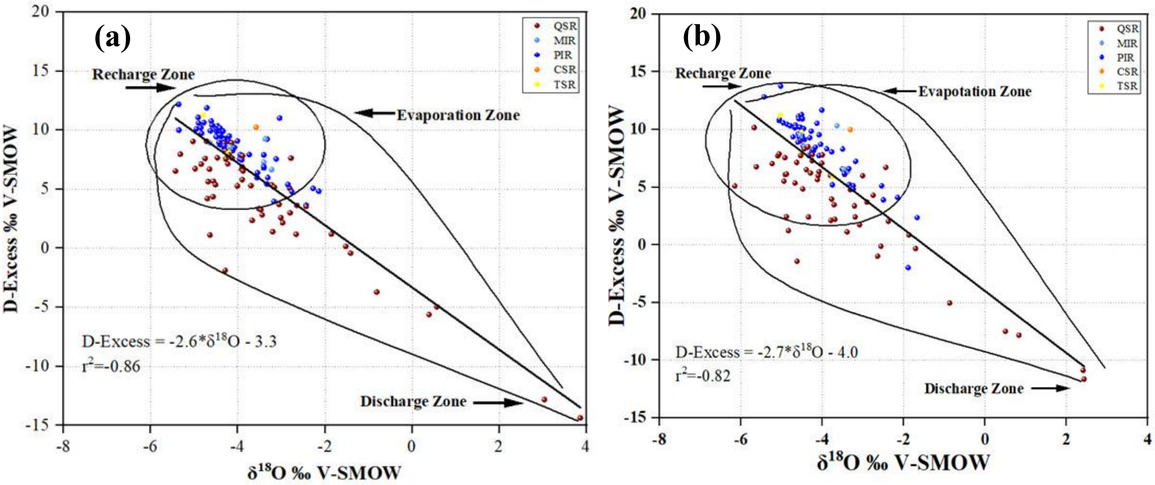


Figure 8.6 D–Excess against $\delta^{18}O$ in groundwater of the KYB (a) wet season (b) dry season. QSR: Quaternary sedimentary rock, MIR: Mesozoic Igneous rock, PIR: Precambrian igneous rock, CSR: Cretaceous sedimentary rock, TSR: Tertiary sedimentary rock.

8.5.7 Spatial Distributions of Deuterium Excess in Groundwater

The spatial distribution of deuterium excess for wet and dry seasons is presented in Figure 8.5 e & f. Figures 8.5 and 8.6 show that D–excess of GW in the fractured basement complex differs from GW in sedimentary formations of the Komadugu–Yobe basin. In general, d-excess of 10 and above is predominantly found for GW in the localised basement fractured and weathered basement aquifers at higher elevations, and d-excess of less than 6 and below is predominantly found for GW in sedimentary Quaternary aquifers at lower elevations. Sreedevi et al., (2021) highlighted the importance of d–excess in identifying GW recharge sources in a semi-arid and arid environment. Mixing of waters from various origins and its kinetic evaporation particularly in the vadose zone coupled with interaction with various geological formations resulted in decreased signatures of d-excess in groundwater. Moreover, changes in precipitation sources, evaporation, and moisture recycling are the resultant factors of this large variability in the d-excess of groundwater (Behrens et al., 2021; Li et al., 2019; Saranya et al., 2021). Figure 8.6 a & b presents the variation of d–excess against $\delta^{18}O$ for wet and dry–season GW samples of the Komadugu–Yobe basin. It would appear from the data that the process of GW recharge is different for fractured basement aquifers than for sedimentary Quaternary aquifers in the KYB.

Given the fractured basement dominates the upland / higher elevations, perhaps this geology and geomorphology reflect the localised isotopic composition of GW recharge when compared with GW from sedimentary formations (generally lower elevations in the Lake Chad basin) (Figure 8.5e and f). Close observation found areas such as Challawa, Rogo, Madaba, Tiga area in Bebeji LGA, Toro and Chiromawa have an elevated level of d–excess for GW in the basement complex region suggesting recharge from a less evaporated water source, possibly influenced by localized rainfall infiltration through the vadose zone, partially weathered, weathered and fractured basement, while localities of Gashua, Hadejia, Guri covering the Hadejia–Nguru wetlands in the Sedimentary Chad formations have low d–excess (more pronounced during dry season) indicative of an evaporated water source (Figure 8.2). This reflects the influence of geological formations and climate on groundwater recharge and the isotopic composition within the aquifer systems. This finding resonated with the work of Goni et al., (2023). Deuterium–excess was observed to be less than 10 in about 80 % of GW samples particularly in the Southeastern parts of the KYB, signifying rainwater evaporation before infiltration. Only GW in higher elevation, and within basement fractured rock have d-excess around 10 (that of the global meteoric line) showing little sign of evaporation during recharge. This suggests relatively young waters of meteoric origin under modern climatic conditions dominate GW recharge.

8.6 Discussion

8.6.1 Rainfall–recharge relationships in KYB and Sahel region of West Africa

The slope of the LMWLs for the 240 groundwater samples in the KYB (wet and dry seasons) supports evaporation as a dominant process (5.4 ± (0.2) and 5.3 ± (0.2) respectively). These are lower than the RMWL (Eq. (8.6)) and GMWL (Eq. (8.5)) indicating an evaporative enrichment effect during recharge processes. This is consistent with other studies across the Sahel, for example, the findings of Vassolo et al., (2023) and Goni et al., (2021), where both the river water and groundwater in the Lake Chad basin experienced the effect of evaporation. GW stable isotope trends intersect the global meteoric water line at ca. -5 ‰ $\delta^{18}O$ and -30 ‰ $\delta^{2}H$, which is 2 ‰ and 14 ‰ lighter respectively than the mean regional/local precipitation (Figure 8.7a). This is indicative of precipitation that leads to groundwater recharge either during the rainy season or at higher elevations (or both). Figure 8.7c shows the distribution of d-excess in the HJKYB with an average value of 2.8 ‰. This tallied with the values recorded in the lowland areas of KYB in this study indicating significant impacts of evaporative enrichment before infiltration. Both areas are situated around the vicinity of Lake Chad.

8.6.2 Comparison with groundwater isotopes found in previous studies

The plot of $\delta^{2}H$ against $\delta^{18}O$ displays variations for GW analysed across the Sahel region of West Africa (Figure 8.7b). As we found in the KYB, other studies have found the stable isotope ratios ($\delta^{18}O$ and $\delta^{2}H$) in groundwater from the Lake Chad Basin (LCB), Iullemeden basin (IB), Liptako–Gourma and Upper Volta system (LG &UVS), Taoudeni basin (TB), and Senegalo–Mauritanian basin (SMB) all exhibit a regression towards a signature that is significantly more depleted in $\delta^{18}O$ and $\delta^{2}H$ relative to the mean composition of rainfall in the surrounding regional GNP stations (Figure 8.7b, Table 8.2) (Huneau 2017; Laurence 2017; Taupin 2017; Travi 2017; Zouari 2017). Moreover, the evaporation lines of the KYB, LCB, IB, LG &UVS, TB, and SMB intersected the RMWL for the Sahel region and GMWL at more depleted $\delta^{18}O$ and $\delta^{2}H$ isotopic signatures like the KYB (Figure 8.7b). The RMWL for the Sahel region was developed by aggregating 15 GNIP stations (Niamey, Bamako, Moruoa, Ndjamena, Kano, Oagadugu, Tombouctou, Sevare, Bankass, Dakar, Louga, Pout, Barago, Ouagadougou, and Bobo-Dioulasso) datasets across the Sahel region obtained from (https://nucleus.iaea.org/wiser/explore/) is defined here as $\delta^{2}H = 6.2 \pm (0.1)\ \delta^{18}O + (2.9 \pm 0.6)$. Groundwater recharge in this region most likely occurs during the months of heavy rainfall (July, August, and September) when the precipitation isotopic signatures are more depleted.

Similar deductions, that groundwater recharge in the Southwestern Lake Chad basin occurs during the months of heavy rainfall were noted by Goni et al., (2021). Lutz et al., (2011) in Mali and Niger indicated that the groundwater recharge specifically occurs in the peak monsoonal months at the prevailing climatic conditions rather than paleo–groundwater recharge under different climatic conditions. Faye et al., (2019) found that groundwater recharge is evident during the months of heavy rainfall in the tropical dry lands of Senegal. Huneau et al., (2011) and Trabelsi et al., (2023) demonstrated the effect of evaporation within the south–eastern Taoudeni sedimentary basin between Burkina Faso and Mali during groundwater recharge. The slopes and intercepts of the evaporation lines in all the major basins of the Sahel region of West Africa are lower than those of the RMWL and GMWL indicating an evaporative enrichment effect during recharge processes. The distribution of d-excess in the Sahel region shows variation from -34.1 to 64.6 ‰ with a mean of 10.1 ‰ (Figure 8.7d). The mean d-excess value of 10.1 ‰ indicates that average precipitation in the entire Sahel region forms under similar conditions to the average global precipitation or occurs under equilibrium conditions (Dansgaard, 1964). This also suggests that the source of moisture-bearing precipitation in the region is likely oceanic (Valdivielso et al., 2024).

8.6.3 Inverse Continental effect across the Sahel region of West Africa

Figure 8.8 presents a boxplot that shows variations in δ^{18}O and δ^{2}H signatures observed in groundwater across various major basins, from West to East, in the Sahel region of West Africa. In the Senegalo–Mauritanian basin, the isotopic signatures ranged from –11.4 to 9.3 ‰ for δ^{18}O, and –81.6 to 29.7 ‰ for δ^{2}H. In the Taoudeni basin, the range of values observed is: –8.6 to 29.8 ‰ in δ^{18}O, and –58.3 to 130.2 ‰ in δ^{2}H. In the region of the Liptako–Gourma & Upper Volta systems, the range of values observed are: –6.5 to 7.2 ‰ in δ^{18}O, and –43.3 to 32.7 ‰ in δ^{2}H. The range of values observed in the Iullemeden basin are: –8.5 to 12.4 ‰ in δ^{18}O and –58.2 to 45.0 ‰ in δ^{2}H. The isotopic signatures in the Komadugu-Yobe basin (this study) ranged from –6.2 to 3.9 ‰ for $\delta^{18}O$, and –44.1 to 16.5 ‰ for $\delta^{2}H$ while in the Lake Chad basin, the range of values observed are: –6.9 to 8.8 ‰ in $\delta^{18}O$, and –53.4 to 43.3 ‰ in $\delta^{2}H$. The continental effect generally refers to a trend from heavier isotopes at the continental margin to lighter isotopes as air masses move landward. From Figure 8.8, there appears to be an 'inverse' continental effect from the coastal west to the eastern Sahel which suggests the source of moisture in the air mass comes from evaporative enrichment, overlain by local orographic effects.

8.6.4 GW isotopes in the KYB within the spatial distribution of GW isotopes in the Sahel

The spatial evolution of $\delta^{2}H$ signatures in groundwater across the Sahel region of Africa is presented in Fig 8.9a. A general increasing trend (as also evident in Figure 8.8) in the enrichment of $\delta^{2}H$ signatures was observed in the Sahel region from the Senegalo–Mauritanian basin in the west to the Lake Chad basin in the east. D–excess values close to and above 10 ‰ are distributed along river Niger in the Niger Republic and Kebbi State in Nigeria (Figure 8.9b). Groundwater in the Taoudeni basin and Liptako–Gourma & Upper Volta system show very low d–excess values. This signifies that the recharge in the regions is produced by heavily evaporated water. The d–excess values in the Lake Chad Basin, Iullemeden Basin, and Senegalo–Mauritanian Basin are mostly positive. This suggests that groundwater in these regions is predominantly recharged directly by precipitation. However, groundwater samples in areas close to Lake Chad, the Taoudeni basin and along river Niger show lower levels of d–excess indicating groundwater recharge that has undergone additional evaporation. This resonates with the findings of Goni et al., (2023) and Huneau et al., (2011). Heavily evaporated water in the parts of the Senegalo–Mauritanian basin and the Lake Chad basin indicates that the Tertiary and Quaternary aquifers may contain old groundwater and additional study of deeper groundwater units is warranted.

8.6.5 Stable isotope observations and inferred groundwater recharge mechanisms in the Sahel

The isotopic signatures of groundwater in the Iullemeden basin (Figure 8.9), and the Senegalo–Mauritanian basin are more depleted and have a higher homogeneity possibly due reduced influence of evaporation processes. The hydrological characteristics of groundwater in the Lake Chad basin along with those of the Taoudeni basin exhibit a more enriched and homogeneous isotopic signature compared to the LG & UVS perhaps due to less complex recharge mechanisms with the minor influence of evaporative enrichment effect during recharge. About half of the groundwater samples from Niger and Chad parts of the Lake Chad basin displayed positive isotopic signatures, indicating a strong evaporative effect while those from Northern Cameroon and Central African Republic, displayed no strong evaporative effect. The latter is the same as the upstream part of KYB close to Kano, Bauch and some parts of Jigawa State. Here aquifer recharge likely occurs in the peak periods (July and August) of rainfall episodes in line with the findings of Mahamat Nour et al., (2022) and Goni et al., (2021). Bello et al., (2019) demonstrated that the groundwater recharge from northern Cameroon originated from modern, less evaporated rainfall infiltrating into the quaternary aquifer. Ette et al., (2017) found the Continental Intercalary aquifer system in the Sokoto parts of the Iullemeden basin gets recharged by modern water (more depleted). However, a significant evaporative effect of recharging rainwater was reported in North–Western Saharan part of the Iullemeden basin by Al–Gamal., (2011). The isotopic datasets of the Liptako–Gourma & Upper Volta system suggested an aquifer by rainfall during heavy rain episodes (August to September) recharge with less evaporative evidence particularly the Liptako–Gourma section. However, the central Upper Volta section spanning over parts of Togo, Benin, and Ghana reveals evaporated groundwater samples in the basement formation region. A similar deduction was done by Loh et al., (2022) in Ghana that the aquifer across the Lake Bosumtwi area gets recharged by modern water that has undergone evaporative enrichment.

Another study conducted by Gibrilla et al., (2017) in Ghana indicated a meteoric origin of recharged groundwater with minimal evaporative enrichment effect. Huneau et al., (2011) identified that the groundwater in the southeastern Taoudeni sedimentary basin is characterized by isotopic compositions very close to the range of present-day regional and global meteoric water lines which indicates no significant effect of evaporation during recharge. Trabelsi et al., (2023) demonstrated the presence of groundwater with varying recharge processes in the Taoudeni aquifer system and that the aquifer gets recharged by direct infiltration of rainwater and/or surface water. The Senegalo–Mauritanian basin is marked with a more depleted isotopic signature of groundwater. Only a few samples showed more enriched signatures. This is indicative of recent recharge by the present–day rainfall characterized by a slight evaporation effect. However, the deeper aquifer systems received their recharge under different climatic conditions in the past. Faye et al., (2019) reported that the shallow groundwaters in the Thiaroye aquifer of Dakar are predominantly of meteoric origin which recharge during the monsoon period (September). The origin of groundwater in the Nouakchott urban area in Mauritania is seawater marked by frequent evaporation uptake as reported by Mohamed et al., (2017).

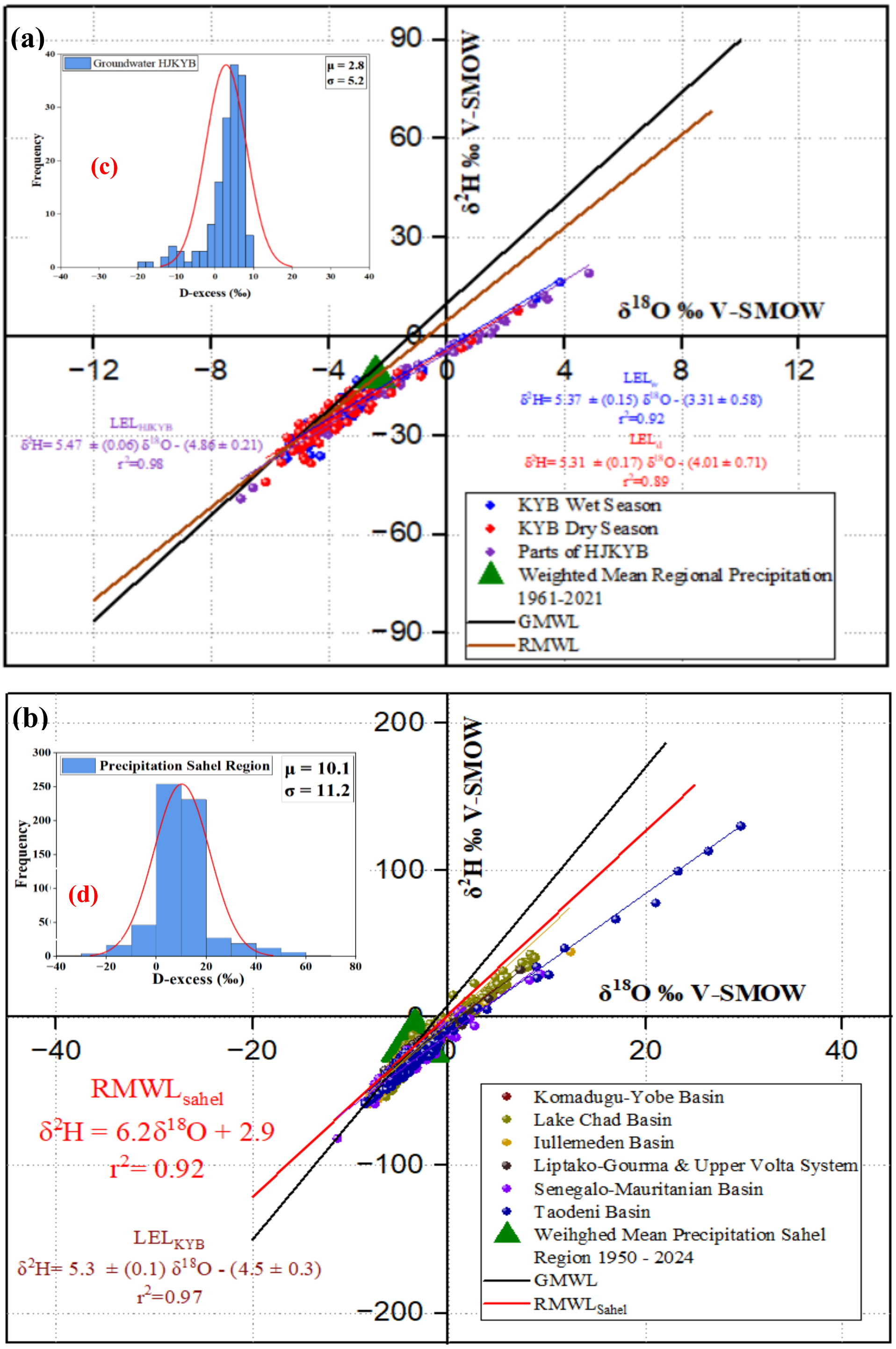


Figure 8.7 (a) Plot of δ^2H and δ^{18}O for wet and dry seasons groundwater samples of KYB (n = 240); Parts of HJKYB (n = 150). Local meteoric water line (LMWL) represents the weighted local meteoric water line. GMWL: Global meteoric water line. LEL: Local evaporation line. (b) Plot of δ^2H and δ^{18}O isotopes composition of groundwater. KYB wet season: δ^2H= 5.37 ± (0.15) δ^{18}O – (3.31 ± 0.58), (r^2=0.96); KYB dry season: δ^2H= 5.31 ± (0.17) δ^{18}O – (4.01 ± 0.71), (r^2=0.94); Lake Chad Basin: δ^2H = 5.51 ± (0.08) δ^{18}O – (4.18 ± 0.31), (r^2 = 0.92); Iullemeden Basin: δ^2H= 6.11 ± (0.10) δ^{18}O – (0.57 ± 0.47), (r^2 = 0.89); Liptako–Gourma & Upper Volta System: δ^2H=5.0 ± (0.07) δ^{18}O – (4.29 ± 0.27), (r^2 = 0.91); Senegalo–Mauritania Basin: δ^2H = 4.97 ± (0.08) δ^{18}O – (10.63 ± 0.45), (r^2 =0.92), Taoudeni Basin: δ^2H = 4.73 ± (0.04) δ^{18}O – (10.14 ± 0.25), (r^2 =0.97). RMWL: Regional meteoric water line; GMWL: Global meteoric water line. (c) Histogram showing the distribution of D-excess for rainfall in parts of HJKYB (d) Histogram showing the distribution of D-excess for precipitation in Sahel region.

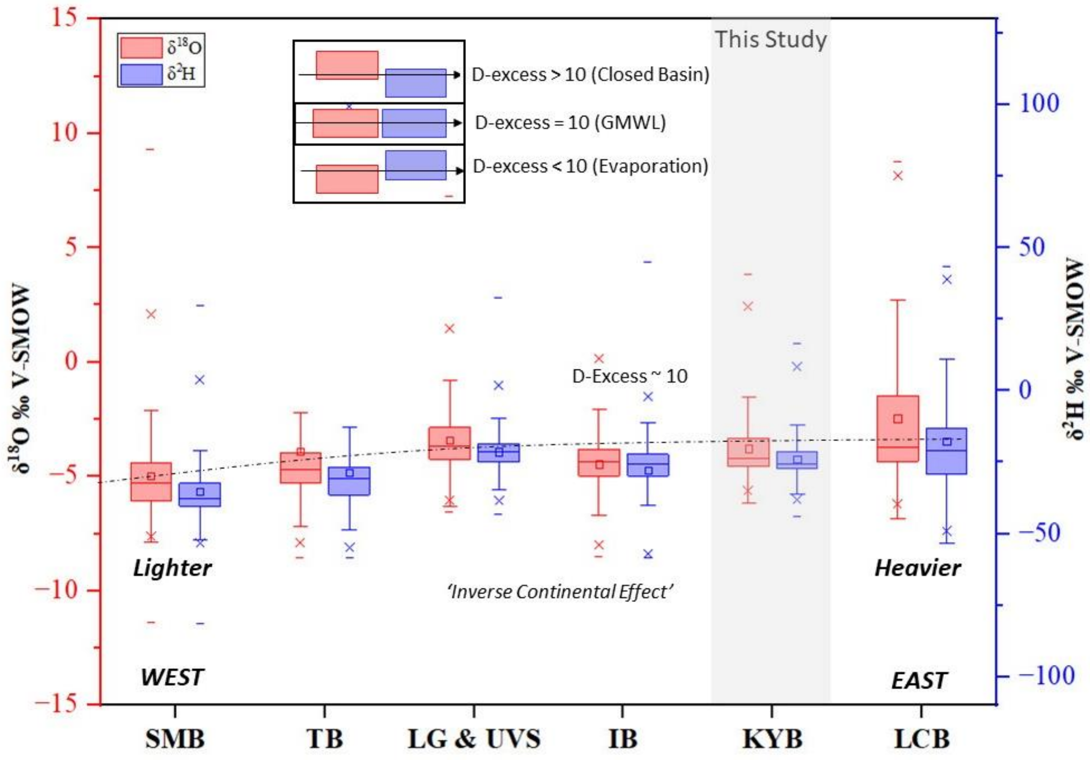


Figure 8.8 Boxplot of the isotopic signatures of groundwater in the Sahel region of west Africa. SMB: Senegalo–Mauritanian basin, TB: Taoudeni basn, LG & UVS: Liptako–Gourma and Upper Volta system, IB: Iullemeden basin, KYB: Komadugu-Yobe basin, and LCB: Lake Chad Basin.

8.6.6 Policy recommendations for sustainable groundwater resources management in the Sahel region of West Africa

This study outcomes not only enhance the capacity of isotopic tools in scientific investigation in the region, but also provide interpretation useful for policymakers, donor agencies, water specialists, and government agencies in the Sahel region of West Africa as they underpin the implementation of IWRM to meet Goal 6 of the SDGs in a timely manner. In order to achieve SDG 6 in the Sahel region of West Africa, integrated water resources management of shared water resources is pivotal, and the following policy recommendations might be considered in support of these efforts:

- Given the hydrological interconnection within the Sahel region and the transboundary nature of various water resources in the region (River Niger, Senegal River, Lake Chad, Volta Lake, Irhazer–Iullemeden aquifer, quaternary aquifer, Senegal–Mali aquifer, and Iullemeden–Tanezrouft aquifer), it is imperative for policymakers, decision-makers, water financers, and the economic community of West African States (ECOWAS) to establish agreements for the management of these shared water resources in light of increased exploitation.

- It is imperative to protect sensitive areas which are potential sources of groundwater recharge in the Sahel region such as the wetlands in the southern region of the Lake Chad basin, the Hadejia–Nguru wetlands, Lake Volta, the Senegal River, Chari–Logone River, the Komadugu–Yobe valley, the river Niger, Nakambe river, Sokoto river, the Salamat Wet Land in Cameroon, Gorgol river, and Oti river from any activities that could potentially disrupt environmental flows and biodiversity. This includes the construction of dams and the implementation of intensive irrigation schemes. It is crucial to prioritize the preservation of wetlands and implement strategies for watershed restoration and sustainable water management, to safeguard the quantity and quality of water resources in the region.
- Regional collaboration between West African countries within the Sahel region should be initiated to promote synergy between counterpart countries exploiting shared aquifers and to employ advanced isotope tracers (radioisotopes, ^{13}C, ^{14}C, ^{36}Cl) for a comprehensive evaluation of the residence time of groundwater and how quickly aquifers get recharged in the region. Moreover, measures should also be taken to evaluate the use of fertilizers in agricultural areas and industrial activities that may potentially contaminate the transboundary aquifers.

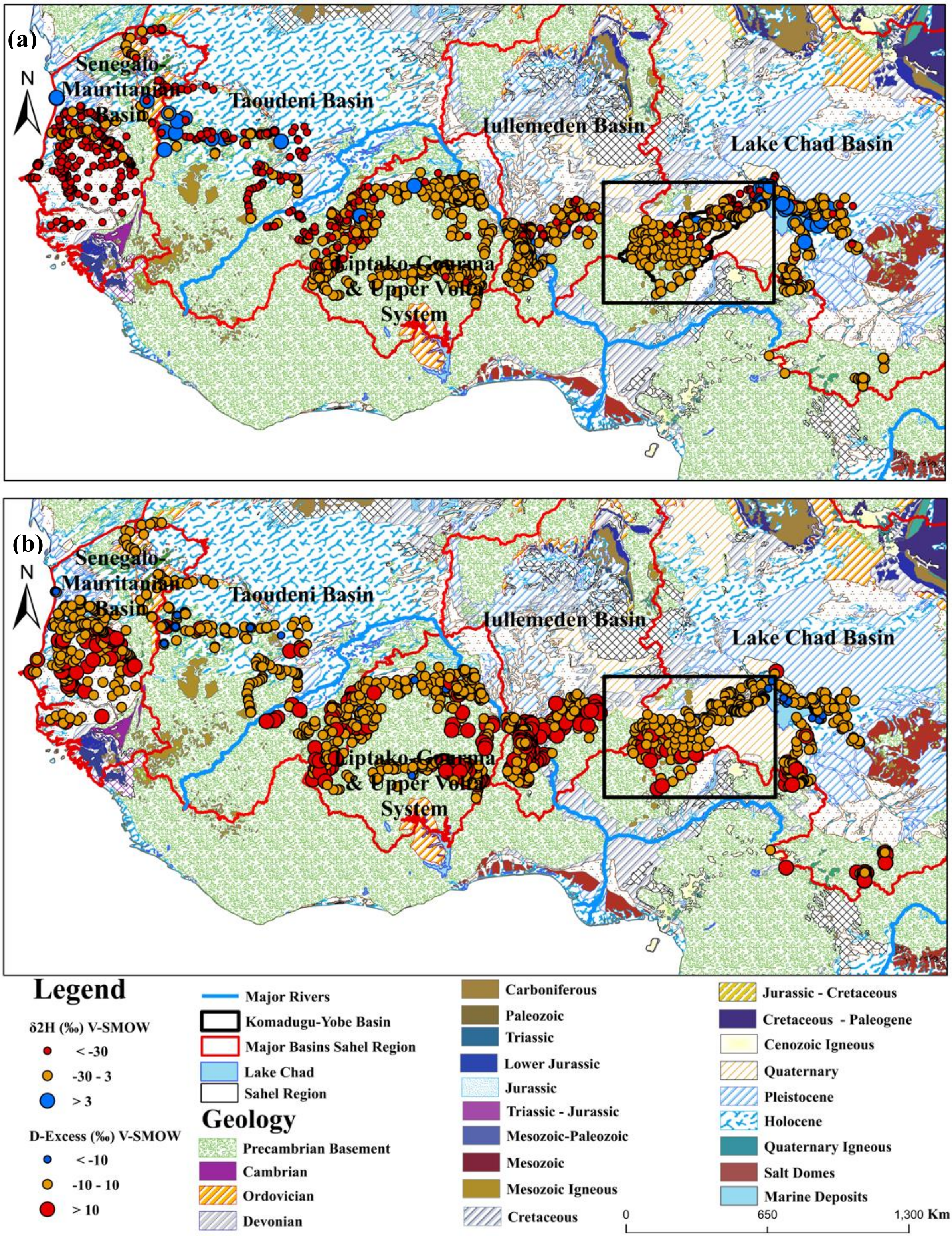


Figure 8.9 (a) Spatial variation of δ^{2}H isotope signature at KYB and across Sahel region of Lake Chad basin, Iul–lemeden basin, Liptako–Gourma & Upper Volta basin, Taoueni basin and Senegalo–Mauritanian basin. (b) Spatial variation of D–Excess at KYB and across the Sahel region of Lake Chad basin, Iullemeden basin, Liptako–Gourma & Upper Volta basin, Taoueni basin and Senegalo–Mauritanian basin.

- It is recommended that GNIP and GNIR stations be maintained across the Sahel, including on the Senegal River, the River Niger, and the Komadugu–Yobe River to increase the spatial resolution of hydrological data for a better understanding of hydrological systems in the region. The installation of more GNIP stations and the reactivation of the dormant GNIP stations would provide an increased dataset for a comprehensive understanding of the hydrological processes in the region. The deeper Pliocene and Continental terminal aquifers, which were inadequately researched, should be thoroughly investigated along with their potential transboundary implications in the Sahel region of West Africa in further studies.

8.7 Conclusion

This study reviewed all published data and developed a regional meteoric water line for the KYB using stable isotope datasets from local and surrounding regional GNIP stations. It also provided the first regional meteoric water line for the Sahel region of West Africa: $\delta^2H = 6.2 (\pm 0.1) \delta^{18}O + 2.9 (\pm 0.6)$. The local meteoric water line is characterized by a lower slope and intercept relative to the global meteoric water line. The circulation of air masses is strongly affected by geographical location and regional orography. The values of groundwater stable isotope show spatially variant isotopic signatures (from –5.4‰ to 3.9‰ ($\delta^{18}O$) and –36.9‰ to 16.5‰ (δ^2H) and from –6.15‰ to 2.43‰ ($\delta^{18}O$) and –44.1‰ to 8.4‰ (δ^2H)) in both the wet and dry seasons influenced by geology and altitude. Evaporative enrichment of isotopic signatures is affected by seasonal variability. Higher d–d-excess values in groundwater displayed a strong correlation with more depleted $\delta^{18}O$ signatures. The variability in isotopic composition of the local and regional precipitation in the transboundary Komadugu-Yobe basin is influenced by the impact of the intertropical convergence zone (ITCZ) and changes in regional orography. Recharges in the Sahel region occur during the months of heavy precipitation. The average precipitation in the entire Sahel region occurs under equilibrium conditions. Future research should include comprehensive and enhanced isotopic characterization, particularly using ^{3}H and ^{14}C to better understand recharge processes in the transboundary Komadugu-Yobe Basin and the wider Sahel region, especially in recharge zones, transboundary water resources, and wetland areas.

8.8 Postface

This chapter has answered and fulfilled RQ4: ‘What role can stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ offer in identifying the origin of groundwater recharge and its mechanisms in the Komadugu-Yobe basin?’ through a published peer-reviewed paper. Groundwater recharge sources/origin and their mechanisms in the Komadugu-Yobe basin were identified (SO13) via stable isotope analysis of 240 groundwater samples collected in 2 sampling campaigns representing wet and dry seasons. Results analysis and interpretation highlighted that groundwater in the basin is recharged mainly through meteoric water with minimal evaporative enrichment in the Precambrian complex parts of the Komadugu-Yobe basin and shows some evaporative enrichment toward the downstream parts of the basin where the geology is Sedimentary quaternary formation. Areas such as Kamadugu-Yobe Valley, Hadejia-Nguru wetland, Chalawa Gorge dam, Tiga dam, KRIP, HVP and areas around Lake Chad were identified as the groundwater recharge origin in the study area. Furthermore, the spatial distribution and seasonal variability of isotopic signatures in the groundwater samples of the Komadugu-Yobe basin and the wider Sahel region were determined and discussed (SO14). These findings form the foundation for future research on nitrate and lead isotope studies. Finally, appropriate policy recommendations for an integrated management of transboundary water resources across the major basins in the Sahel region of West Africa were presented and discussed. It is strongly recommended that transboundary water resources across the Sahel region be monitored and managed regularly, and stringent policies and regulations should be established to prevent any water-related crises in the region which could arise as a result of mismanagement of shared water resources.

9 Discussion, Conclusion, and Recommendations

9.1 Introduction

This chapter presents a discussion of the key findings from the research titled Hydrogeochemistry and isotope hydrology of the Komadugu-Yobe Basin, Nigeria, Sahel region Africa. The thesis successfully fulfilled the main aim of the research to comprehensively assess groundwater resources in KYB and the wider Sahel to support integrated water resources management. This aim arose from an understanding that there is a significant data gap in the assessment of groundwater resources in the basin (as highlighted by the UN-IAEA RAF7021 African programme). Moreover, ongoing conflicts of the Boko Haram insurgency and the farmer-herder crisis coupled with rapid population growth and displaced populations hinder long-term regional groundwater data monitoring and assessment in the basin. The research aim was addressed through four research questions, which were explored through 14 specific research objectives (Figure 9.1), providing a comprehensive understanding of groundwater resources and generating a continuous regional dataset of groundwater stable isotopes in the KYB and the wider Sahel region.

This chapter discusses the results from each research chapter (chapters 5-8), highlighting the key findings and their implications for groundwater sustainability and integrated water resources management (IWRM) and how each research chapter achieved its individual research questions and specific objectives through an integrated discussion. Moreover, it presents the thesis contributions to global and regional knowledge, particularly in the context of Sustainable Development Goal 6 (SDG 6), and the limitations of the study. It concludes with recommendations for future research and practical applications to support sustainable groundwater management in the study region and the wider Sahel.

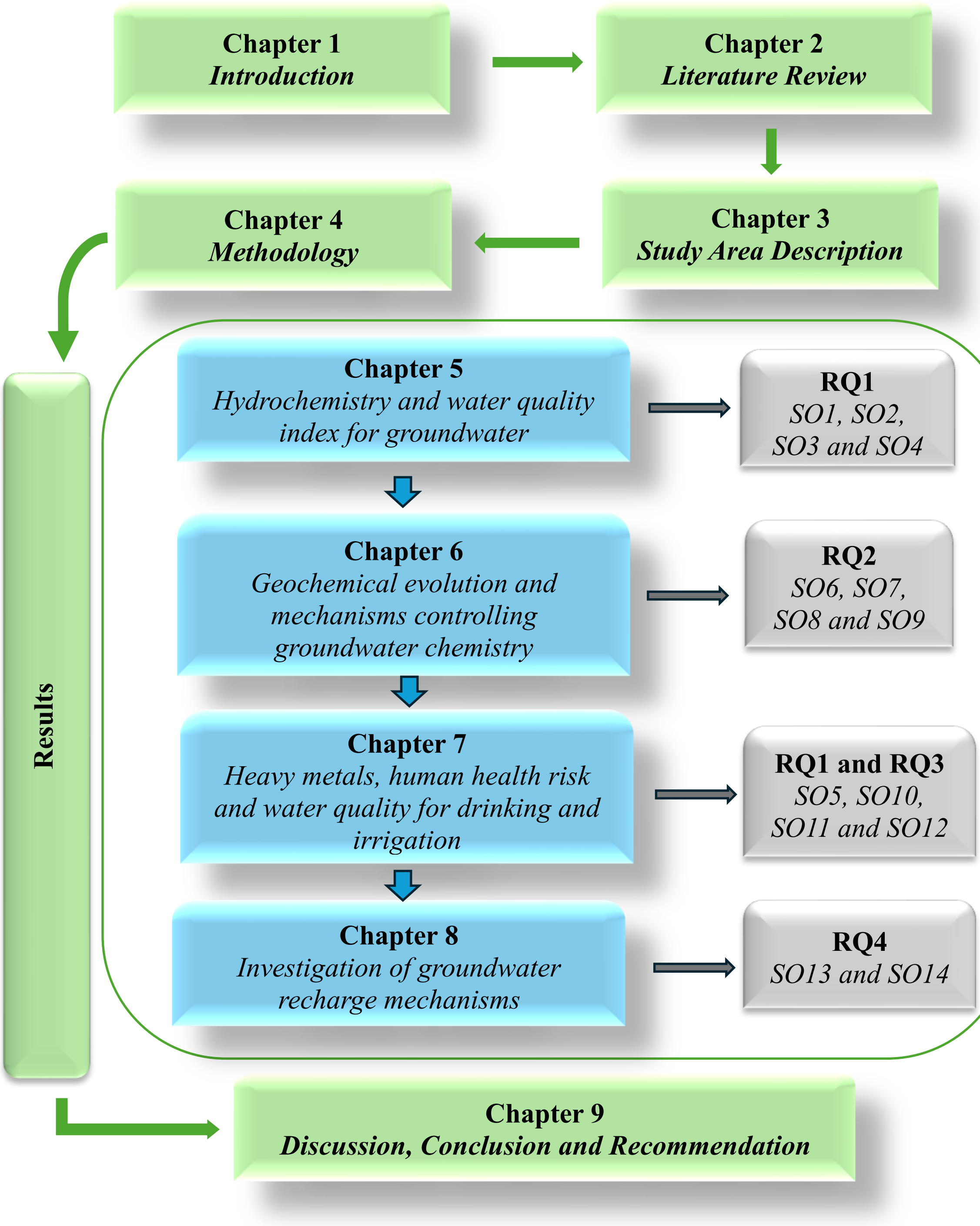


Figure 9.1 Flow diagram of the thesis structure highlighting the research questions and specific objectives addressed in each chapter.

9.2 Summary of Key Findings/Discussion

This thesis has provided invaluable insights into the hydrogeochemical characteristics and groundwater recharge mechanisms within the Komadugu-Yobe Basin, covering various aspects such as overall water quality, groundwater contamination sources, geochemical evolution, processes influencing groundwater chemistry, health risk assessment of heavy metals, and the origins of groundwater recharge. The key findings from each result chapter are discussed and interconnected to provide a comprehensive understanding of the groundwater resources in the basin:

- **Hydrogeochemical Characteristics and Groundwater Quality (Chapter 5)**: This chapter examined the hydrochemical characteristics of groundwater in the KYB and its suitability for drinking. The chapter answered RQ1. SO1 of RQ1 was achieved by comparing various groundwater quality parameters with World Health Organization guidelines for drinking water. The result revealed certain parameters exceeding World Health Organization (WHO, 2018) limits in specific areas. For example, high levels of NO_3 were observed to have exceeded the permissible limits in about 30 % of the groundwater samples indicating potential contamination from agricultural runoff and pit latrines posing serious public health risks mostly in the downstream sections. This calls for a comprehensive assessment of nitrate pollution using isotope tracers and other advanced methodologies. SO2 was fulfilled by performing groundwater quality index analysis to categorise the groundwater into various classes from excellent to unsuitable with 10 % of the groundwater exhibiting poor quality category. SO3 of RQ1 was achieved by employing a Piper diagram and Chadha plot which facilitated the classification of the groundwater into different facies. Most of the groundwater samples were classified as Ca-Mg-HCO_3 type which could be due to the dissolution of carbonate minerals, the presence of CO_2 in the soil water and specific groundwater recharge conditions. This calls for identifying the factors governing the chemistry of groundwater, pCO_2 modelling in groundwater, saturation index modelling and investigation of groundwater recharge (Chapters 6 and 8). The chapter also achieved SO4 of RQ1 by employing spatial analysis using ArcGIS 10.8 to establish the link between geology and water quality parameters. The variation in TDS and F suggested differences in geological formations in the basin. Moreover, TDS, F, Ca, Na and K dominated the Precambrian parts of the basin while the sedimentary parts displayed the presence of NO_3 and SO_4 contaminations. Finally, this chapter underscored the need for targeted interventions to address water quality challenges, particularly in areas with elevated F and NO_3 concentrations.

- **Geochemical Evolution and Mechanisms Controlling Groundwater Chemistry (Chapter 6):** This chapter has successfully addressed RQ2 by identifying the evolution of groundwater and modelling the dominant geochemical processes that control the chemistry of groundwater in the Komadugu-Yobe Basin. Gibbs diagrams, chemometric analysis, bivariate plots, evidential plots saturation indices and pCO_2 modelling demonstrated how geogenic processes (such as rock-water interaction/weathering, mineral dissolution and ion exchange) and anthropogenic processes (such as agricultural runoff, domestic sewage, industrial discharges and pit latrines) contributes to the chemical evolution of groundwater in the basin. The goal of this chapter was to gain an understanding of how geogenic and anthropogenic factors influence the geochemical evolution of groundwater in the aquifer systems to develop sustainable groundwater management strategies. This chapter achieved SO6 of RQ2 by identifying the main geochemical processes influencing groundwater chemistry in the Komadugu-Yobe Basin. Gibbs diagrams, bivariate plots and evidential plots identified rock-water interaction, mineral dissolution, ion exchange and evaporation as the processes controlling the groundwater chemistry. Rock weathering/rock-water interaction was identified as the dominant process influencing the groundwater chemistry indicating significant interaction between groundwater and geological formations followed by ion exchange in the Precambrian parts of the basin and evaporation mostly in the downstream parts of the basin signifying the influence of semi-arid to arid condition on shallow groundwaters. Saturation indices and pCO_2 modelling confirmed carbonate dissolution and silicate weathering and the presence of CO_2 in the plant root zones gravely contributes to high Ca, Mg, and HCO_3 ions in the groundwater. The chapter achieved SO7 of RQ2 by employing chemometric analysis incorporating correlation analysis, principal component analysis and hierarchical cluster analysis to identify the sources of chemical constituents present in the groundwater of the Komadugu-Yobe basin. The chemometric analysis revealed the influence of geogenic, and anthropogenic including agricultural activities and industrial, and evaporation processes on the groundwater quality. Elevated levels of Ca, Na, and Mg in the Precambrian basement parts resulted from geogenic influences from rock minerals weathering and dissolution of biotite, pyroxene, amphibole and Na and Mg feldspars. Regions close to agricultural and urban areas were found to be bedevilled with anthropogenic contamination as high concentrations of NO_3, SO_4 and Cl were observed which could be due to excessive synthetic fertilizer application in irrigated lands, improper waste disposal from homes and industries, and nitrification processes from pit latrines. The groundwater in the upstream parts of the basin is dominated by bicarbonate ions indicating freshly recharged groundwater and evolves as it moves downstream exhibiting high concentrations of calcium, sodium, sulfate and chloride due to water-rock interaction and cation exchange processes. SO8 was achieved by analysing wet and dry season groundwaters and juxtaposing their results. There was no significant difference between the chemistry of wet and dry seasons except that evaporation influence was observed in the downstream sections of the basin during the dry season. A conceptual model was developed to present the geochemical evolution and hydrochemical processes in aquifer systems in the basin thus achieving SO9 of RQ2. Insights from this chapter highlight the need for better pollution control measures and land-use management practices to mitigate the risks of contamination and ensure the long-term sustainability of groundwater resources, particularly in areas where anthropogenic activities are more prominent in the basin.

- **PTEs pollution and Human Health Risk Assessment (Chapter 7)**: This chapter addressed RQ1 and RQ3 by presenting a methodology that integrates chemometric analysis, geochemical modelling and index-based models to identify PTE pollution sources and their speciation and complexation as well as assessing the level of PTEs contamination and their associated human health risks and impacts on groundwater quality. The chapter achieved SO1 and SO5 of RQ1 by employing the irrigation water quality index, groundwater quality index, water pollution index, USSL diagram, Wilcox plot, Doneen's diagram and hydrochemical parameters to determine the suitability of irrigation water. GWQI and WPI revealed a significant number of the groundwater samples grouped into excellent classes dominated mostly in the Precambrian basement based on the GWQI and WPI analysis. However, some groundwaters mostly in the downstream parts of the basin were categorized as highly polluted due to various anthropogenic impacts thus achieving SO1. SO5 of RQ1 was fulfilled through comprehensive analysis of irrigation water quality index and hydrochemical parameters as well as USSL diagram, Wilcox plot, and Doneen's diagram indicating a significant percentage of the groundwater samples were grouped into moderate to high restriction zones with few samples in low and severe restriction zones related to irrigation.

Therefore, the use of this groundwater for irrigation should be done with caution and waters from high restriction zones should be applied on very high salt-tolerant crops with proper drainage systems. Furthermore, the chapter achieved SO10 by identifying the level of PTE contamination in the groundwater through the evaluation of an index-based model of PTEs such as Cdeg, HEI, HPI and mHPI. Pb, Cd, Mn and As were the prevalent contaminants concerning heavy metals with concentrations exceeding the World Health Organization's prescribed limit for drinking water (WHO, 2018). Cd, Pb and As could be influencing factors for CKDu in the basin. Elevated concentrations were observed in regions close to urban areas, industrial sites, agricultural lands, and waste disposal sites, indicating that anthropogenic activities were a major source of heavy metals pollution. Moreover, SO10 was fulfilled by performing correlation analysis, FA/PCA, and R-mode HCA on physicochemical parameters and various heavy metals which suggests that physicochemical parameters and PTEs likely have different geochemical behaviours and originated from distinct geogenic and anthropogenic sources. Similarly, PCA/FA and R-mode HCA highlighted the influence of mixed geogenic and anthropogenic processes from various domestic and industrial discharges, urban waste disposal, mining activities and agricultural practices as the responsible factors for high levels of PTEs in the groundwater. The groundwater was observed to be in oxidizing conditions and favour hematite formation, with some in reducing conditions capable of mobilizing metals. Arsenic predominantly exists in its oxidized form (As^{5+}), However, it existed in a few locations in reduced and toxic species such as As^{3+} probably in deep, and stagnant waters. Biogeochemical processes, including denitrification, are evident, with arsenic interacting with lead to form lead arsenate under oxidizing conditions. In a nutshell, As, Fe and NO_3 speciated to both free and toxic species in the groundwater and thus fulfilling SO11. SO12 of RQ3 was achieved by employing the human health risk assessment model proposed by the US Environmental Protection Agency (USEPA, 2014). The groundwater poses significant non-carcinogenic health risks, as the mean hazard index (HI) is above the threshold limit (>1) for both adults and children. Long-term exposure to this groundwater could result in adverse non-carcinogenic health effects like neurological damage and kidney failure particularly from PTEs like arsenic, cadmium, manganese, and lead. Adults are more susceptible due to longer exposure durations or physiological factors that make them more vulnerable to accumulating these toxic metals. Carcinogenic PTEs, such as As, Cd, Cr, Ni and Pb are present in the groundwater and long exposure to them could cause various types of cancers. The groundwater in the downstream areas is identified as particularly concerning for carcinogenic risks. This might be due to contamination sources upstream or geochemical processes that concentrate these harmful elements in the lower regions of the basin. Consequently, increased attention and potential intervention measures, such as implementation of better land use management practices, stricter enforcement of waste disposal regulations, smart agricultural practices, and prior water treatment with home filtration kit before consumption or alternative water sources, should be prioritized in these areas to mitigate potential long-term health impacts of PTEs contamination in groundwater.

- **Stable Isotopes Analysis for Groundwater Recharge Mechanism (Chapter 8)**: This is the final chapter of the result section and has successfully addressed RQ4. This chapter examined the role stable isotopic analysis can play in assessing groundwater recharge mechanisms in aquifer systems. The chapter employed stable isotopic signatures ($\delta^{18}O$ and $\delta^{2}H$) to analyze groundwater recharge mechanisms assess the impact of seasonal variability on recharge processes in the KYB and compare with the wider Sahel region. The groundwater stable isotopic dataset revealed distinct isotopic signatures that corresponded to local precipitation indicating that the groundwater across the basin is predominantly influenced by meteoric water. The groundwater was found to be more isotopically depleted (indicating recharge from higher altitudes or colder conditions) majorly in the upstream section of the basin, and the downstream areas exhibited enriched isotopic signatures, reflecting evaporative enrichment or interactive recharge process. The local meteoric water line for the transboundary Komadugu-Yobe basin was developed from 3 local and 4 regional GNIP stations: $\delta^{2}H = 6.7\ (\pm\ 0.1)\ \delta^{18}O + 4.1\ (\pm 0.4)$. The local and regional isotopic signatures in the basin varied significantly which was attributed to the impact of intertropical convergence zone (ITCZ) and changes in regional geography and or orography thus fulfilling SO13 of RQ4. The chapter achieved SO14 of RQ4 by comparing stable isotopic datasets from the wet and dry seasons, which revealed more or less significant seasonal variations in the isotopic signatures of the groundwater. Groundwater samples collected during the wet season showed lighter isotopic signatures, indicative of modern recharge from local rainfall. In contrast, samples from the dry season exhibited heavier isotopic signatures, which suggested either evaporative enrichment before infiltration or older groundwater being drawn from underground storages. The seasonal pattern in the basin confirmed that most groundwater recharges occurred during the months of peak rainfall, underscoring the importance of rainfall in the groundwater recharge mechanism in the Komadugu-Yobe basin. However, the presence of evaporation during the dry season and older groundwater recharges to deeper aquifers suggested that deeper aquifers may not be actively replenished at all times raising concern about the long-term sustainability of the basin’s groundwaters. Moreover, SO14 was also achieved by analysing the spatial distribution of isotopic signatures which confirmed the presence of altitude effects in the isotopic signatures of the groundwater. Samples from higher elevations exhibited lighter isotopic signatures (more depleted in $\delta^{18}O$ and $\delta^{2}H$), consistent with rainfall patterns at higher altitudes. However, groundwater from lower altitudes (downstream parts of the basin) and or near surface water bodies was isotopically heavier, reflecting the combined effects of evaporative enrichment and surface water interaction. The regional meteoric water line for the Sahel region was found to be $\delta^{2}H = 6.2 \pm (0.1)\ \delta^{18}O + (2.9 \pm 0.6)$. Groundwater recharges across the Sahel region occur during the months of heavy precipitation while the D-excess analysis across the region suggests that average precipitation in the entire Sahel region exhibits a general continental effect until the ITCZ meets the Congo Basin. The findings from this chapter highlighted the importance of rainfall in sustaining groundwater across the entire region, supporting the need for protecting recharge zones from anthropogenic pollution and over-exploitation and informing strategies for effective integrated water resources management among member states in the Sahel region.

9.3 Thesis Contribution to Knowledge/Novelty

This thesis provided significant contributions to both global and local understanding of groundwater systems, particularly in arid and semi-arid regions. These consist of:

Global Contribution/Novelty:

- The thesis has developed a methodological framework for integrating geochemical modelling, chemometric analysis, index-based models and stable isotopic analysis in groundwater resources assessment, which can be applied in similar regions around the world.
- The thesis enhanced global knowledge on the application of stable isotopes for understanding groundwater recharge mechanisms in regions affected by climate variability, anthropogenic pollution and over-dependence on groundwater.

- The thesis contributed to the understanding of heavy metal speciation and complexation in groundwater systems, which is crucial for addressing contamination from industrial and agricultural sources.
- The study filled a major gap in the Sahel region (as noted by the UN-IAEA RAF7021 African programme) and allows for a continuous dataset of groundwater stable isotopes across the Sahel region.
- The thesis has developed a unique methodology for groundwater sampling in the regions affected by insurgencies such as Boko Haram activities, ISWAP, banditry, and farmer-herder crisis.

Local Contribution/Novelty:

- The study is the first to provide a comprehensive assessment of groundwater quality, geochemical processes, and recharge mechanisms in the transboundary Komadugu-Yobe Basin in a more regional context.
- The thesis provided the first local meteoric water line in the transboundary Komadugu-Yobe basin and the first regional meteoric water line in the Sahel region of West Africa.
- The study provides a clear understanding of the hydrological cycle in the transboundary Komadugu-Yobe basin within the wider Sahel region, in Africa.
- This research fills a critical knowledge gap in characterizing the impact of human activities on groundwater quality and offers practical insights for sustainable groundwater management in the KYB.

9.4 Limitations of the Study

Despite the knowledge the study contributed, the study faced some limitations which involved the following aspects:

- Limited Sampling Timeframe: The study relied on a dataset collected over only two sampling campaigns, during one wet season and one dry season. This limited time frame may not fully capture the long-term variability in groundwater quality and isotopic signatures due to climate variability or inter-annual seasonal changes.
- Limited Access to Some Areas: Security challenges in some parts of the basin hinder physical accessibility to sample those locations, leading to gaps in spatial coverage. However, areas close to those locations were sampled which may not give a true representation. This may result in an incomplete representation of groundwater quality and recharge mechanisms across the entire basin.
- Sampling Density: The number of sampling points may not have been enough to conclude on the variations in groundwater chemistry across the basin, particularly in areas with hydrogeological heterogeneity such as Ringim, Jos, Gumau, Bauchi and Roni, despite efforts to ensure widespread sampling.
- Limited Isotopic Datasets: The study relied on secondary stable isotopic datasets for regional isotopic comparisons, which limits the accuracy of some isotopic analyses.
- Analytical Equipment Sensitivity: The detection limits or calibration precision of the equipment used such as ICP-OES, IC, and Picaro Isotope Analyser may affect the accuracy of some measurements, especially at very low or high concentrations of PTEs or stable isotope signatures.
- Modelling Assumptions: Geochemical models and stable isotopic interpretations rely on some assumptions about equilibrium and homogeneity of aquifer systems which may lead to uncertainties in result analysis.

9.5 Achieving SDG 6 in the Komadugu-Yobe Basin and the Entire Sahel Region: The Way Forward

Access to clean water and sanitation is a fundamental human right. The main aim of the study is to provide insights on groundwater resources that promote sustainable groundwater management and support integrated water resources management in the Komadugu-Yobe Basin and the wider Sahel region, ensuring reliable water quality and availability in the context of climate change, environmental factors and human activities. These aligned with the Sustainable Development Goal 6 (SDG 6), which aims to ensure the availability and sustainable management of water and sanitation for all by 2030 (UN, 2017). Achieving this goal in the transboundary Komadugu-Yobe Basin and the wider Sahel region, bedevilled with acute water scarcity and quality issues, requires a multifaceted approach that incorporates detailed groundwater assessment, state-of-art water management strategies, stringent regulations and policy interventions. Understanding the geochemical factors governing groundwater chemistry, combined with health risk assessments of heavy metal pollution and the recharge mechanisms influencing groundwater origin, is crucial for achieving sustainable groundwater management that supports Integrated Water Resources Management (IWRM) in transboundary basins. The findings from this thesis on the geochemical processes affecting groundwater chemistry, groundwater quality, contamination sources, human health risk assessments, and recharge mechanisms in the Komadugu-Yobe Basin alongside comparisons with the wider Sahel region have provided new insights and a comprehensive understanding of groundwater resources. This new knowledge was generated by successfully addressing the thesis aim through the fulfilment of various research questions and specific objectives and highlighting the urgent need for the way forward towards achieving SDG 6 in the Komadugu-Yobe basin and the wider Sahel region.

1. Ensuring Safe Drinking Water and Sanitation (SDG 6.1 and 6.2)

The findings from the study revealed that groundwater quality in the KYB is affected by pollution from domestic sewage, pit latrines and agricultural runoff which increases nitrate levels, particularly in the downstream section (chapter 6) as well as PTE pollution such as lead, nickel, arsenic, and cadmium (chapter 7). These contaminants pose significant human health risks as discussed in Chapter 7, especially in downstream communities that are solemnly dependent on groundwater for drinking purposes. To ensure safe drinking water in the Komadugu-Yobe Basin and the Sahel region, robust water quality monitoring systems and affordable treatment solutions, such as home filtration kits, and reverse osmosis techniques need to be established in the region. Moreover, the construction of improved sanitation infrastructures such as VIP toilets, ECOSAN toilets and landfills would help reduce groundwater contamination. Additionally, educating communities on proper sanitation and promoting the construction of improved waste disposal systems will reduce pollution and promote sustainable water management in the region thereby, moving the region closer to achieving SDG 6.

2. Improving Water Quality and Reducing Pollution (SDG 6.3)

The study identified key pollution sources, including agricultural runoff, industrial effluents, and poor waste management practices (chapters 6 and 7), which significantly contribute to the pollution of groundwater in the Komadugu-Yobe basin. The presence of these contaminants in the groundwater could pose health threats to the public emphasizing an urgent need to improve water quality across the region. To improve water quality in the Komadugu-Yobe Basin and Sahel region, stricter environmental regulations should be enforced to reduce pollution from agricultural chemicals and industrial effluents, encouraging sustainable agricultural practices like organic farming to reduce chemical into groundwater and drip irrigation to minimize water wastage and soil contamination, improving waste management, and engaging local communities in water conservation efforts. Community engagement is also essential for reducing pollution and ensuring sustainable water management. These measures will not only safeguard public health but also ensure sustainable water management in these vulnerable regions and hence will contribute toward achieving SDG 6.

3. Ensuring Sustainable Water Use and Reducing Water Stress (SDG 6.4)

Chapter 8 identified that groundwater in the KYB and the wider Sahel region is highly dependent on seasonal rainfall for recharge particularly during the months of peak rainfall, making the groundwater in the region vulnerable due to over-extraction, especially during dry seasons when there is no natural recharge process or is minimal and surface water is unavailable. Intensive irrigation farming, over-dependence on groundwater for domestic and drinking purposes and poor management practices have led to unsustainable groundwater use in the region. To achieve SDG 6.4, water-saving technologies like drip irrigation and rainwater harvesting, implementing strict groundwater regulation and management, protecting recharge zones like Hadejia Nguru wetlands, Hadejia Valley, Tiga and Challawa Dams, and forests, and sensitizing local communities on water resource management should be implemented. Farmers should be trained and supported with incentives to adopt advanced and smart agricultural technologies and artificial recharge methods such as managed aquifer recharge (MAR) should be implemented.

4. Integrated Water Resources Management (SDG 6.5)

The findings of the study highlighted that the groundwater systems in the KYB and Sahel are highly influenced by pollution from various geogenic and anthropogenic processes. The impact of agricultural runoff, industrial pollution, domestic sewage, population growth, over-exploitation and urban development has negatively influenced not only groundwater quality but its availability thus exacerbating the challenge of sustainable water management among different countries in the region. To achieve SDG 6.5 in the Komadugu-Yobe basin and the wider Sahel region, a holistic and coordinated approach to water management is highly needed. This involves collaboration among key stakeholders, such as government agencies, NGOs, local communities, and the private sector, to develop integrated water resources management plans. This plan should encourage research and data sharing, land-use planning, water resources management and building institution capacity.

9.6 Recommendations for Future Practice

This study provided valuable insights into various hydrogeochemical processes, general groundwater quality for drinking and irrigation, heavy metal contamination and its associated human health risk and groundwater recharge mechanisms in the Komadugu-Yobe Basin. To ensure sustainable groundwater management in the basin and the Sahel which are bedevilled with impacts of climate change, security issues and over-dependence on groundwater resources, the following recommendations for future practices are highly necessary:

- A robust and continuous groundwater quality monitoring program should be implemented across the transboundary Komadugu-Yobe Basin and the Sahel region, with regular long-term sampling focused on major ions, stable isotopes, radioisotopes, trace metals, and potential contaminants such as nitrates and PTEs, particularly in urban areas, recharge zones and areas with industrial or agricultural activities. This regular long-term sampling will facilitate the detection of any emerging contaminants such as lead, Arsenic, cadmium and nitrate which pose serious human health risks to the local population.
- Integrated Water Resources Management (IWRM) should be implemented in the transboundary Komadugu-Yobe Basin to promote coordinated development and management of water, land, and other related resources, involving stakeholders, local

communities, government authorities, and NGOs in decision-making processes. The study highlighted the complexity of groundwater systems and the impact of anthropogenic activities on water quality as well as over-exploitation and impacts of climate variability, underscoring the need for a collaborative and coordinated approach towards groundwater management.

- Land-use management practices should be implemented to protect critical groundwater recharge zones, particularly in areas with high infiltration rates around the vicinity of Hadejia-Nguru Wetlands and Komadugu-Yobe Valley which were identified as potential groundwater recharge zones through stable isotopic analysis. These areas are essential for maintaining aquifer recharge and should be safeguarded from deforestation, urban development, and industrial encroachment. The study showed that the groundwater in the basin gets recharged through local rainfall making it vital to prevent land degradation that could reduce infiltration.
- Community-based education and awareness initiatives as well as sensitization workshops should be introduced to enhance public understanding of groundwater availability/recharge mechanisms, contamination health risks, and sustainable water management practices. The study successfully identified various groundwater contamination sources, including anthropogenic factors such as agricultural runoff and improper waste disposal as well as geogenic processes such as mineral weathering and dissolution, ion exchange and evaporation, thus emphasizing the importance of public awareness of sustainable groundwater use and improve methods of waste disposal/management.
- This study identified high levels of PTEs, nitrates, and other contaminants in areas affected by industrial and agricultural activities, mining operations and urban development. Therefore, stricter pollution control measures and waste management

regulations should be enforced to reduce groundwater contamination in these areas. This includes regulating fertilizer and pesticide application in agricultural lands, enforcing effluent discharge rules for industries, implementing the polluter pay principle and developing waste treatment facilities to mitigate contamination risks.

- Water-saving technologies, such as smart irrigation systems and rainwater harvesting, should be encouraged in agriculture to reduce water consumption and reduce pressure on groundwater resources. The study indicated that extensive irrigation in the Kano River Irrigation Project (KRIP), Hadejia Valley Project (HVP), and Trimming irrigation projects as well as over-exploitation of groundwater have contributed to groundwater depletion and quality degradation in the basin. This prompted smart irrigation methods and efficient water conservation strategies that will help protect water resources and support sustainable farming.
- Regular health risk assessments should be conducted in areas where high levels of PTEs, nitrates, and other potential contaminants have been prominent in the groundwater. The study highlighted significant human health risks ranging from non-carcinogenic health risks to carcinogenic health risks from utilizing groundwater contaminated with PTEs like Pb, Cd, Mn, Ni, Cr, and As particularly in vulnerable communities around Gashua, Gaidam, Yusufari and Biomari axis. Therefore, regular groundwater assessments for PTEs and potential contaminants would provide an essential dataset for public health interventions and inform decisions on water treatment or alternative water sources.

9.7 Recommendations for Future Research

This study has successfully provided valuable and comprehensive insights into groundwater quality, contamination sources, hydrogeochemical processes, human health risks and recharge mechanisms in the transboundary Komadugu-Yobe basin. However, several research gaps and areas requiring further investigation have emerged. Therefore, to enhance the findings and ensure the sustainability of groundwater resources in the basin and the entire Sahel region, future research should focus on the following recommendations:

- Future research should prioritize long-term groundwater quality monitoring and trend analysis to identify seasonal and inter-annual variations and the potential impact of climate change on water chemistry, recharge, availability and contamination patterns. This study focussed on only single wet and dry seasons which limits its ability to identify long-term trends and the impact of climate change on the overall groundwater chemistry and distribution of contamination sources over the years as monitoring changes in major ions, PTEs and nitrates over time provides in-depth understanding of climate change variability, land use changes, and anthropogenic impacts. Therefore, future studies should focus on establishing observation wells to examine the impacts of these factors on groundwater quality and employ future climate scenarios on groundwater to forecast the impact of extreme events on groundwater quality and prevent potential contamination risks.
- Future research should focus on employing advanced geochemical models and simulation tools to better understand the complex relationship between groundwater, geology, and various contaminants in the Komadugu-Yobe Basin. This study employed various models such as Gibbs diagram, GWB workbench modelling, and Speciation modelling, to mention but a few and identified key hydrogeological processes in the basin. More advanced modelling tools such as reactive transport models and 3D simulation models should be employed in future research to have a deeper insight into contaminants transport through aquifer materials and their interactions with geological formations.

- Future research should focus on detailed hydrogeological characterization and aquifer mapping in the Komadugu-Yobe Basin to enhance understanding of groundwater flow characteristics, groundwater potential and groundwater recharge rates and zones. Although this study has identified key hydrological processes and groundwater recharge zones, a more detailed hydrogeological study using advanced geophysical tools is needed to determine groundwater storage capacity, recharge rates, aquifer yield, and groundwater flow characteristics which will support sustainable groundwater exploitation and management.
- Future research should focus on detailed speciation and bioavailability modelling of PTEs in groundwater, particularly in downstream parts of the basin that are severely contaminated by lead, arsenic, cadmium, and nitrate to understand their toxicity and mobility. Moreover, future studies should investigate PTE speciation using advanced methodologies and assess the bioavailability of PTEs in vegetable plants to develop effective remediation strategies such as phytoremediation, natural adsorbents, and activated carbon.
- Future research should encourage the use of both environmentally stable and radioactive isotopes, such as tritium (^{3}H) and carbon-14 (^{14}C), for groundwater age dating and an in-depth understanding of recharge mechanisms. This study employed stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) to analyse groundwater recharge mechanisms. Hence, incorporating radioactive isotopes would provide more insights into groundwater residence time and its sustainability which would help in identifying modern, older, renewable and non-renewable groundwater resources.

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Appendix A: Supplementary Materials for Paper 2: Geochemical Evolution and Mechanisms Controlling Groundwater Chemistry in the Transboundary Komadugu–Yobe Basin, Lake Chad Region: An Integrated Approach of Chemometric Analysis and Geochemical Modelling.

Table SM6.1 Pearson's correlation analysis results of hydrochemical parameters of wet season.

Parameters	pH	EC	TH	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO^-_3	SO_4^{2-}	NO_3^-	F^-	Fe
pH	1.00												
EC	0.04	1.00											
TH	0.17	**0.82**	1.00										
Na^+	0.06	**0.81**	**0.70**	1.00									
K^+	–0.04	0.41	0.36	0.35	1.00								
Ca^{2+}	0.17	**0.81**	**0.98**	**0.69**	0.37	1.00							
Mg^{2+}	0.13	**0.73**	**0.92**	**0.63**	0.30	**0.83**	1.00						
Cl^-	0.05	**0.83**	**0.79**	**0.93**	0.41	**0.79**	**0.70**	1.00					
HCO_3^-	0.20	**0.61**	**0.77**	**0.59**	0.24	**0.75**	**0.71**	**0.52**	1.00				
SO_4^{2-}	0.11	**0.73**	**0.67**	**0.73**	0.47	**0.68**	**0.55**	**0.69**	**0.57**	1.00			
NO_3^-	–0.12	0.37	0.45	0.16	0.43	0.43	0.44	0.28	0.02	0.25	1.00		
F^-	0.15	0.33	0.41	0.37	0.10	0.40	0.39	0.27	**0.57**	**0.53**	0.01	1.00	
Fe	0.07	–0.16	–0.18	–0.13	–0.12	–0.18	–0.14	–0.11	–0.18	–0.16	–0.17	–0.12	1.00

Table SM6.2 Pearson's correlation analysis results hydrochemical parameters of dry Season.

Parameter	pH	EC	TH	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO^-_3	SO_4^{2-}	NO_3^-	F^-	Fe
pH	1.00												
EC	0.25	1.00											
TH	0.21	**0.70**	1.00										
Na^+	0.17	**0.72**	**0.81**	1.00									
K^+	0.09	0.47	**0.61**	0.39	1.00								
Ca^{2+}	0.22	**0.71**	**0.99**	**0.82**	**0.62**	1.00							
Mg^{2+}	0.19	**0.60**	**0.93**	**0.71**	**0.53**	**0.89**	1.00						
Cl^-	0.11	**0.74**	**0.92**	**0.89**	**0.62**	**0.93**	**0.82**	1.00					
HCO_3^-	0.38	0.29	0.40	0.33	0.01	0.37	0.43	0.26	1.00				
SO_4^{2-}	0.26	**0.67**	**0.84**	**0.76**	**0.67**	**0.86**	**0.71**	**0.79**	0.25	1.00			
NO_3^-	0.06	**0.60**	**0.90**	**0.77**	**0.64**	**0.89**	**0.86**	**0.84**	0.10	**0.79**	1.00		
F^-	0.08	–0.03	–0.02	0.08	–0.07	–0.02	–0.03	–0.04	0.25	0.09	–0.08	1.00	
Fe	0.06	–0.13	–0.10	–0.12	–0.08	–0.10	–0.09	–0.09	–0.08	–0.09	–0.10	–0.07	1.00

Table SM6.3 HCA result of groundwater quality parameters.

Cluster	Chemical Parameters	
	Wet Season	Dry Season
I	EC, TH, Na$^+$, Ca^{2+}, Mg^{2+}, Cl$^-$, HCO$^-_3$, SO$_4^{2-}$, F$^-$	EC, TH, Na$^+$, Ca^{2+}, Mg^{2+}, Cl$^-$, SO$_4^{2-}$, NO$_3^-$
II	K$^+$, NO$_3^-$	K$^+$
III	pH, Fe	pH, HCO$^-_3$, F$^-$, Fe

Table SM6.4 HCA results of groundwater samples.

Cluster	Sampling Location	
	Wet Season	Dry Season
	61, 92, 103, 16, 93, 89, 67, 83, 50, 49, 34, 30, 82, 11, 69, 22, 15, 14, 12, 8, 108, 39, 116, 88, 113, 112, 105, 40, 107, 87, 57, 60, 100, 35, 98, 97, 91, 118, 117, 33, 99, 102, 70, 59, 90, 13, 109, 21, 18, 9, 75, 52, 23, 19, 28, 7	1, 62, 6, 25,115, 77, 94, 12, 36, 24, 64, 95, 17, 84, 55,66, 2, 56, 61, 107, 39, 88, 92, 108, 69, 97, 96, 30, 34, 49, 33, 117, 118, 67, 83, 82, 87, 93,89, 7, 21, 23, 8, 40, 14, 35, 15, 22, 11, 20, 50, 60, 100, 59, 105, 112, 116, 9, 18, 57, 119, 113, 13, 16, 52, 102, 103
II	114, 111, 119, 43, 106, 73, 79, 96, 46, 29, 54, 104, 45, 110, 80, 85, 71, 28, 72, 51, 76, 53, 56, 41, 5, 2, 66, 55, 84, 81, 48, 10, 77, 64, 68, 47, 115, 95, 36, 74, 62, 78, 24, 94, 6, 65, 26, 17, 44, 42, 86, 58, 120, 101, 25, 63, 1	3, 71, 76, 80, 110, 99, 73, 90, 85, 104, 51, 111, 114, 72, 81, 78, 70, 106, 109, 75, 91, 98, 5, 41, 28, 47, 54, 19, 29, 46, 43, 45, 10, 26, 42, 27, 63, 44, 53, 48, 79, 101, 58, 86, 120, 65, 68, 74
III	3, 4, 38, 31, 32, 27, 37	4, 37, 31, 38, 32

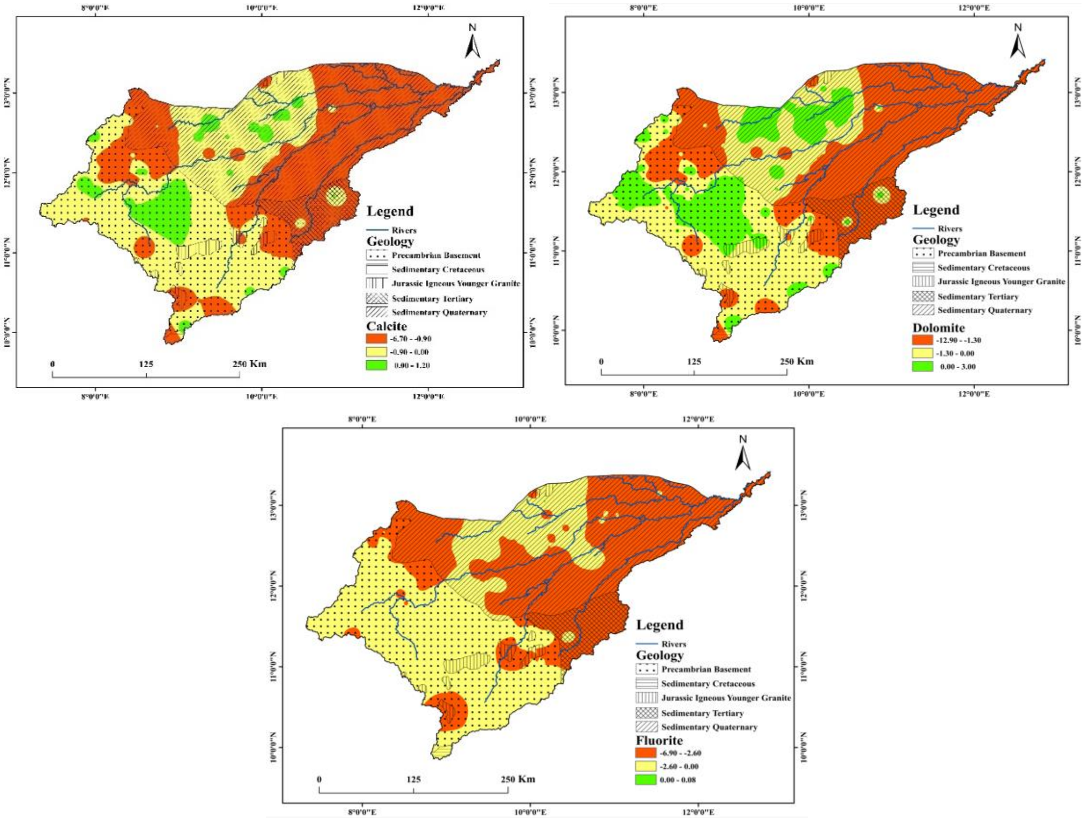

Figure SM6.1 Spatial distribution of saturation indices some selected minerals related to geology and electrical conductivity of wet season groundwater samples.

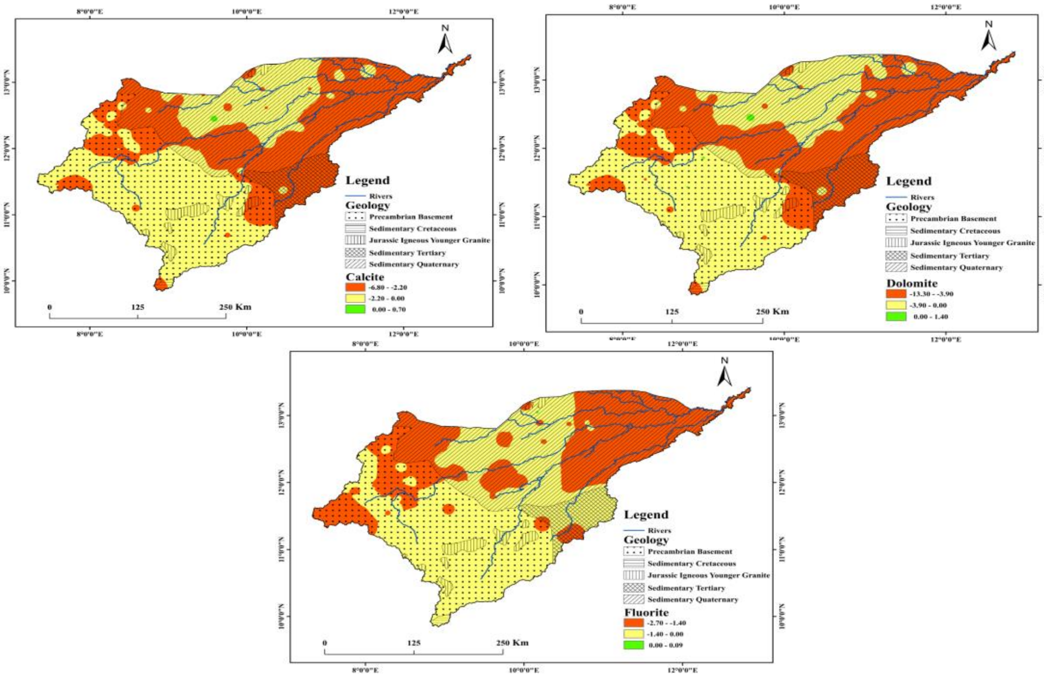

Figure SM6.2 Spatial distribution of saturation indices of some selected minerals related to geology and electrical conductivity of dry season groundwater samples.

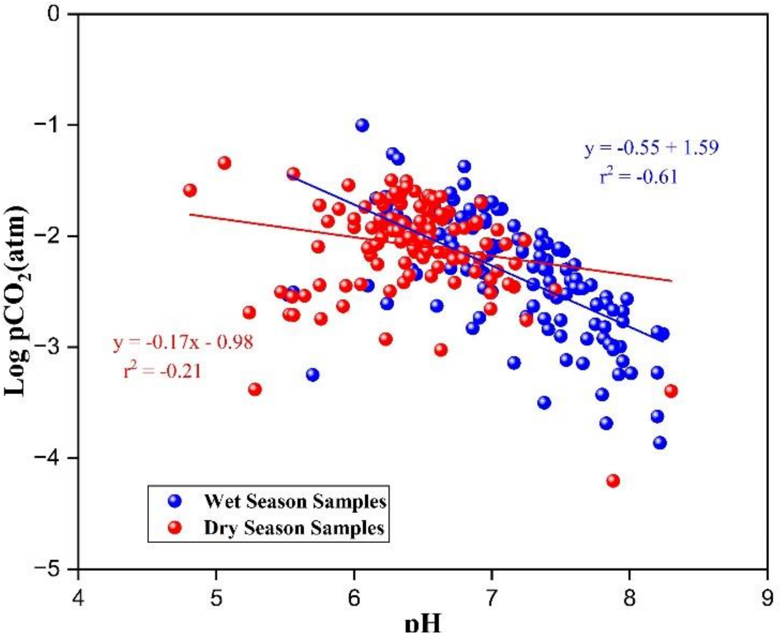

Figure SM6.3 Geochemical relationship between log (pCO_2) vs. pH.

Appendix B: Supplementary Materials for Paper 3: Heavy metals pollution source identification and associated health risk in the groundwater of Komadugu-Yobe basin, Lake Chad region: An integrated approach using chemometric analysis and index-based techniques

Table SM7.1 Heavy metals pollution and health risk assessment ranking criteria (Abba et al., 2024; Dash et al., 2019; Egbueri, 2020; Egbueri et al., 2020; Khan & Umar, 2024; Noor et al., 2024; Sheng et al., 2022; USEPA, 2014; USEPA, 2015).

Method	Pollution or risk level	Classification	Value range
Contamination degree (Cdeg)	Low pollution	I	$CD < 6$
	Moderate pollution	II	$6 \leq CD < 12$
	Considerable pollution	III	$12 \leq CD < 24$
	Very high pollution	IV	$CD \geq 24$
Heavy metal evaluation index (HEI)	Low pollution	I	<10
	Moderate pollution	II	$10 < HEI <2\ 0$
	High pollution	III	> 20
Heavy metal pollution index (HPI)	Low pollution	I	$HPI < 15$
	Moderate pollution	II	$15 \leq HPI \leq 30$
	Moderate-to-heavy pollution	III	$30 < HPI \leq 100$
	Heavy pollution	IV	$HPI > 100$
Modified heavy metal pollution index (mHPI)	Excellent	I	< 50
	Good	II	50 - 100
	Poor	III	100 - 200
	Very poor	IV	200 - 300
	Unsuitable	V	> 300
Cancer risk (CR)	Very low risk	I	$CR \leq 1\times10^{-6}$
	Low risk	II	$1\times10^{-6} < CR \leq 1\times10^{-4}$
	Moderate risk	III	$1\times10^{-4} < CR \leq 1\times10^{-3}$
	High risk	IV	$1\times10^{-3} < CR \leq 0.1$
	Very high risk	V	$CR > 0.1$

Table SM7.2 Ranking criterion of groundwater quality index.

Range of GWQI	Class of water	Wet season		Dry season	
		# samples	% of samples	# samples	% of samples
<50	Excellent	79	65.8	85	70.8
50–100	Good	28	23.3	22	18.3
100–200	Poor	9	7.5	8	6.7
200–300	Very Poor	3	2.5	5	4.2
>300	Unsuitable	1	0.8	0	0
	Total	120	100	120	100

Table SM7.3 Relative weight of irrigation water quality parameters (Abbasnia et al., 2018; Hussein et al., 2024).

Parameters	wi
EC	0.211
Na	0.204
HCO_3	0.202
CL	0.194
SAR	0.189
Total	1

Table SM7.4 The irrigation water quality limiting parameter values (Batarseh et al., 2021).

qi	EC (s/cm	SAR (meq/L) ^0.5	Na (meq/L)	Cl (meq/L)	HCO_3 (meq/L)
85-100	200-750	2-3	2-3	1-4	1-1.5
60-85	750-1500	3-6	3-6	4-7	1.5-4.5
35-60	1500-3000	6-12	6-9	7-10	4.5-8.5
0-35	200<EC≥3000	2<SAR≥12	2<Na≥9	1<Cl≥10	1<HCO3≥8.5

Table SM7.5 Detailed description of input parameters for the human health risk assessments (Barkat et al., 2023; Chen et al., 2023; Jabbo et al., 2022; Liang et al., 2023; USEPA, 2014).

Input parameters for health risk analysis	Unit	Value	
		Adult	Children
Ci	µg/L	Observed value	Observed value
Ingestion rate of water (IR)	L/day	2	1
Exposure duration (ED)	year	30	6
Exposure frequency (EF)	days/Year	365	365
Body weight (BW)	Kg	70	35
Average exposure time (AT) (Non-Cancer)	day	ED×365	ED×365
Average exposure time (AT) (Cancer)	day	70×365	70×365
Exposed skin surface area (SA)	cm^2	18000	6600
Exposure time (ET)	hr/day	1	0.58
Conversion factor (CF)	L/cm^3	1.0×10^{-3}	1.0×10^{-3}

Table SM7.6 The reference dose (RfD, µg/kg/day), slope factor (SF, µg/kg/day) and permeability constant (K_P) of heavy metals through ingestion and dermal contact (Liang et al., 2023; Noor et al., 2024; USEPA, 2014; Wang et al., 2025).

Parameter	$RfD_{ingestion}$(µg/kg/day)	RfD_{dermal}(µg/kg/day)	$SF_{ingestion}$(µg/kg/day)$^{-1}$	SF_{dermal}(µg/kg/day)$^{-1}$	K_P(cm/h)
As	0.3	0.123	1.5×10^{-3}	3.66×10^{-3}	1×10^{-4}
Fe	300	45	-	-	1×10^{-3}
Cd	0.5	0.005	6.10×10^{-3}	3.80×10^{-4}	1×10^{-3}
Co	0.3	16	-	-	4×10^{-3}
Cu	40	12	-	-	1×10^{-4}
Cr	3	0.015	5.0×10^{-4}	1.32×10^{-4}	2×10^{-4}
Mn	20	0.8	-	-	1×10^{-3}
Ni	20	5.4	8.40×10^{-4}	6.40×10^{-4}	2×10^{-4}
Pb	1.4	0.42	8.50×10^{-3}	7.30×10^{-3}	1×10^{-3}
Zn	300	60	-	-	6×10^{-3}

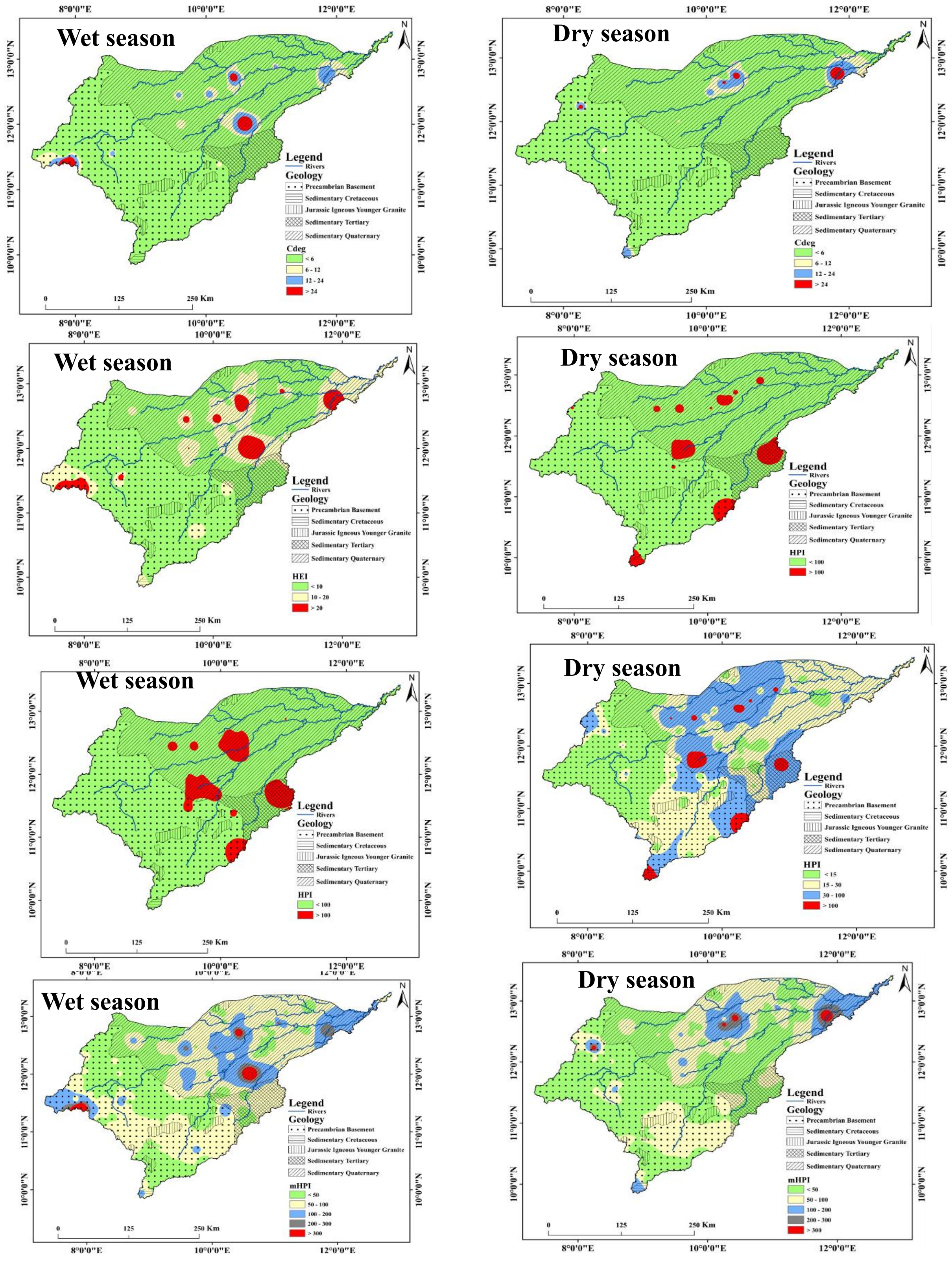

Figure SM7.1 Spatial distribution of trace elements pollution indices.

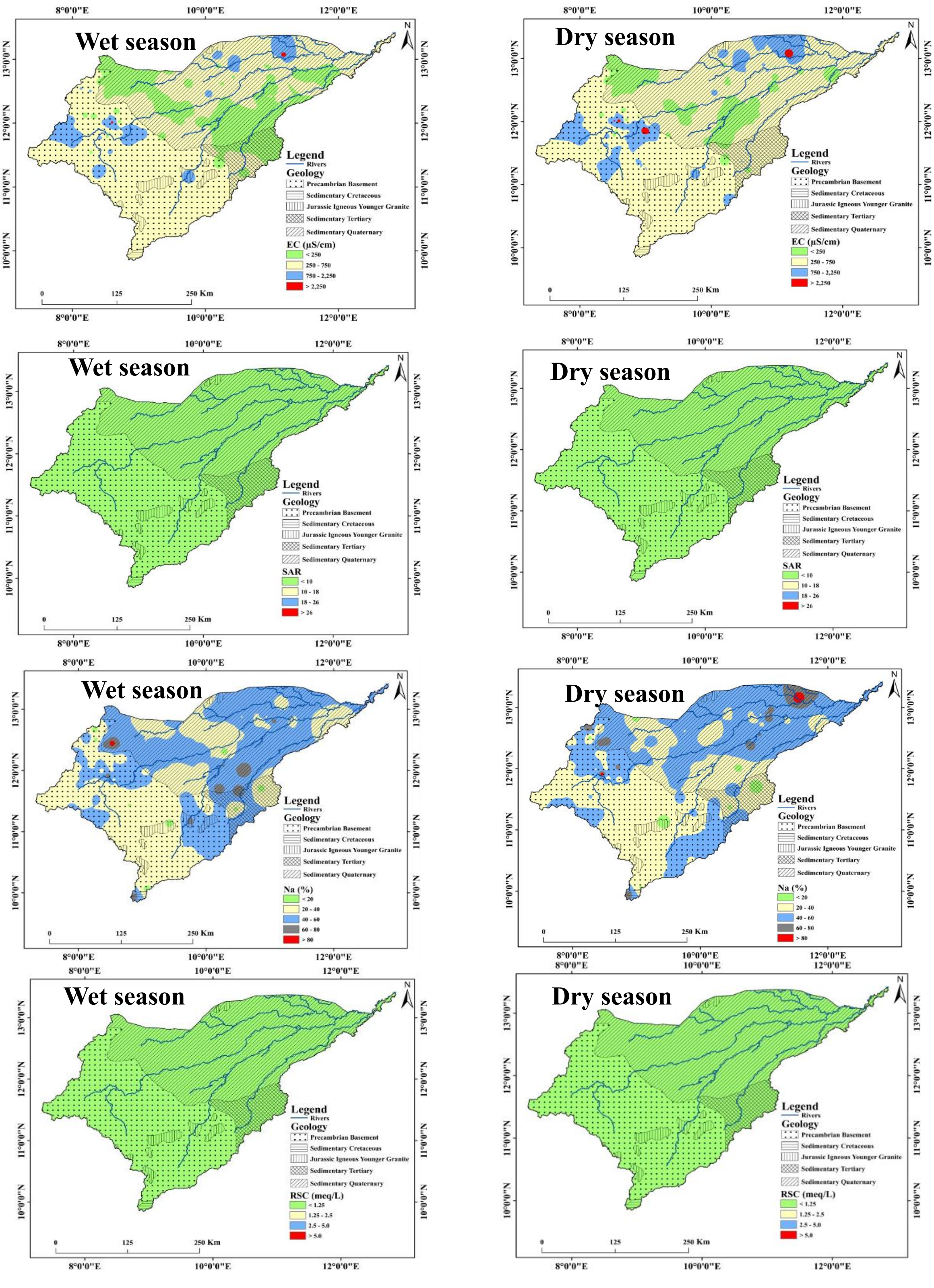

Figure SM7.2 Spatial distribution of irrigation water quality parameters.

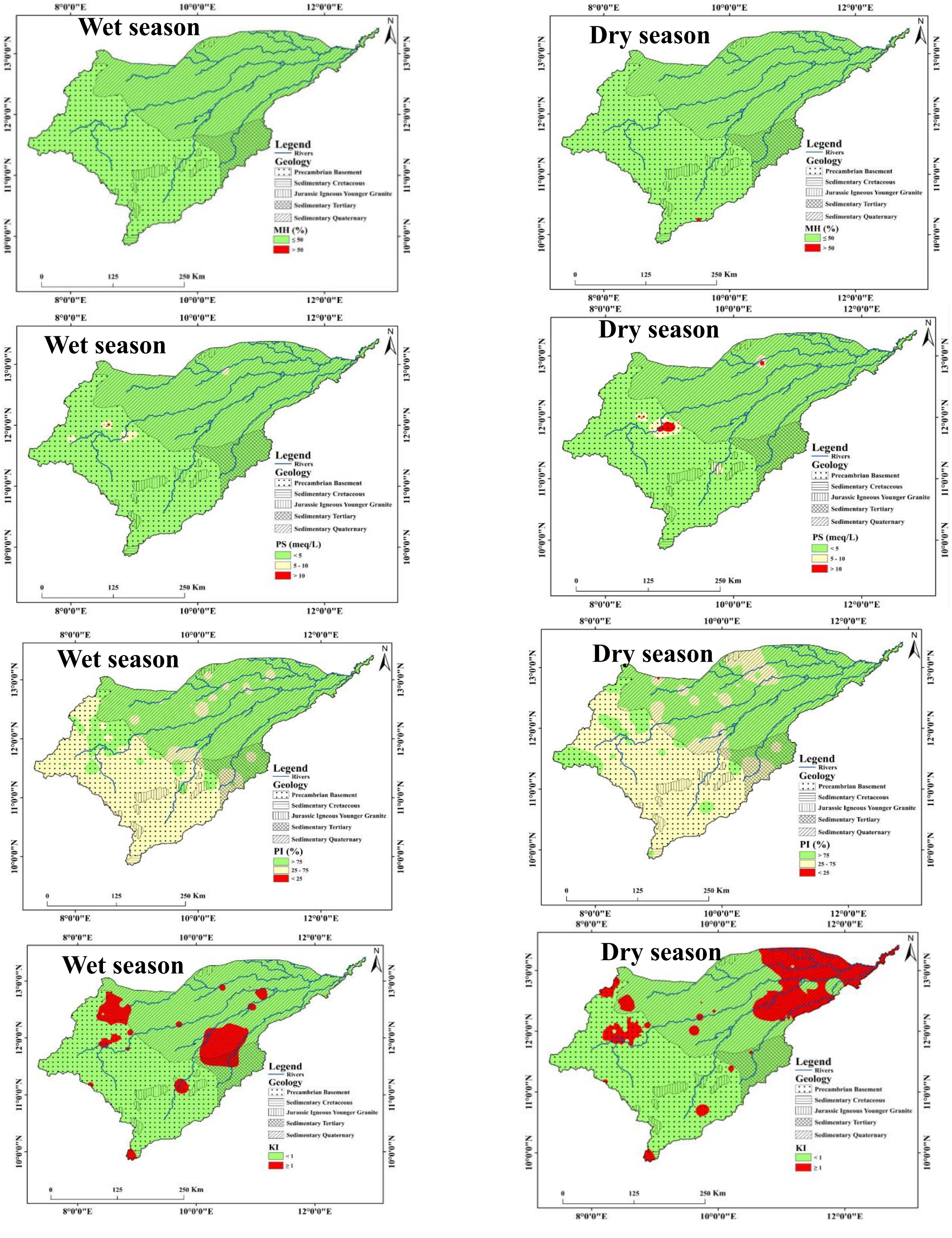

Figure SM7.3 Spatial distribution of irrigation water quality parameters.

Table SM7.7 Irrigation water quality indices.

Criteria	Unit	Range	Classification	Wet season		Dry season	
				# samples	% samples	# samples	% samples
EC		<250	Excellent	50	14.2	38	31.7
		250 - 750	Good	51	42.5	60	50.0
		750 - 2250	Fair/ Medium	17	41.7	18	15.0
		>2250	Poor	2	1.7	4	3.3
SAR		<10	Excellent	120	100.0	120	100.0
		10 to 18	Good	-	-	-	-
		19-26	Poor	-	-	-	-
		>26	Unsuitable	-	-	-	-
Na %	%	<20	Excellent	9	7.5	8	6.7
		20- 40	Good	54	45.0	52	43.3
		40 - 60	Permissible	46	38.3	47	39.2
		60 - 80	Doubtful	10	8.3	10	8.3
		> 80	Unsuitable	1	0.8	3	2.5
RSC	meq/ L	< 1.25	Safe	118	98.3	120	100.0
		1.25 - 2.5	Marginally suitable	2	1.7	-	-
		2.5 - 5	Unsuitable	-	-	-	-
		>5	Harmful	-	-	-	-
PS		<5	Excellent to good	114	95.0	112	93.3
		5 to 10	Good to injurious	4	3.3	3	2.5
		>10	Injurious to unsatisfactory	2	1.7	5	4.2
MH	%	<50	Suitable	120	100.0	119	99.2
		>50	Unsuitable			1	0.8
PI	%	>75	Highly suitable	62	51.7	57	47.5
		25-75	Moderately suitable	58	48.3	62	51.7
		<25	Unsuitable	-	-	1	0.8
KI		<1	Acceptable	101	84.2	98	81.7
		≥1	Unacceptable	19	15.8	22	18.3
IWQI		85 - 100	Excellent	-	-	1	0.8
		70 - 85	Very good	3	2.5	3	2.5
		55- 70	good	45	37.5	48	40.0
		40 - 55	Satisfactory	68	56.7	61	50.8
		0 - 40	Unsuitable	4	3.3	7	5.8

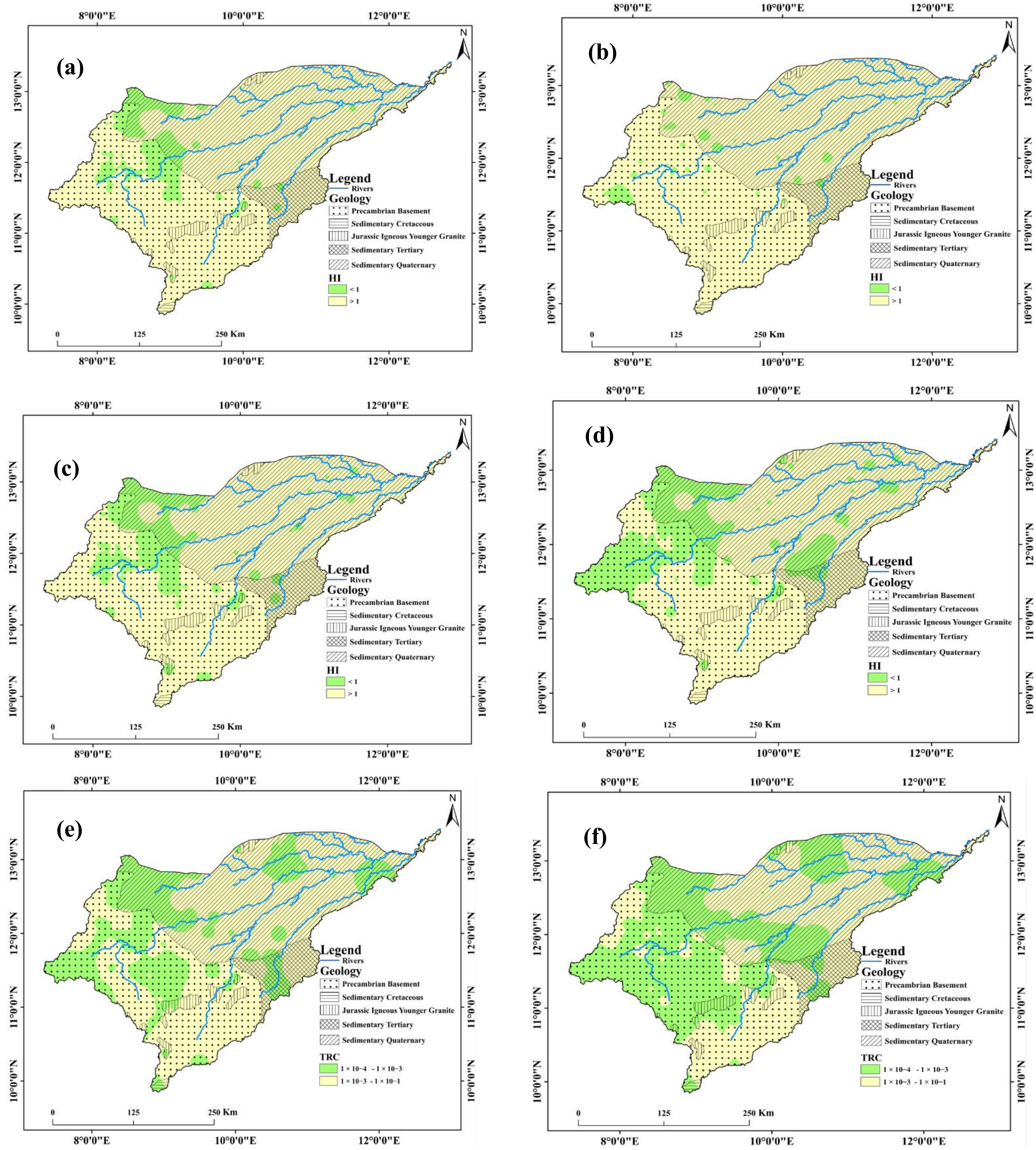

Figure SM7.4 Spatial distribution of (a) non carcinogenic health risk for adults during wet season (b) non carcinogenic health risk for adults during dry season (c) non carcinogenic health risk fir children during wet season (d) non carcinogenic health risk for children during dry season (e) total carcinogenic health risk for adult during wet season (f) total carcinogenic health risk for adults during dry season.

Table SM7.8 Descriptive statistics of HI and TCR for adults and children in wet and dry season.

	Wet season				Dry season			
	HI_{adults}	$HI_{children}$	TCR_{adults}	$TCR_{children}$	HI_{adults}	$HI_{children}$	TCR_{adults}	$TCR_{children}$
Min	0.8	0.8	6.1×10^{-4}	1.2×10^{-4}	0.9	0.8	6.1×10^{-4}	1.2×10^{-4}
Max	4.9	4.9	3.8×10^{-3}	7.6×10^{-4}	5.3	4.8	3.4×10^{-3}	6.8×10^{-4}
Mean	1.4	1.3	1.1×10^{-3}	2.2×10^{-4}	1.4	1.2	1.0×10^{-3}	2.0×10^{-4}
Stdv	0.9	0.8	5.3×10^{-4}	1.1×10^{-4}	0.8	0.7	3.9×10^{-4}	8.0×10^{-5}

Table SM7.9 Correlation matrix of wet season groundwater quality parameters.

Parameter	pH	EC	Eh	DO	Na	K	Ca	Mg	Cl	HCO$_3$	SO$_4$	NO$_3$	F	Fe	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
pH	1																						
EC	0.04	1																					
Eh	0.04	0.22	1																				
DO	-0.25	-0.05	-0.06	1																			
Na	0.06	0.81	0.20	-0.03	1																		
K	-0.04	0.41	0.20	-0.09	0.35	1																	
Ca	0.17	0.81	0.19	-0.18	0.69	0.37	1																
Mg	0.13	0.73	0.19	-0.12	0.63	0.30	0.83	1															
Cl	0.05	0.83	0.20	-0.04	0.93	0.41	0.79	0.70	1														
HCO$_3$	0.20	0.61	0.12	-0.16	0.59	0.24	0.75	0.71	0.52	1													
SO$_4$	0.11	0.73	0.20	-0.04	0.73	0.47	0.68	0.55	0.69	0.57	1												
NO$_3$	-0.12	0.37	0.18	-0.11	0.16	0.43	0.43	0.44	0.28	0.02	0.25	1											
F	0.15	0.33	0.07	-0.16	0.37	0.10	0.40	0.39	0.27	0.58	0.53	0.01	1										
Fe	0.07	-0.16	-0.65	0.14	-0.13	-0.12	-0.18	-0.14	-0.11	-0.18	-0.16	-0.17	-0.12	1									
As	-0.03	-0.02	-0.10	0.08	0.01	-0.07	-0.01	-0.03	-0.06	0.13	-0.04	-0.08	0.17	0.02	1								
Cd	0.19	-0.07	-0.07	-0.17	-0.08	0.01	0.02	-0.09	-0.09	-0.07	-0.09	0.09	-0.07	0.00	-0.04	1							
Co	-0.16	0.13	0.01	0.02	0.17	0.22	0.11	0.12	0.12	0.24	0.08	-0.02	0.03	0.01	-0.01	0.11	1						
Cr	-0.21	-0.05	0.03	0.23	-0.06	-0.06	-0.12	-0.13	-0.10	-0.06	-0.04	-0.11	-0.13	-0.05	-0.03	-0.06	-0.03	1					
Cu	-0.29	-0.01	0.11	-0.12	0.01	0.06	-0.08	-0.07	0.03	-0.15	-0.03	0.01	-0.06	-0.08	-0.04	-0.04	-0.05	-0.06	1				
Mn	0.11	0.22	-0.04	-0.14	0.22	0.08	0.32	0.24	0.22	0.26	0.17	0.05	0.10	0.09	-0.03	0.04	0.26	-0.07	-0.08	1			
Ni	-0.09	0.04	-0.17	0.13	0.07	0.13	0.02	0.08	0.11	0.03	-0.03	-0.01	-0.05	0.48	-0.03	-0.04	0.55	-0.04	-0.04	0.12	1		
Pb	-0.06	0.01	-0.15	-0.08	0.05	-0.10	0.00	-0.01	0.00	0.13	0.10	-0.16	0.18	-0.05	0.01	-0.02	0.09	0.00	0.15	-0.07	0.0002	1	
Zn	0.06	-0.06	-0.07	0.06	-0.12	-0.09	-0.02	0.03	-0.10	0.03	-0.04	-0.05	0.09	0.08	-0.03	0.05	-0.07	-0.12	0.11	0.02	0.13	0.01	1

Table SM7.10 Correlation matrix of dry season groundwater quality parameters.

Parameter	pH	EC	Eh	DO	Na	K	Ca	Mg	Cl	HCO_3	SO_4	NO_3	F	Fe	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
pH	1																						
EC	0.25	1																					
Eh	-0.17	0.16	1																				
DO	0.00	0.00	0.08	1																			
Na	0.17	0.72	0.16	0.01	1																		
K	0.09	0.47	0.13	-0.05	0.39	1																	
Ca	0.22	0.71	0.12	-0.08	0.82	0.62	1																
Mg	0.19	0.60	0.05	-0.15	0.71	0.53	0.89	1															
Cl	0.11	0.74	0.13	-0.04	0.89	0.62	0.93	0.82	1														
HCO_3	0.38	0.29	-0.06	-0.26	0.33	0.01	0.37	0.43	0.26	1													
SO_4	0.26	0.67	0.14	0.01	0.76	0.67	0.86	0.71	0.79	0.25	1												
NO_3	0.06	0.60	0.16	-0.03	0.77	0.64	0.89	0.86	0.84	0.10	0.79	1											
F	0.36	0.22	0.01	-0.12	0.33	0.07	0.23	0.21	0.19	0.48	0.39	0.09	1										
Fe	0.06	-0.13	-0.74	0.01	-0.12	-0.08	-0.10	-0.09	-0.09	-0.09	-0.09	-0.10	-0.09	1									
As	0.14	-0.05	-0.14	-0.15	-0.04	-0.02	-0.01	0.00	-0.04	0.17	-0.05	-0.05	0.03	0.22	1								
Cd	0.02	-0.05	-0.09	-0.16	-0.08	-0.06	-0.05	-0.08	-0.08	0.05	-0.09	-0.05	0.00	0.12	0.16	1							
Co	-0.11	0.08	0.06	-0.04	0.17	0.02	0.02	0.04	0.09	-0.06	0.02	0.10	-0.05	-0.02	-0.01	0.02	1						
Cr	0.05	-0.03	-0.01	0.25	-0.09	-0.05	-0.10	-0.11	-0.10	-0.10	-0.05	-0.08	-0.11	0.07	-0.03	-0.06	-0.03	1					
Cu	-0.22	0.14	0.19	-0.07	0.21	0.20	0.15	0.07	0.20	-0.08	0.11	0.17	-0.08	-0.10	-0.04	-0.11	-0.06	-0.07	1				
Mn	0.04	0.17	-0.04	-0.11	0.26	0.04	0.22	0.16	0.21	0.12	0.19	0.18	0.05	0.13	-0.02	0.03	0.28	0.00	-0.04	1			
Ni	-0.20	0.13	0.05	0.04	0.09	0.04	0.00	0.03	0.12	-0.12	-0.02	0.00	-0.10	-0.07	-0.01	-0.08	0.20	-0.02	0.13	-0.06	1		
Pb	0.05	0.07	-0.08	-0.04	0.09	-0.07	0.00	0.03	0.05	0.07	0.01	-0.02	0.12	-0.04	-0.01	-0.07	-0.07	0.02	0.07	-0.14	0.22	1	
Zn	-0.05	0.09	-0.08	-0.07	0.04	0.10	0.02	0.14	0.09	0.005	-0.04	0.05	0.01	-0.02	0.00	0.00	-0.02	-0.06	0.15	-0.02	0.35	0.09	1

Table SM7.11 Factor loadings for wet and dry season groundwater samples.

Parameter	Wet Season								Dry Season					
	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC1	PC2	PC3	PC4	PC5	PC6
pH	0.14	0.03	**-0.68**	-0.30	-0.25	0.07	-0.02	-0.19	0.24	**0.60**	-0.28	-0.07	0.26	0.12
EC	**0.89**	0.00	0.12	0.05	-0.08	-0.11	-0.08	-0.02	**0.79**	-0.03	-0.01	0.03	0.09	0.13
Eh	0.29	**-0.63**	0.20	-0.08	0.06	0.31	0.35	-0.20	0.18	**-0.60**	**-0.59**	-0.04	-0.27	0.03
DO	-0.16	0.18	**0.41**	**0.42**	-0.40	-0.10	0.25	-0.09	-0.09	-0.27	-0.02	**-0.46**	**0.51**	0.23
Na	**0.86**	0.06	0.09	0.18	-0.04	-0.03	-0.16	-0.08	**0.89**	-0.02	0.02	0.01	0.00	0.18
K	**0.50**	-0.04	0.37	-0.29	0.08	-0.01	0.00	0.23	**0.66**	-0.17	0.15	-0.10	0.06	-0.32
Ca	**0.91**	0.02	-0.08	-0.09	-0.07	-0.05	-0.01	0.01	**0.96**	0.04	0.05	-0.07	0.00	-0.09
Mg	**0.84**	0.05	-0.04	-0.05	-0.07	-0.11	0.10	-0.02	**0.88**	0.08	0.07	0.04	0.00	-0.07
Cl	**0.87**	0.05	0.16	0.04	-0.07	-0.14	-0.17	-0.09	**0.94**	-0.09	0.13	-0.01	0.03	-0.01
HCO3	**0.77**	0.13	-0.30	0.21	0.04	0.20	0.13	-0.01	0.38	**0.56**	-0.35	0.28	-0.08	0.12
SO4	**0.82**	-0.03	-0.01	0.16	-0.01	-0.07	-0.09	-0.03	**0.89**	0.04	-0.04	-0.16	0.09	-0.04
NO3	0.39	-0.22	0.32	**-0.47**	-0.06	-0.27	0.06	0.33	**0.89**	-0.15	0.16	-0.15	-0.03	-0.14
F	**0.51**	0.03	**-0.44**	0.33	0.17	0.02	0.18	0.12	0.33	0.44	**-0.45**	0.22	0.06	0.20
Fe	-0.24	**0.77**	-0.04	-0.05	-0.17	-0.37	-0.21	0.03	-0.16	**0.50**	**0.71**	-0.14	0.20	-0.07
As	-0.01	0.09	-0.19	0.36	-0.06	0.06	0.30	**0.73**	-0.03	0.40	0.18	0.20	-0.11	-0.20
Cd	-0.06	0.03	-0.22	**-0.51**	0.13	0.20	-0.14	0.12	-0.09	0.28	0.13	0.07	-0.37	-0.20
Co	0.20	**0.50**	0.32	-0.11	0.33	**0.58**	0.15	0.03	0.09	-0.14	0.28	-0.05	**-0.46**	**0.60**
Cr	-0.13	-0.10	0.32	0.37	-0.29	0.28	-0.17	-0.21	-0.12	-0.05	0.04	-0.38	0.43	0.23
Cu	-0.05	-0.21	0.26	0.07	**0.66**	-0.35	-0.07	-0.05	0.19	**-0.43**	0.09	0.28	0.01	-0.32
Mn	0.31	0.33	-0.11	-0.25	-0.01	0.25	0.00	-0.17	0.24	0.16	0.27	-0.21	**-0.43**	**0.44**
Ni	0.05	**0.76**	0.34	-0.12	0.14	0.06	0.19	-0.06	0.05	-0.39	0.31	**0.52**	0.15	0.35
Pb	0.03	0.08	-0.18	**0.41**	**0.57**	0.06	-0.35	-0.02	0.04	0.00	-0.06	**0.49**	0.44	0.21
Zn	-0.06	0.16	-0.20	-0.04	0.24	-0.41	**0.62**	-0.35	0.08	-0.15	0.28	**0.58**	0.15	0.04
Eigenvalue	6.15	2.13	1.81	1.60	1.37	1.24	1.07	1.03	6.54	2.27	1.70	1.58	1.43	1.27
Total variance (%)	26.7	9.27	7.89	6.95	5.97	5.41	4.64	4.49	28.4	9.86	7.39	6.87	6.22	5.53
Cumm. Total variance (%)	26.74	36.01	43.90	50.85	56.82	62.23	66.87	71.36	28.42	38.28	45.68	52.55	58.77	64.30

Appendix C: Derivation and Construction of Indices of Groundwater Pollution

Degree of contamination C_{deg}

$$C_{deg} = \sum_{i=1}^{n} Cf_i$$

$$Cf_{i=\frac{C_{Ai}}{C_{Ni}}-1}$$

Where;

Cf_i = Heavy metal contamination factor.

C_{Ai} = Level of heavy metals in groundwater.

C_{Ni} = Limit of heavy metals per regulatory standard.

n = Total number of samples.

Heavy metals evaluation index HEI

$$HEI = \sum_{i=1}^{N} \frac{H_c}{H_{MAC}}$$

Where;

H_C = Level of heavy metals in groundwater.

H_{MAC} = Standard limit of i^{th} heavy metal recommended by local/international body.

Heavy metal pollution index HPI

$$HPI = \left. \frac{HMC}{AL} \middle/ n \right.$$

Where;

HMC = Detected heavy metal concentrations.

AL = Allowable heavy metal limit.

n = Number of samples evaluated.

Modified heavy metal pollution index $mHPI$

$$mHPI = \sum_{i=1}^{n} \left(R_w \times \frac{M_i}{S_i} \right)$$

$$R_w = \frac{W_i}{\sum_{i=1}^{n} W_i}$$

Where;

R_w = Relative weight.

W_i = Assigned weight.

S_i = Standard limit recommended by regulatory body.

M_i = Heavy metal concentrations.

Water pollution index WPI

$$WPI = \sum_{i=1}^{n} PL_i$$

$$PL_i = 1 + \left(\frac{C_i - S_i}{S_i}\right)$$

Where;

C_i = Concentration of variable.

S_i = Standard limit.

For pH:

$$PL_i = (C_i - 7)/(S_{ia} - 7)$$

S_{ia} = Lower limit for pH < 7.

$$PL_i = (C_i - 7)/(S_{ib} - 7)$$

S_{ib} = Upper limit for pH > 7.

Lower limit = 6.5.

Upper limit = 8.5.

Appendix D: Fieldwork Risk Assessment

GENERAL RISK ASSESSMENT FORM (S20)

Persons who undertake risk assessments must have a level of competence commensurate with the significance of the risks they are assessing. It is the responsibility of each Head of Department or Director of Service to ensure that all staff are adequately trained in the techniques of risk assessment. The University document "Guidance on Carrying out Risk Assessments" will be available, in due course, to remind assessors of the current practice used by the University. However, reading the aforementioned document will not be a substitute for suitable training.

Prior to the commencement of any work involving non-trivial hazards, a suitable and sufficient assessment of risks should be made and where necessary, effective measures taken to control those risks.

Individuals working under this risk assessment have a legal responsibility to ensure they follow the control measures stipulated to safeguard the health and safety of themselves and others.

SECTION 1

1.1 OPERATION / ACTIVITY	Complete the relevant details of the activity being assessed.		
Title:	Komadugu-Yobe Basin Nigeria Fieldwork		
Department:	Civil and Environmental Engineering		
Location(s) of work:	Komadugu-Yobe Basin Nigeria (Agricultural, urban and rural area)	**Ref No.**	001
Brief description: Travel to Nigeria from Glasgow UK, Nigeria-based research work including: field data collection (water samples and boreholes and hand dug wells inventories), and meetings with stakeholders in Komadugu-Yobe basin Nigeria			

1.2 PERSON RESPONSIBLE FOR MANAGING THIS WORK			
Name:	Robert Kalin	**Position:**	PI/Professor
Signature:	RK	**Date:**	27.07.2021
Department:	Civil and Environmental Engineering		

1.3 PERSON CONDUCTING THIS ASSESSMENT			
Name:	Abdulrahman Shuaibu	**Signature:**	
Name:		**Signature:**	
Name:		**Signature:**	
Date risk assessment undertaken:	27/07/2021		

1.4 ASSESSMENT REVIEW HISTORY

This assessment should be reviewed immediately if there is any reason to suppose that the original assessment is no longer valid. Otherwise, the assessment should be reviewed annually. The responsible person must ensure that this risk assessment remains valid.

	Review 1	Review 2	Review 3	Review 4
Due date:	../../2021			
Date conducted:	27/07/2021			
Conducted by:	Abdulrahman Shuaibu			

SECTION 2

Work Task Identification and Evaluation of Associated Risks **Page of** **Ref No.**

Component Task / Situation	Hazards Identified	Hazard Ref No.	Who Might be Harmed and How?	Existing Risk Control Measures (RCM)	Likelihood	Severity	Risk Rating	Risk	RCM's
Pre-departure Planning	N/A	0	N/A	All travellers must register for Travel Insurance at http://www.strath.ac.uk/finance/accountingservices/conly/travelinsurance/			NA		
Pre-departure Planning	Political demonstrations or civil unrest erupt when travelling	1	Research student may suffer verbal or physical abuse	Team will regualry check FCO https://www.gov.uk/foreign-travel-advice/nigeria/safety-and-security and Control Risks websites for travel advice/alerts in advance of travel and during trip. If there are instances of unrest, daily communication with team members with local knowledge of affected areas is extremely useful. If cases of unrest are recorded in sampling areas, this must be reported to Supervisor and further risk control measures should be taken	3	4	12	H	N
Pre-departure Planning	Emergency occurs and urgent help is needed i.e. an acute illness or injury which may lead to life loss or long-term health effect	2	Student may sustain injury, harm or death.	Traveller must carry a mobile phone (with battery and credit) at all times. The student must have contact details of the university emergency team, NHS and all partner organisations saved in their phones. Student must carry first aid kit in vehicle while travelling.	3	3	9	M	
Pre-departure Planning	Contact with pathogens and Covid-19	3	Research student or his field assistant may sustain illness and infection during sampling.	The traveller must obtain relevant vaccinations from GP or travel clinic at least 6 weeks in advance of travel. The research student and field assistant must know the route to the nearest hospital at all times of sampling. ▪ The student and filed assistants should know the latest regulations from the Authorities and ensure they have the right approval. ▪ The student and his crew will be required to follow Code of conduct while working during COVID-19 pandemic ▪ The student and the assistants should stay aware of the environment and the people around them	4	4	16	H	

				▪ Members of the team should remember that safety goes both ways. They take care of themselves at home and use the same level of precautions and care as required ▪ Members of the team must wear masks at all time ▪ Members of the team must avoid handshaking and observe recommended physical distance					
Pre-departure Planning	Safety call procedure	4	Traveller may become lost/ injured while working. Safety call procedure will be followed	Traveller will follow programmed safety call procedure, including safety calls for travelling in exceptional or unplanned circumstances	2	2	4	M	
Pre-departure Planning	Driving safety procedure	5	Traveller may sustain serious injury or die if involved in road traffic accident	Traveller will follow programmed driving procedure, including additional measures for long-distance driving (journey plan, safety calls, planned breaks, no driving in dark)	2	2	4	M	
Pre-departure Planning	Accident or medical ill health condition.	6	Traveller may sustain serious injury or die if immediate first aid is not provided	First aid will be kept in vehicle when travelling, and another at accomodation. Traveller will have to completed first aid training from University Security Services, or other qualified organisations.	3	5	15	H	
Flights to Nigeria	Deep vein thrombosis	7	Traveller: DVT	Move around and stretch during long flights	2	2	4	M	Y
General activities	Hygiene	8	All illness	Wash hands+hygiene, use purification tablets as appropriate, observe social distance	3	3	9	M	N
Driving in Nigeria	Exposure to criminal activities, car accident, car becoming stuck in floods and mud, Car breakdown and others	9	Driver, passengers' mobility may be delayed, theft/assault/ injury, violence/extortion/ becoming stranded.	Plan route, drive to conditions, check vehicle safety features, wear seatbelt, avoid night driving, avoid driving alone and areas known of danger, have phone, check weather and news, avoid night travel, plan journey / safety call upon arrival	2	4	8	M	N
General activities in Nigeria	Burns, cuts, scrapes, heat exhaustion etc.	10	All: injury	Take care operating cooking appliances, first aid kit, drink a lot of water, know nearest hospital/ treatment centre	3	3	9	M	Y
General activities in Nigeria	Animals and Insects	11	All: injury and illness from animal bites	The student should keep away from animals, carry first aid kit along, Wear appropriate clothing, Insect repellant, use net whiling sleeping, use anti-malarials, know nearest hospital/ treatment centre	3	3		M	Y

General activities in Nigeria	Food/drink, general tropical and water borne diseases	1 2	All: illness i.e. food poisoning, cholera	Wash hands + hygiene, avoid food that has been left out/ reheated, use purification tablets as appropriate, know nearest route to hospital	2	4	8	M	Y
Pre fieldwork planning	Extreme/Dangerous weather (i.e. flooding, heavy rainfall, high wind, lightening)	13	Student /driver / filed assistant may sustain injury. Mobility may be delayed due to adverse weather condition which may cause accident or anxiety	Before departing for fieldwork, the student and his crew must check for weather forecast for every location of the work ▪ Cancel every plan activity if there is possbility of heavy storm or delay the work until the weather become normal ▪ Speak to local people to understand localised risk and plan aternative route to home in case of sudden weather change ▪ Always carry water to the field to keep hydrated	3	3	9	M	Y
Pre fieldwork planning	All team members must have required PPE and equipment before commencing fieldwork	14	The student/ his assistant may sustain injury or acid burns	Before departing for fieldwork, the team must check that they have the required PPE, and suitable shoes / clothing for the works required for sampling, hand gloves and google in case of acid spillage and the student must have been oriented on standard etiquette and measures.	3	4	12	H	Y
Field work	Handling and transport of hazardous materials (Acids)	16	All: Toxic and acid burns	Store acids appropriately in protective container, make sure it is kept away from people in case of explosion, always wear PPE (i.e gloves and goggles)	2	4	8	M	Y
Field work	Manual Work: Impact injury	17	All: injury	Make sure all equipment is in good working order, make sure correcct tool is being used for each task, wear PPE at all times, plan all equipment lifting and moving, keep work area tidy, store equipment and parts in appropriate place, people not directly working must be outside demarcated work area, first aid kit available	3	3	9	M	Y
Field work	Food/drink poisoning	18	All: illness i.e. food poisoning	Wash hands + hygiene, avoid food that has been left out/reheated ▪ Observe hygiene practices ie handwashing with soap at critical times ▪ Avoid consuming leftovers or reheat food ▪ Carry homecooked food in clean containers to field ▪ Consume well packaged food ▪ Avoid drinking groundwater especially in areas affected by renal failures ▪ Avoid drinking local drinks ▪ Avoid consuming high risk ready to eat foods	2	4	8	M	Y

Field work	Contaminated / poisonous materials	19	All: illness/injury from hazardous materials	Remove all hazard waste from site, store hazard materials correctly, PPE, first aid kit	2	4	8	M	Y
Field work	Fuel handling	20	All: fire and associated injuries / equipment damage	Fuel to be stored in appropriate sealed container, fuel to be kept out of sunlight and away from sources of ignition, fuel should be handled with utmost care	3	3	9	M	Y
Field work	Handling hazardous materials (Acids) at field	21	All: Injury, Toxic, Burns etc	Store hazardous materials appropriately, handle hazardous materials (acid) with care, wear appropriate PPE (i.e. hard hat, boots, gloves, goggles)	3	3	9	M	Y
Field work	Sunburn, heat exhaustion	22	All: injury and illness	Stay out of sun, wear hats, wear suncream, drink lots of water	2	4	8	M	Y
Field work	Animals and insect’s bites	23	All: injury and illness from animal bites, malaria, fleas	Keep away from animals, insects repellants, anti-malarials, first aid kit, appropriate clothing, know nearest hospital/treatment centre	2	3	6	M	Y
Field work	General tropical/ water borne diseases	24	All: illness i.e. cholera	Wash hands, avoid stagnant water, good hygiene, know location of treatment centre	3	4	12	H	Y
Field work	Becoming lost	25	All: becoming stranded	Don't work alone, plan moving between locations, use GPS, have radio/ phone as needed	3	4	12	H	Y
Field work	Bad weather (lightening), Heavy rainfall and wind	26	All: injury	If a lightning storm or high wind develops in the sampling area, sampling should stop, and members should shelter in a safe place until the storm has passed	2	4	8	M	Y
Field work	Team member contract Covid-19	27	Team member may contract covid-19 during sampling	Team Members must observe all preventive measures during sampling. Members must know the route to the nearest hospital at all times. ▪ All Members should know the latest regulations from the Authorities and ensure they have the right approval ▪ Members should stay aware of the environment and the people around them ▪ Members to wear masks, and face shields throughout the sampling time ▪ Members to use individual hand sanitizer throughout the sampling ▪ Members to avoid handshaking and observe recommended physical distance	3	4	12	H	N

SECTION 3

Identified Actions to Improve Control of Unacceptable Risks (as evaluated in Section 2)							**Page of**				**Ref No.**	
Hazard Ref No.	**Risk**	**Recommended Additional Risk Control Measures**	**Implemented Y/N**	**Action By**	**Target Date**	**Completion Date**	**Revised Risk**				**Revision of Risk Signed Off**
							Likelihood	**Severity**	**Risk Rating**	**Risk L, M, H**	
1	H	Political demonstration or civil unrest erupted when travelling: When political protest erupted in any fieldwork location. Sampling should be rescheduled to other locations free from demonstration. Sampling should commence back in the location when the protest is no more occurring in the area.	Y	Travellers			2	5	6	H	
3	H	Contact with pathogens and Covid-19: All team members should get relevant vaccination at least 6 weeks to the commencement of fieldwork. Covid-19 guideline should be observed throughout the sampling period. All members of the team should be provided with face masks and sanitizers throughout the fieldwork, Members are also advised to prevent handshaking and observed recommended physical distance.	Y	Team members			5	7	12	M	
6	H	Car accident and mental ill health condition: When traveng to new or exceptional area or for journeys of long duration, a journey plan must be made and shared with the supervisor and stakeholders prior to leaving (this journey plan should include: map, planned stops, planned safety calls, vehicle inspection etc). History and nature of the roads has to be explored before taking off.	Y	Team members			2	4	9	H	
9	H	Exposure to criminal activities: Team members are advised not to travel early in the morning nor vary late. All field work should finish before 5:00 PM to avoid kidnappers and bandits activities.	Y	Team members			2	3	8	M	
26	H	Bad weather: If extreme weather predictions is observed in the sampling area such as high wind, flooding and heavy storm, all planned activities should be cancelled until a stable condition is regained. Team member should always take plenty water with them to keep hydrated.	Y	Team members			2	4	8	M	

SECTION 4

RECORD OF SIGNIFICANT FINDINGS **Page of**

Ref No.

Where this Section is to be given to staff etc., without Sections 2 & 3,

please attach to the front of this page, a copy of the relevant Section 1 details.

The significant findings of the risk assessment should include details of the following:

- The identified hazards
- Groups of persons who may be affected
- An evaluation of the risks
- The precautions that are in place (or should be taken) with comments on their effectiveness
- Identified actions to improve control of risks, where necessary

Alternatively, where the work activity/procedure is complex or hazardous, then a written Safe System of Work (SSOW) or Standard Operating Procedure (SOP) is advised that should incorporate the significant findings. Such documents should again, have the relevant Section 1 attached. Please state below whether either a SSOW or SOP is available in this case.

Relevant SSOW available Yes ☐ No ☐	Relevant SOP available Yes ☐ No ☐

Significant Findings: (Please use additional pages if further space is required)

Main hazards:

- Covid-19: Covid-19 will be minimised through following standard guidelines and using PPE. Strong hygiene and social distancing in line with the WHO guidelines should be observed. Hand sanitizers and facemasks will be used all through.
- Road accidents: This will be minimised by good driving practice and journey planning
- Becoming stranded - minimised by good journey planning, good communications (phone or radio), using GPS and maps
- Malaria: This will be minimised by using mosquito nets, appropriate clothing and taking anti-malarial drugs.
- Other tropical/ water-borne diseases: minimised by good hygiene and avoiding sources of illness
- Food poisoning: This will be minimised by taking good food, good hygiene, and knowing quality and source of food.
- Sun exposure/ heat stroke/exhausted: This will be minimised by drinking much water, keeping out of sun, wearing sun-cream, hats etc
- Handling hazardous materials: Wear gloves and safety glasses when using tools, or handling hazardous substances

All travellers must arrange travel insurance through the University of Strathclyde.

There were activities of boko haram and bandits in three LGAs of Yobe state in Kamadugu yobe basin last years, fieldwork in these areas will not be undertaken. Hence, secondary data will be obtained from HJRBDA and NIHSA. For other locations, which are free from boko haram activities, team members are advised not to travel early in the morning or leave field vary late. All fieldwork should finish before 5:00 PM to avoid selves from kidnappers and bandit activities.

SECTION 5

RECEIPT OF SIGNIFICANT FINDINGS OF RISK ASSESSMENT **Page** **of**

Please copy this page if further space is required. **Ref No.**

All individuals working to the risk assessment with the Ref. No. as shown, must sign and date this Section to acknowledge that they have read the relevant risk assessment and are aware of its contents, plus the measures taken

(or to be taken by them) to safeguard their health and safety and that of others.

If following review of the assessment revisions are minor, signatories may initial these where they occur in the documentation, to indicate they are aware of the changes made. If revisions are major, it is advisable to produce a new risk assessment and signature page.

NAME (Print)	SIGNATURE	DATE
Abdulrahman Shuaibu		27/07/2021

STANDING TRAVEL ADVICE

Summary

Still current at: 22 July 2021. Updated: 8 July 2021

Latest update:

> The FCDO no longer advises against all but essential travel to Nigeria, based on the current assessment of COVID-19 risks.

The Foreign, Commonwealth & Development Office (FCDO) advise against all travel to: Borno State, Yobe State, Adamawa State, Gombe State, Kaduna State, Katsina State, Zamfara state, riverine areas of Delta, Bayelsa, Rivers, Akwa Ibom and Cross River States.

The FCDO advises against all but essential travel to: Bauchi State, Kano State, Jigawa State, Niger State, Sokoto State, Kogi State, within 20km of the border with Niger in Kebbi State, Abia State, non-riverine areas of Delta, Bayelsa and Rivers States.

On 15 December 2020 the Nigerian Communications Commission (NCC) announced that mobile SIMs must be linked to the Nigerian Identification Number (NIN) of the SIM user. This applies to all residents including foreign nationals. Traveller is advised to seek guidance on compliance from his network operator.

Covid-19 Information

From Monday 28 December 2020 additional arrival procedures will be in place for passengers whose journey starts from the UK or South Africa. Passengers must present their pre-departure permit to fly and a QR code confirming they have booked a test for the seventh day after arrival in Nigeria. They must also provide evidence of a negative COVID PCR result from a test taken within the 72 hours prior to boarding. On arrival these passengers will be processed by the public health authority separately to those from other destinations. UK health authorities have classified Nigeria as having a risk of Zika virus transmission.

Safety and security

Crime

During October 2020, there were a number of large-scale protests (known as #EndSARS protests) in Abuja, Lagos and other locations across Nigeria. Strikes over workers' rights in Kaduna State started on 17 May 2021. Protests have occurred and disruptions to transport and utilities have been reported. Traveller are advised stay away from any political or religious demonstration.

Road Travel

Travel by road in Nigeria can be hazardous. Driver is advised to always wear a seatbelt and avoid travel after dark. Potholes, animals, abandoned vehicles and cyclists can cause serious accidents, as can vehicles travelling at night without lights. Travel between towns by public minibus or pick-up truck isn't recommended; vehicles are often in poor condition and overloaded. Emergency services are basic. Larger coach services do run between the major towns and are more reliable.

When driving in Nigeria you should always carry a valid driving licence with you, a copy of your passport and your id card; you may need to produce it at police check points because of the equipment you are carrying. An introduction letter from the department is also needed signifying that the student is collecting the sample for research purposes.

Political situation

- Spontaneous demonstrations related to governance and economic issues can occur. You should avoid political rallies and street demonstrations.

Health

- Cases of COVID 19 are increasing at an alarming rate. You should follow the health advice issued by the ministry of health.

- Visit your health professional at least 4 to 6 weeks before your trip to check whether you need any vaccinations or other preventive measures. Country specific information and advice is published by the National Travel Health Network and Centre on the TravelHealthPro website and by NHS (Scotland) on the fit for travel website. Useful information and advice about healthcare abroad is also available on the NHS Choices website.
- If you need emergency medical assistance during your trip, you should contact emergency response team and ask for an ambulance. You should contact your insurance/medical assistance company promptly if you are referred to a medical facility for treatment.

Terrorism

Terrorists are very likely to try to carry out attacks in Nigeria. Most attacks are conducted by Boko Haram or Islamic State West Africa (ISWA) and occur in Borno, Yobe and Adamawa States in the Northeast. The groups have previously shown intent and capability to conduct kidnaps in Nigeria. Foreign nationals, including humanitarian workers, are likely targets for kidnap. Humanitarian hubs and humanitarian workers have been targeted during attacks in the Northeast, including Monguno, Borno State on 13 June 2020. There have also been significant attacks in Gombe, Kano, Kaduna, Jos and Bauchi States and in the Federal capital, Abuja. Further attacks are likely. Attacks could be indiscriminate and could affect western interests as well as places visited by tourists. You should avoid places where crowds gather, including political meetings, religious gatherings and places of worship, markets, shopping malls, hotels, bars, restaurants, transport hubs and camps for displaced people.

Lastly, around 117,000 British nationals visit Nigeria each year. Most visits are trouble-free.

Specific Actions Taken to Avoid Terrorism Issues During the Fieldwork

The following actions were taken during the fieldwork campaigns to avoid risks associated with terrorism activities and ensure successful collection of groundwater sample in the Komadugu-Yobe basin:

- Prior to the fieldwork, we have established close collaboration with local security agencies, including the police, and community vigilante to get familiarized with high-risk areas and obtain necessary permissions and ensure security escorts during sample collection in high-risk areas. We also held meetings with traditional rulers, community leaders, and local government officials to explain the purpose of the research, in order to gain their support, establish rapport with the local population and avoid suspicion during sample collection.

- A reconnaissance visit was conducted in the study area to identify safe and accessible sampling sites, areas with bad roads, insecure areas and areas requiring special attention.

- Risk assessments were performed to evaluate the security situation in each potential location, potential threat during fieldwork, avoiding areas with ongoing conflicts or reports of insurgent activities.

- Sampling was planned to minimize time spent in each sampling location. The team usually arrived, collected samples, and departed quickly to reduce exposure to potential risks. 3 people team conducted the fieldwork to avoid attracting public attention. Also, sampling was limited only to areas near settlements or places deemed safe by security assessments. Fieldwork was scheduled for daylight hours only, avoiding early mornings or late evenings sampling. Local people were employed to collect samples from insecure locations that are known with history of groundwater contamination.

- Constant communication was maintained with security contacts using mobile phones. Power bank was used in case of power outage and phone battery run down. Reliable vehicles were used for transportation, equipped with necessary supplies and tools for quick departure if required. The vehicle was regularly serviced to avoid wear and tear of essential parts. Emergency evacuation plans were developed in case of eventualities.

- Detailed records of activities, locations visited, and observations were documented, and regular updates were shared with supervisors, local stakeholders and institutional contacts in a WhatsApp group to keep them informed about felid work progress and safety of the team.

Travel Documents

- Team members identification cards should be in their possession at all times.

Appendix E: Review Comments and Authors Responses for Paper 1 (Chapter 5)

water-2856035

AUTHORS RESPONSE TO REVIEW COMMENTS
(incl. Cover Letter)

Fidelia Zhang, Assistant editor, MDPI

Dear Ms. Fidelia Zhang,

Thank you for the review comments to our paper. Please find attached our revised manuscript and responses enclosed.

We would like to indicate that the Review Comments made on our paper were comprehensive and generally supportive of our work and its publication. This is especially true for almost all the reviewers who provides more in-depth technical review, and comments: “The argument is of sure interest to the Water' journal readers”. We have produced a positive response to all comments that have allowed the manuscript enhancement.

We trust that you would find this revised manuscript suitable for publication in your journal. Please do not hesitate to contact us if any aspects require further clarification.

Our review response is as follows below.

Kind regards,

Abdulrahman Shuaibu

AUTHORS RESPONSE TO REVIEWER 1 COMMENTS (Round 1)

Comments and Suggestions for Authors

Comment 1

Remove dot from the paper title.

Response

The dot has been removed from the paper title as recommended.

See Line 3 of the revised manuscript.

Comment 2

I suggest not use abbreviation in the Keywords as: “SDG 6”.

Response

The Keywords: “SDG 6” has been removed as recommended.

See line 34 of the revised manuscript.

Comments 3

In Table 2, add the abbreviations of HDL, MPL and PAMPL below the table.

Response

The abbreviations of HDL, MPL and PAMPL were added below Table 3.

See Line 337 and 3338 in the revised manuscript.

Comment 4

WHO has guidelines, pl. use “guideline/s” instead “standard/s”.

Response

WHO standards were replaced by WHO guidelines throughout the paper.

See Line 26, 290, and 327.

Comment 5

Add the limitations of your study to the end of Discussion.

Response

The study limitations were stated in the introduction section of the manuscript.

Comments 6

Please refer to the recent article to improve the literature review, methodology and discussions:

I. Characteristics, water quality index and human health risk from nitrate and fluoride in Kakhk city and its rural areas, Iran

Response

The referred article was thoroughly read, understood, and utilized in the literature review, methodology and discussions section of the manuscript as recommended.

AUTHORS RESPONSE TO REVIEWER 2 COMMENTS (Round 1)

Comments and Suggestions for Authors

Re-water 2856035

The research provides important information about the quality of groundwater in the Sahel region. The article should be published. Authors should consider the following comments:

Thank you so much for taking your time to read our paper thoroughly and make positive comments that would improve the quality of the manuscript.

Comment 1

L179 – were the samples frozen?

Response

The samples were not frozen but rather kept at a temperature of ~ 4°C before shipping them to Civil and Environmental Engineering Laboratory, University of Strathclyde, Glasgow for analysis.

Comment 2

L180 – add the city and country of the university.

Response

The city of the University was added as recommended.

See Line 186 of the revised manuscript.

Comment 3

L188 – unnecessary repetition of the place where samples were analyzed.

Response

The place where samples were analyzed was removed as was stated earlier in the Groundwater Sampling and Field Measurement section.

See Line 209 and 210.

Comment 4

L219 – add abbreviation (GWQI).

Response

The abbreviation (GWQI) was added in Line 240 as recommended.

Comment 5

Change the table numbering order. For example, Table 3 should have number 1 - because the first one is mentioned in the text. However, Table 1 should be number 2, because it is discussed second in order.

Correlations between indicators should be calculated.

Response

The Table numbering was corrected in order, Table 1 was first mentioned in the text, then 2 …. and arranged in the Results and Discussion section in the same order.

See Line 329 to 338 of the revised manuscript.

AUTHORS RESPONSE TO REVIEWER 3 COMMENTS (Round 1)

Comments and Suggestions for Authors

The purposes of the manuscript water-2856035 have been to provide information valuable to stakeholders, government institutions, and decision-makers involved in sustainable management of groundwater resources in Nigeria and the wider Sahel region through a geochemical study.

Although the work is not of great scientific significance in that techniques already known to the scientific community are applied, the work is well written, and I think can be of use to government institutions.

However, I think some things need to be fixed before publication and my comments are in the attached file.

I believe the manuscript may be published only after **moderate** revision.

Thank you for taking your time to read our article. Your comments were comprehensive and supportive to the work and its publication. The comments were in-depth and technical and would be of interest to the reader of the article and were properly addressed.

Comment 1

1. it does not make sense to indicate the model in the abstract.

Response

The equipment model number has been removed in the abstract as recommended.

See line 21 of revised manuscript.

Comment 2

2. it does not make sense to indicate the model in the abstract.

Response

The equipment model number has been removed in the abstract as recommended.

See line 22 of revised manuscript.

Comment 3

3. It is important to consider also the dissolution rates of the various minerals. These topics are much discussed in the literature, see for example: Marini, L., 2006. Geological sequestration of carbon dioxide: thermodynamics, kinetics, and reaction path modeling. Elsevier.

Response

The dissolution rate of various minerals has been considered, added, and cited in the main text in the introductory section of the manuscript.

See Line 52 to 54 of the revised manuscript.

Comment 4

4. Major tectonic lineaments should be added in Figure 1.

Response

The major tectonic lineaments were added in Figure 1 as recommended.

Comment 5

5. Why was the redox potential (Eh) not measured?

Response

The redox potential (Eh) is beyond the scope of this work. However, since it is ongoing research, it is going to be considered in the subsequent study.

Comment 6

6. In addition to the charge balance, precision and accuracy data should also be reported.

Response

The ionic balance error analysis is sufficient to tell the accuracy of the chemical analysis. However, these other indices would be duly considered in the upcoming publication.

Comment 7

7. To evaluate the chemical composition of the water it is not enough to use the Piper diagram because it does not take into account (as proposed by the authors) salinity, I suggest using a TIS salinity diagram, as proposed by: Apollaro, C., Caracausi, A., Paternoster, M., Randazzo,

P., Aiuppa, A., De Rosa, R., Fuoco, I., Mongelli, G., Muto, F., Vanni, E. and Vespasiano, G., 2020. Fluid geochemistry in a low-enthalpy geothermal field along a sector of southern Apennines chain (Italy). *Journal of Geochemical Exploration*, *219*, p.106618.

Response

We would like to indicate that there is no evidence of geothermal water, and the study area is not close to coastal areas. Therefore, TIS salinity diagram is not relevant in the discussion of the chemical composition of the groundwater of the study area.

Comment 8

8. Use box plots to better describe and visualize these characteristics and variations.

Response

We would like to indicate that if we use box plot, we cannot be able to present some of the important information presented in the Tables. Thank you so much for your suggestions.

Comment 9

9. Indicate the meaning of the acronyms in the legend: HDL, MPL and PAMPL

Response

The meaning of the acronyms: HDL, MPL and PAMPL were presented below the table in the legend as recommended.

See Line 337 and 338.

Comment 10

The presence of calcite is ubiquitous in all types of rocks, even crystalline ones, as already highlighted by: White, A.F., Schulz, M.S., Lowenstern, J.B., Vivit, D.V. and Bullen, T.D., 2005. The ubiquitous nature of accessory calcite in granitoid rocks: implications for weathering, solute evolution, and petrogenesis. *Geochimica et Cosmochimica Acta*, *69*(6), pp.1455-1471.

Response

The recommended article backing the argument has been cited and appropriately referenced as requested. Thank you.

See citation number 74 Line 350 in the revised manuscript.

Comment 11

11. Indicate what types of fertilizers the authors think are used!

Response

The type of fertilizers used in the study area were indicated as requested.

See Line 351 in the revised manuscript.

Comment 12

12. The TDS also depends on the water-rock interaction time, therefore on the (more or less long) path of the water!

Response

Water-rock interaction time was added among the factors contributing to high TDS values in the Precambrian basement part of the study area.

See Line 367 in the revised manuscript.

Comment 13

13. a (medical) work where this is highlighted should be cited. Kidney stones are oxalates, not carbonates!

Response

We would like to indicate that the presence of calcium carbonate (CaCO3) and calcium phosphate and Calcium oxalate are the most common causes of kidney stone.

See Line 374 and 375 in the revised manuscript.

Comment 14

14. In tab. 15 is marked 13.

Response

12.5% was marked 13% to tally with the percentage in Table 5 as recommended.

See Line 380 and 381 in the revised manuscript.

Comment 15

15. Mg could also derive from the dissolution of mafic minerals. These minerals are very resistant to alteration, with a low dissolution rate. see for example the work: Bloise, A., Belluso, E., Critelli, T., Catalano, M., Apollaro, C., Miriello, D. and Barrese, E., 2012. Amphibole asbestos and other fibrous minerals in the meta-basalt of the Gimigliano-Mount Reventino Unit (Calabria, south-Italy). *Rendiconti online della società geologica italiana*, pp.847-848.

Response

The dissolution of mafic minerals has been included and cited accordingly as requested.

See Line 401 in the revised manuscript.

Comment 16

16. Insert a bibliographical reference

Response

Bibliographical reference has been cited as requested.

See Line 489 in the revised manuscript.

Comment 17

17. Are you sure of the presence of halite in Precambrian deposits?

Response

Halite is not present in the Precambrian basement. It was a mistake and was removed. Thank you so much for this fruitful observation.

See Line 504 in the revised manuscript.

Comment 18

18. The presence of sulphides cannot be overlooked, as evidenced by: Vaughan, D.J., 2006. Sulfide mineralogy and geochemistry: introduction and overview. Reviews in Mineralogy and Geochemistry, 61(1), pp.1-5.

Response

The reference has been read and cited in the sulphate section of the manuscript as requested.

See Line 513 in the revised manuscript.

Comment 19

19. The colors in the diagram are very confusing to the reader. the ED, RWD and PD zones are not very evident. It is therefore advisable to draw the graph again!

Response

The diagram was redrawn and the ED, RWD and PD zones were revised as recommended.

See Line 616 in the revised manuscript.

Comment 20

20. To evaluate the chemical composition of the water it is not enough to use the Piper diagram because it does not take into account (as proposed by the authors) salinity, I suggest using a TIS salinity diagram, as proposed by: Apollaro, C., Caracausi, A., Paternoster, M., Randazzo, P., Aiuppa, A., De Rosa, R., Fuoco, I., Mongelli, G., Muto, F., Vanni, E. and Vespasiano, G., 2020. Fluid geochemistry in a low-enthalpy geothermal field along a sector of southern Apennines chain (Italy). *Journal of Geochemical Exploration*, *219*, p.106618.

Response

We would like to indicate that there is no evidence of geothermal water, and the study area is not close to coastal areas. Therefore, TIS salinity diagram is not relevant in the discussion of the chemical composition of the groundwater of the study area.

Comment 21

21. Conclusions should be revised taking into account the previous comments.

Response

The conclusion of the manuscript was thoroughly revised as recommended.

See Line 688 to 713 of the revised manuscript.

Comment 22

22. The recommended works must be added in the references:

Marini, L., 2006. *Geological sequestration of carbon dioxide: thermodynamics, kinetics, and reaction path modeling*. Elsevier.

White, A.F., Schulz, M.S., Lowenstern, J.B., Vivit, D.V. and Bullen, T.D., 2005. The ubiquitous nature of accessory calcite in granitoid rocks: implications for weathering, solute evolution, and petrogenesis. *Geochimica et Cosmochimica Acta*, *69*(6), pp.1455-1471.

Vaughan, D.J., 2006. Sulfide mineralogy and geochemistry: introduction and overview. Reviews in Mineralogy and Geochemistry, 61(1), pp.1-5.

Bloise, A., Belluso, E., Critelli, T., Catalano, M., Apollaro, C., Miriello, D. and Barrese, E., 2012. Amphibole asbestos and other fibrous minerals in the meta-basalt of the Gimigliano-Mount Reventino Unit (Calabria, south-Italy). *Rendiconti online della società geologica italiana*, pp.847-848.

Apollaro, C., Caracausi, A., Paternoster, M., Randazzo, P., Aiuppa, A., De Rosa, R., Fuoco, I., Mongelli, G., Muto, F., Vanni, E. and Vespasiano, G., 2020. Fluid geochemistry in a low-enthalpy geothermal field along a sector of southern Apennines chain (Italy). *Journal of Geochemical Exploration*, *219*, p.106618.

Response

The recommended works were read and those that are relevant to the paper were utilized adequately and referenced accordingly. Thank you so much for taking your time to source these wonderful articles that are worthy of being cited in our manuscript.

AUTHORS RESPONSE TO REVIEWER 4 COMMENTS (Round 1)

Comments and Suggestions for Authors

Reviewer' comments: This contribution presents a good case study concerning the quality of groundwater in in the Komadugu-Yobe Basin, Sahel Region. After revision, many comments can be cited:

Thank you so much for taking your time to read our paper and finding it worthy of publication in Journal of water.

Comment 1

1. There is no information concerning the habitation and activities in region.

Response

The information concerning habitation and economic activities in the region were highlighted in the study area setting section.
See Line 122 to 125 of the revised manuscript.

Comment 2

2. Add brief description of the groundwater collection procedure.

Response

This was explicitly presented in the Groundwater Sampling and Field Measurement section as requested.

See Line 178 to 186 of the revised manuscript.

Comment 3

3. Does the period between the collection of the samples in Komadugu-Yobe Basin (Nigeria) and the analysis conducted in the Department of Civil and Environmental Engineering 180 Laboratory at the University of Strathclyde (Glasgow) can has an influence in the obtained results?.

Response

We would like to indicate that the period between the collection of the samples in Komadugu-Yobe Basin (Nigeria) and the analysis conducted in the Department of Civil and Environmental Engineering Laboratory at the University of Strathclyde (Glasgow) is not over 180 days and has significantly influence the quality of the results obtained in the study.

Comment 4

4. At what depth is the Groundwater's for this region?

Response

The sampling depth of the groundwater in the study area varies from 22 to 75 m below the ground level.

Comment 5

5. It was interesting to give in information concerning the effect of over-extraction or the cultivation, if it exists, on the water quality.

Response

We would like to draw your attention to the results and discussion section of the manuscript where we clearly discussed the effect of over-exploitation and various rain fed and irrigation farming taking place in the basin on the overall quality of the groundwater.

See Line 351 to 352, 370, 426, 488……..

Comment 6

6. For Table 2, what is the meaning of HDL, MPL and PAMPL?
7.

Response

The meaning of HDL, MPL and PAMPL were presented below Table 2.

See Line 337 and 338 of the revised manuscript.

Comment 7

7. Give a small discussion concerning Table 3.

Response

Small discussion concerting Table 1 was given in the 2.7 Groundwater Quality Index section under Materials and Methods.

See Line 222 to 263 of the revised manuscript.

Comment 8

To summarize, this work is one of the best works that I have seen in this area, the presentation and discussion of results are conducted with a very good manner. It is clear that this work has a great importance for the policy makers and can be considered as a very good base for a new study in different area. To conclude, I think that this article should undergo minor revisions before being published.

Response

Thank you so much for your fruitful comments and suggestions. They have really improved the quality of the work and would give the reader of the article a comprehensive understanding of the work.

Appendix F: Review Comments and Authors Responses for Paper 2 (Chapter 6)

EJRH-D-24-01518
AUTHORS RESPONSE TO REVIEW COMMENTS
(incl. Cover Letter)

Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow G1 1XJ, UK

Editor-in-Chief
Journal of Hydrology: Regional Studies,
Elsevier Publishers,
Netherlands.

Dear Denis Hughes, PhD,

Thank you for the review comments to our paper. Please find attached our revised manuscript and responses enclosed.

We would like to indicate that the Review Comments made on our paper were comprehensive and generally supportive of our work and its publication. This is especially true because the reviewer provides more in-depth technical review, and comments: “The argument is of sure interest to the Journal of Hydrology: Regional Studies readers”. We have produced a positive response to all comments that have allowed the manuscript enhancement.

We trust that you would find this revised manuscript suitable for publication in your journal. Please do not hesitate to contact us if any aspects require further clarification.

Our review response is as follows below.

Kind regards,
Engr. Abdulrahman Shuaibu

AUTHORS RESPONSE TO REVIEWER 1 COMMENTS (Round 1)

Editor and Reviewer comments:

Reviewer #1: Review report - EJRH-D-24-01518

Geochemical Evolution and Mechanisms Controlling Groundwater Chemistry in the Transboundary Komadugu-Yobe Basin, Lake Chad Region: An Integrated Approach of Chemometric Analysis and Geochemical Modelling.

The research topic of this manuscript is within the aim and scope of the JHRS. The manuscript is well organized, and the authors employed a integrated approach to evaluate geochemical processes governing water chemistry. However, the manuscript needs major revision.

Detailed comments

Comment 1

Abstract - Add the details about number of wells, samples and analysis details.

Response

Total number of samples collected was added in the abstract as requested. However, number of wells and details of analysis were documented in detail in the methodology section of the paper.

Comment 2

Introduction - add research gap. Too many researchers worked in the study area as mentioned. What is the novelty of this manuscript? So add few more sentences regarding this.

Response

The research gap and the study novelty statement including the research objectives were added in the last paragraph of the introduction section of the manuscript as requested.

Comment 3

Methods - add number wells samples.

Response

Total number of boreholes and hand-dug wells utilized for wet and dry season groundwater sampling was added in the methodology section as requested.

Comment 4

Analysis - Fe is not analysed and it is included in PCA . check it.

Response

Fe was analysed and included accordingly in analysis section. It was analysed using inductively coupled plasma optical emission spectrometry (ICP–OES, iCAP 6200, Thermo Fisher Scientific) together with Ca, Na, Mg and K.

Comment 5

Lines 219-222. Avoid the repetition. Merge the sentence

Response

The sentence in lines 219-222 were rewritten as recommended.

Comment 6

Geochemical modelling - What is the database used? Add in the text

Response

The database used for geochemical modelling was Geochemist's WorkBench GWB software 17.0 and was included in the text accordingly.

Comment 7

The results and discussion section should be supported by the recent citations.

Response

Results and discussion section was supported by recent citations mostly 2022-2024 journals as requested.

Comment 8

Fe is included in all sections; but, not analysed. How?

Response

Fe was analysed and included in the methodology section. We initially forgot to include it in the list of analytes.

Comment 9

Table 1. NO_3 concentration is too high. Recheck data quality or add justification

Response

The data quality was verified and the justification for the high nitrate concentration was appropriately added in the text (See line 374 – 380 of the revised manuscript). The high nitrate concentrations presented in Table 1 during the wet and dry seasons were measured in open dug wells and boreholes, where significant pollution is attributed to agricultural activities and leachate from unimproved pit latrines, particularly in the downstream areas of the basin. This finding aligns with a study by Goni et al., (2023), conducted in parts of the Hadejia-Jama'are-Komadugu-Yobe Basin, a section of the transboundary Komadugu-Yobe basin which reported high nitrate concentrations, with a maximum value of 1,003 mg/L measured in a dug well affected by agricultural pollution**.** (https://doi.org/10.1007/s10040-023-02637-2).

Comment 10

4.2.2- PCA - the clarity in the writing is very poor. Better to discuss wet and dry season separately. Rewrite

Add citations and compare with international studies

Response

Section 4.2.2 of the manuscript has been rewritten. The wet and dry season results are discussed separately, as requested, and the findings are compared with recent international studies.

Comment 11

Figure 4. Not clear. Use different colours each cluster group.

Response

Different colours were used to differentiate various cluster groups in Figure 4 as recommended.

Comment 12

Line 495 dolomitic carbonate? Use the term dolomite

Response

Dolomite was used instead of dolomitic carbonate as requested.

Comment 13

Figure 8f. check the diagram. Some errors may be in dry season samples.

Response

Figure 8f. was checked and corrected according as requested.

Comment 14

Conclusion - Reduce the length. Use bullet points.

Response

The conclusion section of the manuscript has been summarized in bullet points, as requested.

EJRH-D-24-01518R1 (Round 2)
AUTHORS RESPONSE TO REVIEW COMMENTS

Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow G1 1XJ, UK

Editor-in-Chief
The Journal of Hydrology: Regional Studies,
Elsevier Publishers,
Netherlands.
Dear Denis Hughes, PhD,

Response to Reviewers

We are pleased to revise our manuscript in accordance with the suggestions of the reviewers and editor, as this manuscript significantly benefits from their insightful comments. Below are the responses to the comment made for your kind perusal.

Editor and Reviewer comments:

Editor: Please change the format of the abstract to conform with this journal's requirements (see website or previously published papers for more details).

Response

The abstract has been revised to align with the journal's required format, as requested. Please refer to lines 17 to 36 in the updated version of the manuscript.

Reviewer #1:

Comment 1

The manuscript is revised substantially based on the reviewer comments. However, the fonts in the figures and legends are too small and invisible. Please check the figures 2, 3, 4 and 8.

Response

The highlighted figures have been reviewed, and their font sizes have been increased for better visibility, as requested.

Comment 2

Further, Dolomite carbonate is used in table 3. This should be corrected.

Response

Dolomitic carbonate in Table 3 has been corrected to Dolomite as recommended.

Comment 3

After correcting these issues, this manuscript is suitable for publication.

Response

All the highlighted issues have been thoroughly addressed. Thank you for taking the time to provide a comprehensive review of the manuscript.

Comment 4

I recommend the highlighter options for corrections instead of track change option.

Response

The highlighter options were used for the corrections as recommended.

We hope our responses to the reviewers and editor's comments have been adequately addressed, and we look forward to your positive feedback and the acceptance of our manuscript for publication.

Thank you
Yours Sincerely
Abdulrahman Shuaibu.

Appendix G: Review Comments and Authors Responses for Paper 4 (Chapter 8)

Reviewer Comments (if applicable):

Editor: This study is interesting, but the manuscript shows major quality issues and needs to be revised importantly. I reject the study for the moment but would like to encourage them to resubmit it after attending all comments, accordingly, including them in the resubmission. If you intend to resubmit, please select me as editor. The manuscript will be treated as a new submission. The authors have indeed interrelated the atmosphere and hydrosphere but have failed to include the lithosphere properly. I am between rejection and major revision, but I prefer to give them an opportunity.

Thank you so much for your comprehensive and constructive comment on our manuscript. We sincerely appreciate your acknowledgment of the potential of our study and your willingness to give us an opportunity for resubmission to your reputable Journal. We understand your concerns regarding the quality issues and the need for significant improvement, particularly in addressing the integration of the lithosphere into the study. We have addressed all the comments and suggestions provided by you and the reviewers. We have also provided detailed rebuttals to the comments and suggestions we disagreed with, particularly those from Reviewers 4 and 5. We are grateful for this opportunity to resubmit, and we have ensured that the revised manuscript adheres to the highest quality standards. We have selected you as the editor, as we highly value your expertise and guidance. Thank you again for your constructive review comments and for encouraging us to refine and improve the quality of our work.

Reviewer #1: The map in figure 1 has a scale of thousands of kilometres when I believe that should be more detailed including the geology of the study basin.

Figure 1 Situation figure first, then a detailed Geological/Hydrogeological map of the basin and then the map with the groundwater control and sampling network.

Figure 1 has been rearranged as recommended. A detailed Geological/Hydrogeological map of the basin, along with a map indicating groundwater control and sampling points, has been added as requested (see Figure 1b in the revised version of the manuscript).

Line 156: the heading is not numbered.

The heading in Line 156 has been numbered appropriately.

Point 2.2. It is needed a more detailed geological or hydrogeological map, as well as a groundwater level map to see how the GW flows. Nor would it be superfluous for the authors to prepare along with the detailed map of the geology of the basin, some geological sections to help the reader understand all the explanation between lines 157 and 176.

We would like to indicate that we have presented a detailed geological map of the study area with groundwater level contours and GW flow direction (See Fig. 1b in the revised version of manuscript). Moreover, detailed hydrogeological cross-section AA' was also presented to enhance the readers understanding of geological and hydrogeological characteristics of the basin (See Fig. 2 in the revised version of the manuscript).

I believe that the use of the GNIP's stations are not appropriate. They are stations that, according to the map in Figure 1c, are located half a thousand kilometres away and although the authors say in line 216 and 217, that the stations share similar climatic conditions with the study area they are too far apart for me.

The authors did not only used GNIP stations in developing the regional meteoric water line, rather they used local stations across the region and additional incorporated GNIP stations to have a more regional representation of meteoric water. These regional GNIP stations have similar climatic characteristics in some respects. Note that, the concept of meteoric water line is to understand isotopic composition of precipitation, which reflects the movement and origin of air masses that contribute moisture to a particular area. So, incorporating GNIP and surrounding local stations in the development of regional meteoric water line is appropriate and has been proven effective by various research worldwide.

The authors use only two sampling campaigns (2021 and 2022). This isotopic database is weak to conclude the regional functioning of an aquifer.

We would like to indicate that we have incorporated datasets from previous research in some parts of the basin (Gon et al., 2001 between 1992 and 1997, Goni 2006 in 2001 and 2018, Goni et al 2023, Mbonu and Travi 1994 between 1988 and 1989) and a more regional dataset collected across the entire Sahel region through UN-IAEA RAF 7021, 7019 and 7011 projects spanning from 2011- 2023 to describe the regional functioning of the aquifer.

Section 3.7 of line 380, which is the spatial distribution of the isotopic composition of groundwater, seems to be nonsense and has no hydrogeological basis whatsoever. They assume that the Precambrian basement, which they do not say what lithology it is, is an aquifer when I should understand that they are metamorphic or igneous rocks. The geology/Hydrogeology of the article is scarce.

Thank you for highlighting the need for clarity and more discussion regarding Section 3.7 and the geological/hydrogeological framework in the manuscript. While we respect your view, we believe the use of the term "**nonsense**" is not appropriate. We aim to clarify any misunderstandings and address your comments constructively. In the revised version of the manuscript, we have explicitly stated that the Precambrian basement is overlain by fresh basement, fractured basement, weathered basement, and partially weathered basement, which serve as aquifers and provide groundwater storage and flow. Additionally, a detailed discussion on the geology and hydrogeology of the study area has been included in Section 2.2 of the revised manuscript. Regarding the spatial distribution of the isotopic composition of groundwater, the revised manuscript appropriately relates the study findings to the geology and hydrogeology of the region to ensure scientific interpretation and the influence of hydrogeological processes to groundwater.

Authors talk about groundwater recharge inputs, as if there were a connection and an input or transfer of water resources from the Precambrian basement to the sedimentary zones to the east, but without hydrogeological foundations.

The term "groundwater recharge inputs" has been revised appropriately, and the hydrogeological foundations are now presented in detail in Section 2.2 of the revised manuscript. Furthermore, hydrogeological connections have been thoroughly incorporated into the discussion of results in the revised manuscript.

I think that the map in figure 4 should be prepared differentiating the Precambrian unit from the sedimentary ones, even differentiating the sedimentary units because they have different lithology. In figure 4, each hydrogeological unit should be differentiated. So, the authors have to treat the samples of the Precambrian unit on the one hand and the sedimentary units on the other hand. Due to the amount of data, they have, they could even GW line maps or isoscapes. I think these maps translate what is the main problem of this article which is that they do not take into account at all the hydrogeology of the area.

Thank you for your comment regarding Figure 4 and the need to better differentiate the Precambrian and sedimentary units, as well as to incorporate hydrogeological considerations into the result discussion. We have revised Figure 4 to differentiate the Precambrian basement from the sedimentary geology. Each hydrogeological unit is now represented with unique hatching symbols to clearly distinguish the geological formations. This ensures that the lithological differences are effectively visualized. Additionally, groundwater line maps have been overlain on the geological map in Figure 2 of the revised manuscript. All discussions related to groundwater line maps were referred to the figure for better comprehension.

In this article, authors mix several things and lose the scientific sense. First, they take samples from a basin with two campaigns and try to establish the recharge pattern of the aquifers of the basin, but they use stations of the GNIP network located half a thousand kilometers away. There is no attempt to study the hydrogeology of the basin, in fact, they do not create any detailed map of the basin, nor do they make geological or hydrogeological cross sections. The section on groundwater recharge mechanisms is either non-existent or tremendously sparse. In the discussion section, they do not discuss the data on recharge mechanisms in the basin, but directly deal with the comparison of these data with all the data collected in the region. Secondly, they have compared their data with data from other publications and other studies to establish comparisons with this western region of Africa. Thirdly, they have generated a section that are recommendations for the management and sustainable use of resources, subway, as if it were a report rather than a scientific work. I believe that this article has to be focused more from the scientific point of view and eliminate what is the part of the recommendations for management. They should focus on the scientific part but they have to work much more on the hydrogeological part of the area, plus discuss how the recharge works or even provide data or quantify the recharge. At least give it a try.

Thank you for your detailed and constructive comments and suggestions. We are grateful for the opportunity our manuscript based on your valuable comments and suggestions. While GNIP stations were utilized in our analysis, the study also incorporated data from all available local stations within and surrounding the study area to develop the Regional Meteoric Water Line (RMWL). This approach has been widely validated by previous research and is proven to be effective in regions with sparse isotopic data. We have included a detailed geological discussion and a hydrogeological cross-section which provides an in-depth explanation of the various lithologies present in the basin and discussed the groundwater flow directions in the revised manuscript. The discussion section of the revised manuscript now incorporates a comprehensive discussion of the recharge mechanisms in the basin and the wider Sahel (see section 4.1 and 4.4). The section on groundwater management and sustainable use provided at the end of discussion section is intended to provide actionable insights for Integrated Water Resources Management (IWRM) and to promote groundwater sustainability in the Sahel region. This component complements the scientific analysis by addressing the practical implications of the research. Thank you again for your thorough review and insightful suggestions.

Reviewer #2: The manuscript introduces a study of the origin of precipitation producing groundwater recharge in the Komadugu-Yobe Basin (which is located in central-western Africa and is part of the large Chad Lake watershed) and a discussion on the origin of air mases producing groundwater recharge across the western Sahel. To achieve this goal, the study focusses mainly on the existence (or not), and on the seasonal and spatial distribution, of isotopic fractionation processes that modify the isotopic signature of precipitation during groundwater recharge, and tries to relate the existence (or not) of evaporation with different factors: with the precipitation season (dry and wet), with altitude, with the lithology (the manuscript says "the geology"), and with the origin of the air mases producing precipitation.

In my opinion, the manuscript has a wide scope not well reflected neither in the title nor in the content. The title should focus on the origin of air mases producing recharge in the Komadugu-Yobe basin and the whole western Sahel, and not in the existence or not of evaporative fractionation during recharge (although this fact contributes to deduce the origin of precipitation).

The content should be synthesized and clarified, going to the focus of the work. Those are some ideas to achieve that:

Thank you for taking your time to review our manuscript and provide insightful and constructive comments. We really appreciate your comments regarding the scope, title, and content of the manuscript. We have revised the revised the scope of the manuscript and streamlined our discussion and results sections to align with the title and the main objective of the manuscript as recommended. These valuable comments have ensured consistency between the title and the content of the manuscript.

- The text is written as very long, difficult to follow-up paragraphs. Some long paragraphs like section 4.4 are particularly difficult to understand because they are very dense. Single messages must be written as short and separated paragraphs. To provide an example: the conclusions must be separated in at least 7 paragraphs: 1) from line 619 to the sentence ending in "moisture sources" in line 624; 2) from the sentence starting in "The variability" in line 619 to the sentence ending in "air masses" in line 627; 3) from the sentence starting in " The results (must be "values", not results) of groundwater " in line 627 to the sentence ending in ""altitude" in line 630; 4) from the sentence starting in "Evaporative" in line 630 to the one ending in "signatures" in line 632; 5) from the sentence starting in "The variability" in line 632 to the ne ending in "condition" in line 637; 7) from the sentence starting in "Finally" to the end of the conclusions in line 640.

We really appreciate your suggestion regarding the structure and readability of the text, particularly in section 4.4 and the conclusions. We have reviewed and revised the text to break down long paragraphs into shorter ones for improved readability and comprehension particularly in the result and discussion section. In the conclusions section, we have restructured the content as requested. We are confident these revisions improve the clarity and flow of the manuscript.

- Some more geological and hydrogeological information is needed to understand some discussion and conclusions. The description of the regional geology is scarce and disordered. The geology must be described in term of ages, materials and relative permeability. Por example, the text in line 157 says that the area is underlain by impermeable Precambrian basement, but any reference is made to the rocks forming this basement. Many sampling wells are located in those materials, then most probably the Precambrian materials are not impermeable.

The geological and hydrogeological features of the study area were discussed in detail as recommended. Various geological formations and their lithostratigraphy were presented. Additionally, the hydrogeological cross-section AA’ was illustrated in Figure 1, highlighting auriferous materials overlying both the Precambrian basement and sedimentary parts of the basin. The Precambrian basement is overlain by fresh basement, fractured basement, weathered basement, partially weathered basement, and overburden soils. Groundwater occurs in the weathered and fractured basement, where it occurs within fractures, fissures, and joints.

Moreover, the geological map and legend in Figure 1 are incorrect: the legend and the figure duplicate ages (Pleistocene and Holocene are the same than Quaternary; Cretaceous and Jurassic are different ages of the Mesozoic, so there cannot be a lithological class called "Cretaceous-Jurassic", neither can be a class called "Jurassic Carboniferous"; etc.). The geology in figures 1 and 8 should be reviewed, corrected and simplified, and the geological legend must be ordered correctly in chronological order. Using the simplified geological classes shown in the legend of Figure 5 could be a good point.

The legend of the geological map in Figure 1 was revised as requested. Various geological formations were reordered chronologically, from the oldest to the most recent formations: Precambrian Basement Complex, Cambrian, Ordovician, Devonian, Carboniferous, Paleozoic, Triassic, Lower Jurassic, Jurassic, Triassic-Jurassic, Paleozoic-Mesozoic, Mesozoic, Mesozoic Igneous, Cretaceous, Jurassic-Cretaceous, Cretaceous-Paleogene, Cenozoic Igneous, Quaternary, Pleistocene, Holocene, Quaternary Igneous, Salt Domes, and Marine Deposits. Pleistocene and Holocene are classified within the Quaternary Period, with Pleistocene being the earlier epoch and Holocene being the current epoch of the Quaternary. Additionally, the lithological classes "Cretaceous-Jurassic" and "Jurassic-Carboniferous" were corrected to align with standard geological terminology. The Cretaceous-Paleogene boundary refers to the transition between the Cretaceous Period and the Paleogene Period, also known as the K-Pg Boundary. The Jurassic-Cretaceous designation marks the transition between the Jurassic and Cretaceous periods. These updates have been incorporated into Figure 1, which was corrected and simplified as requested.

- Some information on the depth of the sampled wells is necessary. Some differences in isotopic values could be supported by the depth of sampled groundwater.

The depth of sampling was presented in contour lines in Figure 2. in the revised version of the manuscript.

- The isotopic composition ranges and the D-excess values of groundwater samples taken in the dry and wet seasons are practically the same. The discussion based on the altitude (orography) effect is week and should be improved.

We would like to clarify that we have explicitly stated there is no much significant difference between the wet and dry season datasets. Additionally, the altitude effect on isotopic composition and D-excess has been thoroughly reviewed, as requested.

- The spatial distributions of □18and □2 values in Figure 4 are random. Only and D-excess values seem to have some relationship with either altitude, geology or may be well depth. This aspect deserves a more detailed discussion.

The section has been thoroughly discussed by analysing the relationship between isotopic distribution and altitude, geography, and well depths, as requested.

- A minimum information on the characteristics of the intertropical convergence zone and its role on precipitation is needed

Information on the characteristics of the Intertropical Convergence Zone (ITCZ) and its influence on precipitation across the Sahel region has been incorporated into the result and discussion section of the manuscript as requested.

- The content of section 4.3 is relevant for the countries in the zone, but it is not a result of the work introduced in the manuscript. Then, to focus the manuscript on the core of the work, this section should be eliminated. Some of the main ideas in this section can be moved to the conclusions.

Section 4.3 is an integral part of the study. It highlights the inverse continental effect in the study area and the whole of Sahel region describing the sources of moisture in the air masses.

- The graphical abstract has much information to be understood in a glimpse. It would benefit of being simplified.

The graphical abstract has been refined in a simple format as requested.

- Some highlights are longer that allowed.

The highlights were revised and summarized as requested.

- Highlight 4 mentions recharge from surface water, but this aspect is not discussed in the manuscript.

Surface water has been removed as it was not discussed in the manuscript.

The text needs also a in depth reviewing of formal aspects. For example:

- The standard isotopic names and symbols must be used. For example: the Deuterium excess can be written "D-excess" or "d", but not "d-excess"; an empty space must be between the numeric value of a particular stable isotope and the symbol ‰; the title (and several sentences across the manuscript) says "environmental stable isotopes of d18O and d2H", but it should say "using the stable isotopes 18O and 2H", because they are always environmental and because "□" refers to the way in which contents are expressed, but is not part of the isotopes name.

- Isotopic values should not be confused with signatures. They are not synonyms. An isotopic signature is the fingerprint of the precipitation found in groundwater or surface water.

The text has been thoroughly reviewed, and all standard names and symbols have been appropriately represented as recommended.

- In line 221, Eq. 3, delta is ‰, not in mm.

The unit of the delta sign was corrected as recommended.

- In line 222 the text is unclear. It should be: "Pi is the precipitation amount in the ith month, and □i is the isotopic composition of the precipitation in the ith month."

The text was made cleared as requested.

- When writing the mathematical function of meteoric isotopic lines, using the parenthesis correctly is relevant. For example, it should be: d2H = 6.11 (± 0.10) d18O - 0.57 (± 0.47), not d2H = 6.11 (± 0.10) d18O (-0.57 ± 0.47).

All mathematic Equations were checked as correctly as recommended.

- Some values in Table 1 lack the minus "-".

The minus values in Table 1 were included as requested.

- Text in lines 290 to 294 must be moved to section 2.4 in Methods.

Text in the lines were moved to section 2.4 in the Methods as recommended. See line 210 to 2017 in section 2.4 of the revised manuscript.

- Explain the meaning of "w" and "d" in the legend of Figure 3a.

The meaning of "w" and "d" which is “wet” and “dry” were added in the legend of the Figure as requested.

- In all the figures including legends related to numerical classes: please, be aware that it is impossible to have the following set of classes, for example:

≤ -4

-4 -1

≥ -1

They must be:

<-4

-4 -1

> -1

This applies for any legend consisting in numerical classes.

All figures including legends related to numerical classes in the manuscript were revised to the format recommended.

- The text needs a sound review of English writing.

The English writing errors as mentioned has been revised thoroughly as requested.

Thank you so much for your comprehensive comments and valuable suggestions.

Reviewer #4: Understanding GW recharge process using stable Isotopes depends on climate, temperature, and precipitation patterns and also reflects environmental conditions at the time of water's origin. During rainfall season here rainfall is seasonal and shows how much of the groundwater is replenished during the rainy season versus the dry season. but the study has not distinguished between groundwater that is recharged from surface water and that which comes from precipitation. The isotopic signature of surface water is often different from that of precipitation, allowing researchers to trace the sources of recharge. Stable isotopes can differentiate between water that is primarily sourced from wetland infiltration and that which originates from direct rainfall, groundwater recharge is enhanced artificially, where surface water is infiltrated into aquifers. They have not estimated the proportion of recharge derived from rainfall and other sources like rivers. They discuss the evaporation processes. But not providing insights into the water balance and recharge rates. The use of the stable isotope mixing models are to be elaborated with interpretations, they have not used the tritium and carbon-14, to estimate the age of groundwater to determine how long water has been in the system and how quickly the aquifers are being replenished.

Thank you for your comprehensive and insightful comments on our manuscript. We would like to indicate that we acknowledge the importance of distinguishing between groundwater recharged from surface water and direct precipitation, as well as understanding recharge processes, water balance, and recharge rates.

At present, our research focuses exclusively on groundwater and precipitation datasets collected from local GNIP stations and surrounding regional stations. Surface water sources were not considered in this study due to the scope and dataset limitations. However, we recognize the significance of incorporating these datasets and plan to include them in future studies as part of an ongoing research (RAF 7021) in the Sahel region of Africa, supported by the UN-IAEA. Regarding the use of isotopic mixing models, it is not possible now as we are at the stage of developing a conceptual understanding of the groundwater system. The use of tritium and ^{14}C isotopes to estimate groundwater age and recharge rates is indeed valuable and is beyond the scope of the present phase of the research due to financial constraints. However, we plan to incorporate these methods in subsequent phases to gain deeper insights into the age of groundwater and the recharge rates of aquifers.

They have not clearly mention whether recharge mechanisms occur via direct infiltration of rainfall or through lateral flow from surface water bodies. Whether the rate of recharge is slow or fast (i.e from recent rainfall or ancient precipitation (relict groundwater) and surface water that will provide a valuable information for sustainable water use in these areas. What about the geological and hydrogeological conditions in that area that is highly variable and how effectively application of isotopic tracers for this transboundary complex groundwater flow systems be delineated is a big question that has not been attempted, for that they have to integrate isotopic data with remote sensing, climate models etc., to improve the understanding of recharge dynamics.

We would like to indicate that we have explicitly stated that groundwater recharge in Komadugu-Yobe Basin occurs predominantly through the direct infiltration of rainfall in the revised manuscript. We did not use tritium or other isotope-based dating techniques in this phase of the research, we observed that recharge appears to be relatively fast in specific areas, particularly around the verge of Lake Chad and the Hadejia-Nguru Wetlands. Rapid infiltration occurs in these regions due to favourable geological and hydrogeological conditions. We also incorporated geological hydrogeological cross section and discussed the influence of geology and hydrogeology on recharge mechanisms in the results section of the revised manuscript. We have integrated isotopic data with remotely sensed datasets in the revised manuscript. However, the application of tritium, ^{14}C, and climate models is beyond the scope of this study and will be addressed in future phases of our ongoing research.

They have discussed the ITCZ movement that moves from north and south of the equator throughout the year, whether it influenced by the ITCZ, during the wet season, when the ITCZ is overhead, rainwater typically has a distinct isotopic signature (usually lower $\delta^{18}O$ and $\delta^{2}H$ values due to the strong convection processes and higher humidity). In regions influenced by the ITCZ, the isotopic composition of rainfall is often more depleted in heavier isotopes during the rainy season compared to the dry season. This seasonal variability has not been traced in groundwater to identify how rain from different times of the year contributes to recharge. Since the groundwater has a more isotopically depleted signature suggests recent recharge, enriched groundwater has older water, that is not brought out clearly in the discussion, particularly when the aquifers that are recharged intermittently. Similarly, the isotope values here are not clearly indicative of the evaporation processes during the dry season.

We have expanded our discussion of the ITCZ and its role in influencing recharge processes during the wet and dry seasons. We have specifically addressed how the ITCZ impacts the isotopic composition of rainfall by causing isotopic depletion during the rainy season due to strong convection processes and higher humidity. We have also discussed its role in the origin of air masses that bring rainfall to the Sahel region and its implications for recharge mechanism in the revised manuscript.

Further clear-cut discussion where they have isotopes fall on RMWL or GMWL indicate the recent meteoric water, often from local rainfall. In most of the sample's groundwater enriched in heavy isotopes compared to the RMWL then it will have to indicate evaporation during recharge and how about the role of ancient Precambrian Groundwater whether that has or hasn't interacted much with recent precipitation. Since isotopic values fall between LMWL whether it clearly indicate the mixing between shallow meteoric water and deeper groundwater. What about the past climatic changes and their effect on groundwater recharge.

We would like to clarify that the study focuses exclusively on shallow groundwaters. The potential mixing between shallow meteoric water and deeper groundwater, as well as the role of ancient Precambrian groundwater, will be explored in on going RAF 7021 project in the region. However, we have explicitly discussed the influence of weathered and fractured basement rocks on the isotopic composition of the groundwater.

From this study how did they delineate the role of groundwater in each border area of this transboundary region, whether the lateral or vertical mixing is dominant and how these interconnections will help one side or either side of groundwater resource; how did this study contribute to the management of interconnected transboundary GW system particularly to this area is missing completely.

Delineation of groundwater recharge contributions from transboundary countries is not within the scope of this study. Instead, our focus was on characterizing the isotopic composition of groundwater and understanding recharge processes within the study area and the wider Sahel region. Also, the results of the study were used to develop policy recommendations for sustainable groundwater management in the Sahel region in order to support IWRM and informed decision making in the revised manuscript.

Objectives has to be redefined; lacuna and limitations has to be spelt out.

The objectives of the manuscript were redefined, and various research gaps and limitations were explicitly spelt out such as a gap due to insufficient isotopic data from local GNIP stations, leading to a reliance on augmented datasets from surrounding regional stations e.t.c. The study does not extensively address the isotopic characterization of deeper aquifers and long-term climatic impacts on recharge processes.

Reviewer #5: This paper addresses a specific issue regarding the recharge of groundwater in the study area and proposes an examination of the relationship between hydrogen and oxygen isotopes, as well as D-excess. However, the interpretation of hydrogen and oxygen isotopes presented in the paper is somewhat unpersuasive and lacks robustness. Moreover, it appears that the authors lack a clear understanding of the interplay between recharge, runoff, and discharge of groundwater in volcanic regions. Given the current version, the paper is not deemed suitable for publication in the Science of the Total Environment.

Major comments:

The author believes that groundwater in the study area solely originates from precipitation within the watershed. Therefore, they attempt to delineate recharge by analyzing the hydrogen and oxygen isotope characteristics of groundwater during wet and dry seasons, concluding that recharge comes from heavy precipitation during the wet season. However, as shown in Fig,3a, no discernible difference in the hydrogen and oxygen isotopes of groundwater is observed between wet and dry seasons. Additionally, the weighted average of local precipitation is enriched in comparison to groundwater, hinting that groundwater may not originate solely from local precipitation. Therefore, the author may reconsider his research approach by examining the possibility of exogenous water recharge.

Research has confirmed the existence of a deep circulation form of groundwater in volcanic rock areas, referred to as basalt groundwater (Wang W., 2023; Wang W., 2024). Recharge from high-altitude leakage areas (such as the Tibetan Plateau internal flow area) can recharge to low-altitude areas (Chen J. S., 2009; Chen J. S., 2012; Liu X., 2024). Studies conducted in the endorheic region of Tibet have verified that the leakage volume amounts to 54 billion m^3/year, equivalent to the discharge of the Yellow River (Yong B., 2021). Groundwater can replenish across watersheds (Chen J. S., 2009; Chen J. S., 2012; Zhang Y. T., 2023; Wang W., 2024; Liu X., 2024). The authors are encouraged to review the relevant references.

In the Cameroon volcanic region of southern Nigeria, where precipitation can reach up to 10,000 mm/year, groundwater may exist in a state of deep circulation and outward discharge. The author should take note of this and revise the paper accordingly.

Thank you for your comments. We really appreciate you taking your time to provide valuable comments and suggesting references regarding exogenous recharge and deep groundwater circulation.

We would like to indicate that, the manuscript has explicitly acknowledged that there is no significant difference in the hydrogen and oxygen isotopic signatures of groundwater during wet and dry seasons. The suggestion to consider exogenous water recharge is interesting. However, it falls outside the scope of the current study, which focused on movement of airmasses and precipitation and its contribution to groundwater recharge in Komadugu-Yobe basin and the wider Sahel region.

Regarding the references provided, they discussed on volcanic regions and high-altitude recharge processes which we believed are entirely not relevant to the current study. The study area does not exhibit volcanic activity similar to that described in the references provided. Our study focuses on sedimentary and basement aquifers of KYB without any evidence of deep circulation and significant outward. We understand that the reviewer has not fully understand the main objective and the focus of the research. We have revised the manuscript thoroughly to ensure that the key focus and objectives of the study were discussed explicitly to address any potential misunderstanding regarding the scope of the study.

Minor comments:

1. Table 1 could be more clear if it presented the changes in the form of a plot.

Table 1 would be more effective if presented as a table rather than a figure, allowing readers to clearly view the ranges and duration of the isotopic datasets.

2. The precipitation points depicted in Figure 2b could benefit from classification according to the various GNIP stations.

Figure 2b has been updated to classify the precipitation points based on the respective GNIP stations.

3. All plots that showed distribution of isotopes can be scaled up to display the different points more clearly.

We would like to indicate that we have revised some of the isotope distribution plots for an improve clarity of different points.

Appendix H: Raw Hydrochemical and Stable Isotopic Dataset

Field physicochemical parameters measurement during wet season.

Sample ID	Location Name	Geological Fm.	Lat	Long	Eev. (m)	Sample Source	DTW (m)	pH	DO (mg/l)	Temperature (°C)	EC (µS/cm)	TDS (mg/L)	Eh (mV)
L01	Filin-Tanda	QSR	12.88	11.04	332	HB	21.8	6.06	6.1	28.3	957	612	120
L02	Rijiyar-Gabas	MIR	13.14	13.05	368	DW	28.2	6.28	7.2	28.7	454	291	40
L03	Lamisu	QSR	13.05	10.17	347	MB	55.0	7.07	6.4	28.6	960	614	18
L04	Aisami	QSR	12.88	10.45	341	HB	36.0	7.52	7.1	28.2	1657	1060	85
L05	Doguwar-Kuka	QSR	12.88	10.56	337	HB	31.0	7.04	4.7	26.1	430	275	-100
L06	Jaji Maji	QSR	12.90	10.80	339	HB	34.0	6.24	6.4	27.4	541	346	120
L07	Bukarti	QSR	12.89	10.91	338	HB	36.0	6.99	8.6	28.7	186	119	17
L08	Usur	QSR	12.87	10.98	342	HB	32.0	6.16	7.5	27.1	140	90	96
L09	Yunusari	QSR	13.15	11.54	332	MB	69.0	6.62	11.2	28.5	250	160	12
L10	Yusufari	QSR	13.07	11.17	332	HB	48.0	6.23	7.6	27.1	2746	1757	113
L11	Kachallri	QSR	12.98	11.11	333	HB	43.0	6.42	8.6	27.6	219	140	36
L12	Gadar-Dinya	QSR	12.88	10.95	338	HB	38.0	6.31	6.8	27.9	182	116	117
L13	Balle	QSR	12.83	11.69	327	HB	41.0	6.97	7.5	25.6	124	79	-332
L14	Bayamari	QSR	12.77	11.50	338	HB	37.0	6.70	7.9	28.3	153	98	92
L15	Sabon-Fegi Kankare	QSR	12.79	11.36	335	HB	42.0	6.54	9	28.5	136	87	158
L16	Zango-Ii Gashua	QSR	12.88	11.06	335	HB	33.0	6.94	7.8	27.3	108	69	-390
L17	Karage	QSR	12.81	10.86	335	HB	34.0	7.36	6.2	30.1	855	547	64
L18	Garin-Alkali	QSR	12.81	11.06	339	MB	55.0	6.84	8.2	30.3	232	148	119
L19	Gololo	QSR	12.32	10.69	345	HB	43.0	6.95	7.6	28.2	338	216	96
L20	Jakusko	QSR	12.37	10.78	346	MB	65.0	6.67	11.7	28.7	196	125	128
L21	Kwarso Girgir	QSR	12.56	10.93	340	HB	44.0	6.86	6.8	28.3	171	109	45
L22	Gasamu	QSR	12.73	10.97	335	HB	42.0	6.70	7.4	28.5	90	58	290
L23	Lambu	PIR	11.99	8.36	485	HB	45.0	7.05	6.3	27	228	146	280
L24	Garo	PIR	11.96	8.10	525	HB	47.0	6.52	7.1	28.5	470	301	322
L25	Shanono	PIR	12.05	7.99	591	HB	52.0	7.00	8.1	26.7	1017	651	-110

Field physicochemical parameters measurement during wet season.

Sample ID	Location Name	Geological Fm.	Lat	Long	Elev. (m)	Sample Source	DTW (m)	pH	DO (mg/l)	Temperature (°C)	EC (µS/cm)	TDS (mg/L)	Eh (mV)
L26	Getso	PIR	11.88	7.89	568	HB	45.0	7.5	5.8	27.2	1356	868	282
L27	Karaye	PIR	11.78	8.02	537	DW	33.0	7.4	7.2	26.7	1850	1184	382
L28	Kogo	PIR	11.62	8.17	553	HB	37.0	7.2	7.4	26.5	438	280	152
L29	Madobi	PIR	11.77	8.29	495	HB	33.0	7.6	5.2	27.5	353	226	374
L30	Gasau	PIR	11.91	8.46	468	DW	42.0	6.6	6.8	26.4	219	140	290
L31	Sir Sunusi Specialist Hospital	PIR	12.01	8.60	469	HB	45.0	7.5	9.3	28.6	2503	1602	379
L32	Fagge D2	PIR	12.01	8.52	465	HB	36.0	7.4	4	30.3	1964	1257	20
L33	Jogana	PIR	12.03	8.71	467	HB	44.0	6.9	8.4	28.7	64	41	-119
L34	Zakiarai	PIR	12.10	8.89	415	HB	42.0	6.9	5.9	28.8	275	176	110
L35	Karakawa	QSR	12.15	9.16	391	HB	37.0	7.8	5.7	27.8	245	157	180
L36	Malikawa	PIR	11.97	9.04	431	HB	45.0	7.2	7.1	27.6	522	334	45
L37	Alkala	PIR	11.86	9.00	441	DW	32.0	7.7	6.6	26.4	1403	898	162
L38	Wudil	PIR	11.81	8.84	417	HB	47.0	7.6	4.7	25.8	1787	1144	110
L39	Dawakin-Kudu	PIR	11.85	8.55	446	DW	28.0	8.2	3.8	25.7	199	127	145
L40	Danhassan	PIR	11.79	8.52	439	HB	49.0	7.9	4.6	26.7	170	109	-210
L41	Bunkure	PIR	11.67	8.55	482	HB	42.0	6.9	5.6	26.9	376	241	-362
L42	Rano	PIR	11.56	8.58	532	HB	45.0	8.0	5.6	26.5	930	595	135
L43	Kibiya	PIR	11.53	8.65	499	DW	38.0	7.4	6.1	25.3	376	241	174
L44	Baure	PIR	11.43	8.80	579	HB	45.0	8.2	5.8	27.5	663	424	150
L45	Sumaila	PIR	11.54	8.96	478	HB	45.0	7.8	5	27.3	446	285	123
L46	Panda	PIR	11.61	9.04	446	HB	46.0	7.6	6.2	27	304	195	188
L47	Kachako	PIR	11.54	9.27	455	HB	44.0	7.0	3.5	26.2	546	349	144
L48	Gano	PIR	11.84	8.73	446	DW	38.0	6.8	7.6	25.8	590	378	303
L49	Dawakin-Tofa	PIR	12.11	8.33	483	HB	49.0	6.7	7.4	26.8	106	68	170
L50	Kiyawa	PIR	12.12	8.19	507	HB	45.0	6.8	9.6	26.3	197	126	190

Field physicochemical parameters measurement during wet season.

Sample ID	Location Name	Geological Fm.	Lat	Long	Eev. (m)	Sample Source	DTW (m)	pH	DO (mg/l)	Temperature (°C)	EC (µS/cm)	TDS (mg/L)	Eh (mV)
L51	Sarkin-'Ya	PIR	12.13	8.10	539	HB	44.0	6.9	7.2	27.1	238	152	205
L52	Bichi	PIR	12.23	8.24	527	HB	45.0	7.0	8.2	27	270	173	148
L53	Tudun Makeri	PIR	12.31	7.95	571	HB	53.0	6.8	7	26.2	484	310	-145
L54	Kusada	PIR	12.46	7.97	538	HB	47.0	8.2	4.5	27.3	424	271	210
L55	Ingawa	PIR	12.64	8.05	511	DW	37.5	7.8	4.2	26.8	775	496	162
L56	Roni	PIR	12.67	8.26	480	HB	50.0	7.4	9.6	26.5	320	205	197
L57	Shagari Quarters	PIR	12.64	8.40	490	HB	47.0	8.2	5.8	27	193	124	230
L58	Chiromawa	PIR	11.64	8.40	499	HB	42.0	7.8	6.6	25.7	693	444	103
L59	Kofa	PIR	11.55	8.28	555	HB	45.0	7.3	7.4	25.3	197	126	-338
L60	Rogo	PIR	11.83	7.56	607	HB	42.0	7.8	4.7	25.1	290	186	-224
L61	Fulatan	PIR	11.39	7.86	681	HB	38.0	7.5	9.4	25.5	315	202	-435
L62	Ikara	PIR	11.17	8.22	683	DW	37.5	7.3	8.6	25.2	705	451	35
L63	Tudun-Wada	PIR	11.25	8.41	578	DW	28.2	6.8	4.2	25.6	1025	656	-48
L64	Falgore	PIR	11.11	8.58	590	HB	52.0	6.4	6.6	25.5	395	253	-306
L65	Kunchi	PIR	12.50	8.27	482	HB	42.0	6.9	4.6	26.3	789	505	12
L66	Makoda	QSR	12.42	8.43	478	DW	44.5	6.3	3.8	26.5	388	248	-9
L67	Danbatta	QSR	12.44	8.52	464	HB	43.0	5.7	8	27.5	39	25	20
L68	Ganduje	PIR	12.22	8.45	460	HB	47.0	6.7	5.3	27.3	480	307	-280
L69	Minjibir	PIR	12.17	8.66	453	DW	29.3	6.7	6.2	26	15	10	84
L70	Dutse	QSR	11.79	9.34	419	HB	45.0	7.5	4.9	25.6	156	100	-185
L71	Kangire	PIR	11.49	9.49	453	HB	50.0	7.4	3	27.4	513	328	165
L72	Buji Gari	PIR	11.52	9.67	428	HB	48.0	6.2	4.7	28.3	274	175	160
L73	Nasaru	MIR	11.23	9.60	458	HB	45.0	7.4	4	28	360	230	-268
L74	Warji	MIR	11.18	9.75	451	HB	45.0	6.8	3.2	26.4	1004	643	199
L75	Kafin-Madaki	PIR	10.69	9.76	572	HB	42.0	7.0	4	26.5	385	246	126

Field physicochemical parameters measurement during wet season.

Sample ID	Location Name	Geological Fm.	Lat	Long	Elev. (m)	Sample Source	DTW (m)	pH	DO (mg/l)	Temperature (°C)	EC (µS/cm)	TDS (mg/L)	Eh (mV)
L76	Zaranda	PIR	10.23	9.51	716	HB	40.0	6.3	3.8	25.7	538	344	105
L77	Gumau	MIR	10.26	9.01	833	HB	47.0	6.6	6	25.6	624	399	200
L78	Yankwano Jos	CSR	9.95	8.88	1145	DW	27.5	6.5	2.9	25.2	532	340	38
L79	Toro	PIR	10.06	9.07	985	DW	30.8	8.0	2	25.5	320	205	62
L80	Zanguro	PIR	10.43	9.98	523	HB	46.0	7.6	3.5	27.2	527	337	168
L81	Kwanar Marga	PIR	10.76	10.28	495	HB	44.0	7.6	5.4	26	602	385	107
L82	Kari	TSR	11.24	10.56	421	MB	65.0	6.1	9.6	27.6	158	101	50
L83	Giade	PIR	11.39	10.20	466	HB	45.0	6.2	3.3	27.3	68	44	-372
L84	Gwaram	PIR	11.28	9.89	433	DW	45.0	7.2	3.5	27.4	593	380	204
L85	Yana	MIR	11.41	10.02	430	HB	45.0	7.4	3.8	28.4	412	264	207
L86	Sirko	TSR	11.36	10.47	469	HB	42.0	7.2	4.4	26.3	690	442	210
L87	Dagauda	TSR	11.71	10.86	407	DW	33.2	7.9	5.8	26.8	235	150	205
L88	Garin-Gabako	QSR	11.89	11.03	389	DW	27.4	7.8	4.6	26.5	60	38	-190
L89	Unguwar Dan-Kawo Azare	QSR	11.69	10.19	405	HB	40.0	5.6	5.6	27.6	99	63	226
L90	Puchikuwa	QSR	12.09	10.27	369	HB	36.0	7.5	3.8	29.6	102	65	-277
L91	Tashena	QSR	12.30	10.29	359	HB	39.0	7.4	5.6	29	110	70	51
L92	Kankare Gamawa	QSR	12.01	10.60	378	HB	47.0	7.0	5.5	29.2	86	55	-422
L93	Bulkachuwa	TSR	11.65	10.52	407	MB	72.0	5.5	10.6	29.7	108	69	22
L94	Jama'are	QSR	11.67	9.93	407	HB	40.0	6.9	5.4	28.7	702	449	223
L95	Kiyawa	QSR	11.78	9.61	400	HB	45.0	7.4	5.6	27.5	466	298	33
L96	Gwampai	QSR	12.00	9.62	390	HB	43.0	7.8	4.5	28.5	241	154	202
L97	Miga	QSR	12.24	9.71	370	HB	37.0	7.4	4.2	26.4	94	60	188
L98	Yangyami	QSR	12.25	9.36	394	HB	40.0	7.5	3.2	28.6	71	45	162
L99	Maishada	QSR	12.45	9.59	356	HB	46.0	7.7	4.4	28.7	347	222	-400
L100	Kwanar-Dinya	QSR	12.61	9.76	359	HB	45.0	7.7	3.8	27	173	111	152

Field physicochemical parameters measurement during wet season.

Sample ID	Location Name	Geological Fm.	Lat	Long	Eev. (m)	Sample Source	DTW (m)	pH	DO (mg/l)	Temperature (°C)	EC (µS/cm)	TDS (mg/L)	Eh (mV)
L101	Hadejia	QSR	12.46	10.05	359	HB	39.0	7.5	3.8	27.7	985	630	178
L102	Saleri	QSR	12.62	10.25	350	HB	40.0	7.4	4.3	27.6	198	127	-328
L103	Guri	QSR	12.73	10.42	349	HB	38.0	7.9	10.2	27.7	200	128	-405
L104	Kirikasamma	QSR	12.70	10.25	348	HB	48.0	8.0	3.5	26.8	447	286	160
L105	Kadiluworiya	QSR	12.90	10.20	347	HB	52.0	7.9	6.4	27.6	155	99	165
L106	Malammadori	QSR	12.57	9.88	360	HB	49.0	7.8	11.5	26.8	359	230	-267
L107	Azauna	QSR	12.01	9.94	371	HB	45.0	7.7	6.2	26.3	196	125	182
L108	Auyo	QSR	12.33	9.94	360	HB	33.0	7.5	4.2	26.3	337	216	205
L109	Kaugama	QSR	12.47	9.73	361	HB	42.0	7.3	6.2	28.5	277	177	185
L110	Gumel	QSR	12.62	9.39	367	HB	48.0	7.9	4.7	28.5	404	259	201
L111	Maigatari	QSR	12.81	9.44	368	MB	75.0	7.8	4.2	28.4	235	150	217
L112	Tashar-Garba	QSR	12.74	9.10	374	HB	40.0	8.0	2.2	28.3	121	77	204
L113	Babban Mutum	QSR	12.82	9.00	382	DW	62.0	8.0	10.4	28.5	106	68	198
L114	Fankami	QSR	12.44	9.24	375	HB	51.0	8.2	8.7	29.5	188	120	183
L115	Sugungu	QSR	12.33	8.96	390	HB	47.0	7.3	7.1	27.4	473	303	226
L116	Garu	QSR	12.58	8.74	400	HB	50.0	7.9	7.8	26.6	87	56	-358
L117	Gwarandama	QSR	12.85	8.70	407	HB	48.5	7.2	6.2	27.8	37	24	205
L118	Ishiyawa	QSR	13.05	8.44	404	DW	41.8	7.4	7.3	27.4	46	29	199
L119	Malafa	PIR	12.09	8.50	487	DW	38.6	7.2	6.2	27.6	390	250	104
L120	Kura	PIR	11.77	8.42	478	HB	48.0	6.7	6.8	26.8	851	545	117

Field physicochemical parameters measurement during dry season.

Sample ID	Location Name	Geological Fm.	Lat	Long	Elev. (m)	Sample Source	DTW (m)	pH	DO (mg/l)	Temperature (°C)	EC (μS/cm)	TDS (mg/L)	Eh (mV)
L01	Filin-Tanda	QSR	12.88	11.04	332	HB	22.8	6.45	5.8	30.1	984	630	92
L02	Rijiyar-Gabas	MIR	13.14	13.05	368	DW	31.1	6.12	7.1	31.5	705	451	184
L03	Lamisu	QSR	13.05	10.17	347	MB	57.5	6.89	6.9	32.3	880	563	80
L04	Aisami	QSR	12.88	10.45	341	HB	36.5	6.79	7	31.8	1846	1181	190
L05	Doguwar-Kuka	QSR	12.88	10.56	337	HB	32.0	6.57	5.5	30.1	492	315	-186
L06	Jaji Maji	QSR	12.90	10.80	339	HB	36.0	6.13	7.1	30.7	820	525	216
L07	Bukarti	QSR	12.89	10.91	338	HB	38.0	6.53	10.2	29.2	225	144	211
L08	Usur	QSR	12.87	10.98	342	HB	32.0	6.20	7.8	28.8	173	111	197
L09	Yunusari	QSR	13.15	11.54	332	MB	73.0	7.25	10.7	32	428	274	29
L10	Yusufari	QSR	13.07	11.17	332	HB	51.0	6.99	6.9	31.4	3560	2278	147
L11	Kachallri	QSR	12.98	11.11	333	HB	44.0	6.73	9.1	30.4	355	227	177
L12	Gadar-Dinya	QSR	12.88	10.95	338	HB	39.0	6.19	7.3	28.6	289	185	218
L13	Balle	QSR	12.83	11.69	327	HB	41.0	6.48	8	30.6	118	76	-405
L14	Bayamari	QSR	12.77	11.50	338	HB	37.0	6.30	7.9	30.8	271	173	120
L15	Sabon-Fegi Kankare	QSR	12.79	11.36	335	HB	43.0	6.34	9.5	31.2	179	115	179
L16	Zango-Ii Gashua	QSR	12.88	11.06	335	HB	33.0	6.37	6	28.3	126	81	-355
L17	Karage	QSR	12.81	10.86	335	HB	33.0	6.54	6.4	29.8	863	552	215
L18	Garin-Alkali	QSR	12.81	11.06	339	MB	58.0	7.04	8.6	30.8	433	277	159
L19	Gololo	QSR	12.32	10.69	345	HB	45.0	6.34	7.1	28.5	207	132	180
L20	Jakusko	QSR	12.37	10.78	346	MB	69.0	6.56	9.5	27.6	330	211	159
L21	Kwarso Girgir	QSR	12.56	10.93	340	HB	45.0	6.33	6.2	31.3	144	92	162
L22	Gasamu	QSR	12.73	10.97	335	HB	44.0	6.20	8.4	31.4	63	40	165
L23	Lambu	PIR	11.99	8.36	485	HB	46.0	6.35	7.2	29.2	317	203	160
L24	Garo	PIR	11.96	8.10	525	HB	48.0	6.12	6.8	27.8	502	321	186
L25	Shanono	PIR	12.05	7.99	591	HB	54.0	6.10	5.4	29.5	1266	810	190

Field physicochemical parameters measurement during dry season.

Sample ID	Location Name	Geological Fm.	Lat	Long	Elev. (m)	Sample Source	DTW (m)	pH	DO (mg/l)	Temperature (°C)	EC (µS/cm)	TDS (mg/L)	Eh (mV)
L26	Getso	PIR	11.88	7.89	568	HB	47.0	6.52	5	30	1656	1060	-14
L27	Karaye	PIR	11.78	8.02	537	DW	36.0	7.17	7.9	28.8	1404	899	188
L28	Kogo	PIR	11.62	8.17	553	HB	38.0	6.58	8.3	29	506	324	142
L29	Madobi	PIR	11.77	8.29	495	HB	34.0	6.53	4.4	28.4	359	230	132
L30	Gasau	PIR	11.91	8.46	468	DW	45.0	5.53	6.8	28.3	304	195	203
L31	Sir Sunusi Specialist Hospital	PIR	12.01	8.60	469	HB	46.0	6.62	8.6	28.4	2660	1702	222
L32	Fagge D2	PIR	12.01	8.52	465	HB	37.0	6.38	5.6	28.8	2407	1540	179
L33	Jogana	PIR	12.03	8.71	467	HB	45.0	5.64	8.1	30.7	61	39	172
L34	Zakiarai	PIR	12.10	8.89	415	HB	43.0	5.75	4.2	30.2	218	140	161
L35	Karakawa	QSR	12.15	9.16	391	HB	38.0	6.28	5.1	31.1	236	151	145
L36	Malikawa	PIR	11.97	9.04	431	HB	48.0	6.30	8.4	30.8	347	222	147
L37	Alkala	PIR	11.86	9.00	441	DW	34.0	7.16	6.4	30.5	3320	2125	165
L38	Wudil	PIR	11.81	8.84	417	HB	48.0	6.33	5.8	39.5	2090	1338	170
L39	Dawakin-Kudu	PIR	11.85	8.55	446	DW	30.0	6.36	5.3	24.6	138	88	178
L40	Danhassan	PIR	11.79	8.52	439	HB	50.0	6.32	5.7	26.6	97	62	196
L41	Bunkure	PIR	11.67	8.55	482	HB	43.0	6.69	7	27.8	422	270	-190
L42	Rano	PIR	11.56	8.58	532	HB	45.0	6.87	6.8	28.6	1189	761	191
L43	Kibiya	PIR	11.53	8.65	499	DW	40.0	7.46	5.2	26	500	320	165
L44	Baure	PIR	11.43	8.80	579	HB	45.0	6.92	4.8	29.8	734	470	76
L45	Sumaila	PIR	11.54	8.96	478	HB	45.0	6.96	4.6	30	574	367	102
L46	Panda	PIR	11.61	9.04	446	HB	46.0	6.64	6	30.1	274	175	50
L47	Kachako	PIR	11.54	9.27	455	HB	44.0	6.34	5.5	30.2	467	299	73
L48	Gano	PIR	11.84	8.73	446	DW	40.5	6.66	7.3	28	599	383	53
L49	Dawakin-Tofa	PIR	12.11	8.33	483	HB	49.0	5.94	2.9	29.2	98	63	-61
L50	Kiyawa	PIR	12.12	8.19	507	HB	46.0	6.61	6.7	29.5	305	195	135

Field physicochemical parameters measurement during dry season.

Sample ID	Location Name	Geological Fm.	Lat	Long	Elev. (m)	Sample Source	DTW (m)	pH	DO (mg/l)	Temperature (°C)	EC (μS/cm)	TDS (mg/L)	Eh (mV)
L51	Sarkin-'Ya	PIR	12.13	8.10	539	HB	45.0	6.40	7	29.6	344	220	126
L52	Bichi	PIR	12.23	8.24	527	HB	47.0	6.47	8	31.1	252	161	-417
L53	Tudun Makeri	PIR	12.31	7.95	571	HB	55.0	7.24	5.4	29.9	617	395	102
L54	Kusada	PIR	12.46	7.97	538	HB	48.0	7.04	4	30	418	268	103
L55	Ingawa	PIR	12.64	8.05	511	DW	39.5	5.47	4.5	31	555	355	172
L56	Roni	PIR	12.67	8.26	480	HB	51.0	5.92	8.3	28.5	452	289	168
L57	Shagari Quarters	PIR	12.64	8.40	490	HB	48.0	7.12	6.2	32.9	176	113	168
L58	Chiromawa	PIR	11.64	8.40	499	HB	44.0	6.27	6	28.5	827	529	63
L59	Kofa	PIR	11.55	8.28	555	HB	46.0	6.42	6.4	29.7	216	138	-265
L60	Rogo	PIR	11.83	7.56	607	HB	42.0	6.44	3.2	29.3	293	188	191
L61	Fulatan	PIR	11.39	7.86	681	HB	40.0	6.26	4.8	29.5	356	228	178
L62	Ikara	PIR	11.17	8.22	683	DW	40.0	6.99	8.1	26.6	529	339	83
L63	Tudun-Wada	PIR	11.25	8.41	578	DW	30.5	6.89	5.1	27.3	1504	963	88
L64	Falgore	PIR	11.11	8.58	590	HB	53.0	6.17	6.3	29.2	412	264	-187
L65	Kunchi	PIR	12.50	8.27	482	HB	44.0	6.44	4.2	31.7	626	401	-66
L66	Makoda	QSR	12.42	8.43	478	DW	48.0	6.16	4.6	31.1	392	251	177
L67	Danbatta	QSR	12.44	8.52	464	HB	44.0	5.28	9.3	31.6	120	77	188
L68	Ganduje	PIR	12.22	8.45	460	HB	48.0	6.63	4.2	31.2	354	227	155
L69	Minjibir	PIR	12.17	8.66	453	DW	33.5	6.05	6.2	29.1	64	41	109
L70	Dutse	QSR	11.79	9.34	419	HB	46.0	6.88	4.4	28.6	189	121	112
L71	Kangire	PIR	11.49	9.49	453	HB	52.0	7.10	3.1	30.7	355	227	62
L72	Buji Gari	PIR	11.52	9.67	428	HB	49.0	6.66	4.3	30.4	462	296	151
L73	Nasaru	MIR	11.23	9.60	458	HB	46.0	6.54	5.2	29.6	365	234	-337
L74	Warji	MIR	11.18	9.75	451	HB	45.0	6.00	3.6	29.4	851	545	55
L75	Kafin-Madaki	PIR	10.69	9.76	572	HB	43.0	6.27	3.5	28	493	316	123

Field physicochemical parameters measurement during dry season.

Sample ID	Location Name	Geological Fm.	Lat	Long	Elev. (m)	Sample Source	DTW (m)	pH	DO (mg/l)	Temperature (°C)	EC (µS/cm)	TDS (mg/L)	Eh (mV)
L76	Zaranda	PIR	10.23	9.51	716	HB	41.0	6.56	3.9	28	718	460	130
L77	Gumau	MIR	10.26	9.01	833	HB	49.0	6.45	5.6	28	641	410	152
L78	Yankwano Jos	CSR	9.95	8.88	1145	DW	30.5	5.75	3.3	26.2	595	381	88
L79	Toro	PIR	10.06	9.07	985	DW	33.0	6.80	2.4	27.1	552	353	175
L80	Zanguro	PIR	10.43	9.98	523	HB	47.0	6.73	4.2	28.8	415	266	26
L81	Kwanar Marga	PIR	10.76	10.28	495	HB	45.0	6.40	6	29.5	833	533	83
L82	Kari	TSR	11.24	10.56	421	MB	69.0	5.55	10.5	27.6	199	127	29
L83	Giade	PIR	11.39	10.20	466	HB	48.0	5.24	4.6	28.8	90	58	-141
L84	Gwaram	PIR	11.28	9.89	433	DW	47.5	6.48	4	29	779	499	57
L85	Yana	MIR	11.41	10.02	430	HB	46.0	6.38	4.7	30.3	473	303	31
L86	Sirko	TSR	11.36	10.47	469	HB	43.0	6.30	5.1	28.5	760	486	-215
L87	Dagauda	TSR	11.71	10.86	407	DW	35.5	5.56	5.4	30.1	443	284	210
L88	Garin-Gabako	QSR	11.89	11.03	389	DW	29.2	5.81	5.8	30.4	348	223	189
L89	Unguwar Dan-Kawo Azare	QSR	11.69	10.19	405	HB	41.0	4.81	6.3	30.1	103	66	223
L90	Puchikuwa	QSR	12.09	10.27	369	HB	38.0	6.27	3.6	31.2	73	47	-173
L91	Tashena	QSR	12.30	10.29	359	HB	39.0	6.55	8.2	30.6	70	45	130
L92	Kankare Gamawa	QSR	12.01	10.60	378	HB	48.0	5.89	5.8	32	244	156	161
L93	Bulkachuwa	TSR	11.65	10.52	407	MB	76.0	5.06	11.4	31.5	381	244	211
L94	Jama'are	QSR	11.67	9.93	407	HB	41.0	5.96	4.5	30.2	216	138	185
L95	Kiyawa	QSR	11.78	9.61	400	HB	48.0	6.00	5.8	29.8	454	291	158
L96	Gwampai	QSR	12.00	9.62	390	HB	44.0	6.63	5.3	30.4	202	129	109
L97	Miga	QSR	12.24	9.71	370	HB	38.0	6.23	4	30.2	133	85	135
L98	Yangyami	QSR	12.25	9.36	394	HB	42.0	6.21	3	30.2	78	50	114
L99	Maishada	QSR	12.45	9.59	356	HB	48.0	8.30	5.6	31.1	609	390	-279
L100	Kwanar-Dinya	QSR	12.61	9.76	359	HB	46.0	6.50	3.4	32.2	244	156	136

Field physicochemical parameters measurement during dry season.

Sample ID	Location Name	Geological Fm.	Lat	Long	Elev. (m)	Sample Source	DTW (m)	pH	DO (mg/l)	Temperature (°C)	EC (µS/cm)	TDS (mg/L)	Eh (mV)
L101	Hadejia	QSR	12.46	10.05	359	HB	40.0	6.58	5.2	30.7	918	588	141
L102	Saleri	QSR	12.62	10.25	350	HB	41.0	6.50	4	32.2	177	113	-406
L103	Guri	QSR	12.73	10.42	349	HB	40.0	6.61	5.2	30.6	351	225	-420
L104	Kirikasamma	QSR	12.70	10.25	348	HB	49.0	6.63	4.3	31.4	233	149	143
L105	Kadiluworiya	QSR	12.90	10.20	347	HB	53.0	6.53	7.1	31.2	165	106	-332
L106	Malammadori	QSR	12.57	9.88	360	HB	51.0	6.72	10.8	32.5	350	224	145
L107	Azauna	QSR	12.01	9.94	371	HB	46.0	6.17	6.8	31.1	333	213	150
L108	Auyo	QSR	12.33	9.94	360	HB	35.0	6.08	4.1	30.8	312	200	162
L109	Kaugama	QSR	12.47	9.73	361	HB	43.0	6.91	6.5	32	460	294	139
L110	Gumel	QSR	12.62	9.39	367	HB	49.0	6.48	4.8	31.8	400	256	129
L111	Maigatari	QSR	12.81	9.44	368	MB	79.0	6.36	3.3	32.5	509	326	130
L112	Tashar-Garba	QSR	12.74	9.10	374	HB	44.0	6.43	3.82	32	146	93	140
L113	Babban Mutum	QSR	12.82	9.00	382	DW	66.0	7.88	10.8	32.7	137	88	107
L114	Fankami	QSR	12.44	9.24	375	HB	52.0	6.55	8.2	31.1	307	196	131
L115	Sugungu	QSR	12.33	8.96	390	HB	49.0	5.74	7	30.4	703	450	176
L116	Garu	QSR	12.58	8.74	400	HB	51.0	6.99	8.1	28	133	85	-342
L117	Gwarandama	QSR	12.85	8.70	407	HB	49.0	5.56	6.8	31.3	54	35	177
L118	Ishiyawa	QSR	13.05	8.44	404	DW	43.5	5.76	8.6	27.4	131	15	23
L119	Malafa	PIR	12.09	8.50	487	DW	40.2	6.79	6.3	31.4	372	264	12
L120	Kura	PIR	11.77	8.42	478	HB	49.0	6.18	7.2	28	921	612	-130

Major ions (mg/L) and stable isotopes (‰) during wet season.

Sample ID	Na	K	Ca	Mg	Cl	HCO_3	SO_4	NO_3	F	$\delta^{2}H$	$\delta^{18}O$
L01	94.43	50.22	72.11	18.78	110.21	336.52	28.35	0.32	0.47	-13.6	-1.85
L02	23.74	22.07	38.81	11.38	21.52	225.46	8.41	27.38	0.08	-19.9	-3.40
L03	92.52	2.48	80.82	10.93	98.40	258.48	133.06	38.62	2.34	-36.2	-4.29
L04	216.96	19.39	78.60	43.18	293.54	284.54	75.87	36.29	0.66	11.5	3.04
L05	41.07	8.86	46.12	9.30	32.67	235.89	0.57	0.16	0.40	16.5	3.86
L06	49.31	6.23	47.93	15.44	51.73	78.68	11.68	180.42	0.03	-21.6	-2.97
L07	20.86	2.27	12.54	2.58	15.54	97.75	1.70	0.26	0.47	-24.7	-3.44
L08	10.38	6.04	11.79	3.28	3.86	78.26	2.22	2.20	0.11	-11.7	-1.41
L09	33.17	2.41	28.48	0.51	29.56	66.20	24.59	3.40	0.15	-31.6	-4.84
L10	25.88	6.62	45.16	11.30	25.34	70.81	30.19	125.57	0.001	-26.8	-4.01
L11	18.60	4.18	17.79	4.88	11.82	23.81	8.34	82.14	0.001	-31.8	-4.68
L12	11.54	7.25	15.78	4.34	18.12	49.94	10.00	35.48	0.08	-20.1	-2.66
L13	6.54	3.01	13.45	3.48	2.29	76.37	0.10	0.15	0.08	-17.4	-2.81
L14	14.23	2.86	10.38	2.98	10.85	75.57	7.44	1.32	0.04	-19.4	-2.80
L15	8.78	4.41	14.65	3.13	12.65	78.47	0.80	0.68	0.001	-17.5	-2.64
L16	8.45	2.38	5.57	1.72	1.79	49.13	0.12	0.18	0.13	-20.4	-3.22
L17	18.88	59.59	91.25	23.35	36.96	151.08	45.98	313.92	0.17	-24.3	-3.70
L18	36.04	5.27	7.91	2.34	6.45	136.76	10.48	0.13	0.01	-33.4	-4.70
L19	32.27	14.67	21.21	4.89	29.10	148.14	13.27	0.25	0.39	-31.2	-5.03
L20	15.73	3.46	16.23	3.63	4.22	99.07	5.75	16.47	0.32	-36.9	-5.43
L21	20.68	3.91	10.28	3.30	0.74	109.95	0.89	0.14	0.08	-27	-3.67
L22	6.43	2.03	9.55	2.49	0.84	64.69	0.40	0.10	0.001	-21.5	-3.01
L23	16.18	5.68	19.29	6.19	11.44	107.98	2.21	28.34	0.24	-26.4	-4.49
L24	57.42	6.70	38.13	7.18	96.00	45.47	16.69	108.21	0.13	-21.4	-3.17
L25	84.90	6.57	82.42	41.66	129.69	264.35	27.30	69.97	0.26	-26	-4.49

Major ions (mg/L) and stable isotopes (‰) during wet season.

Sample ID	Na	K	Ca	Mg	Cl	HCO3	SO4	NO3	F	δ2H	δ18O
L26	90.06	11.53	112.38	57.83	156.79	267.56	34.18	149.33	1.25	-19.3	-3.40
L27	115.30	95.52	139.76	33.34	210.70	287.49	89.94	149.60	0.63	-17.3	-2.76
L28	24.37	3.98	40.85	14.28	33.58	181.58	7.33	44.02	0.64	-24.7	-4.12
L29	22.34	3.83	30.74	8.04	11.89	159.18	3.29	19.71	0.34	-28.6	-4.90
L30	28.96	7.10	6.44	0.97	23.63	14.25	11.13	48.37	0.10	-26.5	-4.41
L31	284.80	8.94	124.20	24.43	372.45	287.73	86.94	0.98	0.57	-22	-3.74
L32	141.30	16.51	227.00	33.41	345.33	268.08	60.48	78.56	0.45	-13.1	-2.27
L33	5.06	3.38	2.91	0.89	2.73	13.43	0.17	11.65	0.04	-28.2	-4.91
L34	30.11	5.44	16.29	4.38	41.49	18.89	2.22	66.36	0.10	-25.2	-4.31
L35	22.88	6.01	17.68	4.98	18.25	94.04	7.80	12.31	0.220	-20.1	-3.16
L36	39.41	5.49	57.43	9.65	48.13	139.50	11.48	99.30	0.137	-29.5	-4.95
L37	142.20	78.20	93.90	23.10	222.11	216.45	75.89	0.001	0.66	-24.7	-4.22
L38	210.10	17.97	118.40	31.51	332.15	258.20	30.28	0.001	0.63	-15.8	-2.43
L39	16.16	1.86	18.60	3.76	14.86	38.32	37.92	6.99	0.22	-21.2	-3.33
L40	15.61	2.63	15.10	3.66	5.34	87.64	0.88	6.89	0.15	-22.5	-3.56
L41	19.08	0.11	38.05	11.42	10.89	220.10	2.00	12.84	0.57	-25.6	-4.38
L42	41.98	11.49	116.70	21.51	47.71	290.05	37.60	30.09	0.67	-13.3	-3.04
L43	23.81	1.28	49.07	3.47	11.76	169.18	14.82	0.33	0.33	-30.7	-5.36
L44	32.53	2.93	78.29	29.63	26.90	252.74	35.51	12.51	0.72	-25.8	-4.49
L45	23.94	2.62	50.87	10.97	26.85	204.86	6.36	37.18	0.36	-24.1	-4.08
L46	17.06	4.43	31.62	7.71	1.67	178.39	0.78	3.90	0.39	-28.9	-4.83
L47	31.57	11.67	69.31	11.17	70.09	163.88	19.37	34.54	0.307	-28.6	-4.85
L48	49.47	44.48	47.78	9.90	99.20	162.81	25.89	55.04	0.57	-22	-3.55
L49	12.78	4.21	10.13	1.32	3.33	36.19	0.22	31.55	0.22	-24.1	-3.96
L50	12.15	4.55	23.77	4.41	22.70	43.39	2.96	42.16	0.25	-25.8	-4.36

Major ions (mg/L) and stable isotopes (‰) during wet season.

Sample ID	Na	K	Ca	Mg	Cl	HCO3	SO4	NO3	F	δ2H	δ18O
L51	22.32	12.70	20.05	2.80	26.41	52.46	5.60	51.87	1.10	-25	-4.36
L52	14.83	0.11	27.64	6.37	38.39	92.95	6.81	8.87	0.24	-27.6	-4.78
L53	52.33	2.86	39.91	7.85	6.33	253.98	8.93	6.76	1.01	-20.4	-3.40
L54	31.62	6.32	54.88	15.21	38.98	232.50	5.16	32.37	0.31	-26	-4.32
L55	67.14	64.90	44.03	12.50	155.03	15.12	15.44	187.45	0.07	-24.8	-4.34
L56	8.40	1.98	33.60	17.89	1.72	206.99	3.89	0.09	0.14	-32.8	-5.35
L57	15.84	2.42	15.23	5.59	17.19	23.23	8.92	54.37	0.03	-26.5	-4.49
L58	28.41	6.97	69.09	23.65	110.93	184.57	22.22	66.42	0.12	-20.3	-3.40
L59	20.15	2.64	15.48	2.37	15.93	80.55	1.39	17.23	0.39	-26.3	-4.59
L60	21.91	3.79	28.11	4.94	30.82	81.34	10.76	39.93	0.230	-25.7	-4.41
L61	25.98	7.80	21.87	9.98	79.15	28.49	0.34	20.62	0.079	-24.1	-4.20
L62	83.70	13.33	54.83	7.94	121.53	54.16	47.97	157.79	0.22	-26.5	-4.43
L63	118.70	12.74	90.40	15.83	140.68	379.32	56.09	2.66	0.65	-12.3	-2.14
L64	18.54	1.69	45.70	12.33	83.64	61.16	4.91	72.25	0.20	-25.4	-4.47
L65	28.99	5.82	100.60	40.62	65.37	215.40	20.76	221.77	0.44	-24.6	-4.12
L66	17.89	72.02	15.28	4.37	32.02	65.21	18.49	112.11	0.12	-25.4	-4.30
L67	2.70	1.85	0.23	0.05	2.82	1.48	0.33	3.49	0.001	-24.2	-4.14
L68	21.70	6.02	57.24	13.04	29.72	161.92	10.52	86.86	0.15	-25.3	-4.31
L69	4.51	1.07	15.09	0.30	1.66	57.75	0.50	2.96	0.07	-26.1	-4.61
L70	6.89	1.86	15.93	4.24	2.32	87.32	1.74	0.11	0.31	-25.6	-4.31
L71	25.39	1.59	64.90	11.84	45.77	167.83	3.98	75.42	0.56	-23.6	-3.94
L72	11.13	40.53	16.50	4.31	8.23	87.20	9.47	41.96	0.620	-20.5	-3.31
L73	12.11	2.39	45.65	9.39	16.72	136.78	13.90	10.93	0.51	-28.2	-4.64
L74	126.14	15.22	42.80	12.31	147.33	125.14	39.00	42.82	0.001	-19.1	-3.22
L75	31.79	4.69	35.30	6.29	58.55	102.66	3.48	39.94	0.22	-23	-4.01

Major ions (mg/L) and stable isotopes (‰) during wet season.

Sample ID	Na	K	Ca	Mg	Cl	HCO_3	SO_4	NO_3	F	δ^2H	$\delta^{18}O$
L76	49.34	4.52	35.70	20.65	40.29	214.36	15.45	23.27	1.11	-17.4	-3.33
L77	49.64	4.42	53.64	19.53	99.60	113.60	15.73	68.11	0.00	-17.7	-3.37
L78	72.45	21.14	31.77	6.75	105.45	23.02	6.53	148.56	0.34	-18.4	-3.58
L79	11.97	1.86	41.14	10.33	7.40	159.99	5.50	11.90	0.49	-25.8	-4.71
L80	48.57	0.11	47.12	12.80	30.11	156.28	18.17	111.44	0.95	-17.4	-3.12
L81	54.97	60.51	55.84	7.41	55.38	151.53	40.08	109.69	0.39	-23.8	-3.91
L82	9.34	14.77	9.17	3.06	7.26	12.13	1.17	81.40	0.04	-25.5	-4.21
L83	6.26	2.03	6.19	0.69	8.25	9.46	4.49	8.72	0.39	-25.8	-4.31
L84	43.44	44.47	50.06	11.72	63.74	142.43	35.87	90.00	0.16	-25.1	-4.41
L85	22.98	2.98	37.29	17.22	29.10	134.30	2.71	62.99	0.348	-24.8	-4.17
L86	24.69	6.48	87.55	24.85	66.44	216.85	34.76	12.54	0.187	-27.1	-4.80
L87	7.42	2.28	34.48	4.18	3.47	81.48	0.51	50.80	0.05	-26.6	-4.28
L88	5.70	1.09	9.74	0.68	4.15	23.77	0.32	4.07	0.03	-34.6	-5.32
L89	16.98	1.97	5.87	0.60	19.22	7.83	0.45	30.77	0.001	-26	-4.28
L90	15.11	2.43	6.41	1.68	0.87	57.69	0.85	0.14	0.12	-25.4	-4.13
L91	1.87	1.94	13.54	2.11	1.75	39.24	0.44	2.28	0.06	-30.4	-4.75
L92	12.41	2.93	3.34	0.76	3.03	37.35	0.90	0.29	0.11	-24.8	-3.52
L93	13.73	1.00	3.92	0.84	4.99	7.31	0.20	30.89	0.001	-25.7	-4.22
L94	31.00	10.42	82.72	17.08	82.84	38.86	14.82	228.61	0.04	-14.6	-2.78
L95	37.58	9.19	52.02	7.88	42.50	114.57	9.14	80.62	0.00	-23.3	-3.89
L96	16.13	4.70	29.44	7.25	5.45	146.93	5.02	0.87	0.35	-26.7	-4.23
L97	10.05	3.39	5.06	1.62	2.16	45.82	1.13	0.56	0.095	-28.7	-4.72
L98	7.47	2.47	7.50	1.53	0.88	41.23	0.93	0.49	0.14	-24.6	-3.91
L99	36.10	2.99	29.40	5.53	7.00	164.25	13.04	6.23	0.46	-33.1	-4.98
L100	10.08	2.73	21.67	4.39	8.41	60.58	2.01	19.53	0.21	-32.2	-4.57

Major ions (mg/L) and stable isotopes (‰) during wet season.

Sample ID	Na	K	Ca	Mg	Cl	HCO3	SO4	NO3	F	δ2H	δ18O
L101	66.64	24.38	99.40	20.70	111.14	199.50	28.35	122.01	0.29	-25.4	-3.90
L102	9.71	3.85	26.04	4.64	10.47	88.12	0.86	0.00	0.09	-2.5	0.39
L103	16.71	4.89	19.13	4.04	8.82	77.88	13.09	0.20	0.13	-15.9	-2.43
L104	36.86	5.04	54.21	11.12	26.04	200.77	8.00	31.39	0.46	-0.4	0.57
L105	16.48	3.33	11.41	2.38	2.05	73.11	1.13	0.05	0.10	-10.2	-0.81
L106	26.74	5.48	37.25	7.83	29.59	146.89	6.49	27.20	0.16	-24.3	-3.90
L107	10.83	4.21	16.23	3.87	4.53	33.74	3.36	44.66	0.07	-28.1	-4.47
L108	30.06	16.87	22.34	5.98	8.64	111.80	51.74	1.89	0.08	-24.2	-3.20
L109	26.72	6.09	22.65	3.48	28.97	117.59	6.81	11.15	0.00	-30.5	-4.65
L110	34.80	6.64	42.54	10.82	15.78	173.86	14.96	51.79	0.857	-24.5	-3.47
L111	22.71	4.20	18.02	4.97	7.86	103.65	10.21	1.38	0.525	-36	-4.64
L112	8.65	3.13	12.92	3.67	1.32	67.35	3.67	2.41	0.16	-30.8	-4.56
L113	3.08	3.59	15.34	1.93	1.86	60.02	0.85	0.00	0.06	-25.7	-4.20
L114	17.06	3.45	17.90	2.92	1.36	94.53	2.48	1.51	0.80	-30.7	-4.51
L115	38.62	10.98	39.51	11.74	90.06	38.68	4.22	86.07	0.04	-20.7	-3.05
L116	8.21	5.15	5.74	1.64	1.17	47.24	1.47	0.05	0.13	-12	-1.52
L117	2.99	1.07	2.74	0.89	1.28	11.51	0.29	5.18	0.00	-26.6	-4.27
L118	2.69	2.16	1.87	0.35	2.98	7.89	0.45	2.56	0.00	-24.5	-3.88
L119	30.63	7.16	41.81	4.87	40.08	168.25	2.64	0.48	0.17	-27.1	-4.63
L120	73.80	9.44	83.89	27.90	121.80	183.43	12.77	125.99	0.14	-17.4	-2.85

Major ions (mg/L) and stable isotopes (‰) during dry season.

Sample ID	Na	K	Ca	Mg	Cl	HCO_3	SO_4	NO_3	F	δ^2H	$\delta^{18}O$
L01	82.48	4.79	9.59	3.33	96.48	59.02	25.87	2.41	0.21	-36.6	-4.88
L02	15.89	17.90	15.97	4.30	21.63	28.91	5.91	57.00	0.09	-20.7	-3.38
L03	96.93	3.50	73.65	9.65	77.02	133.39	126.18	37.05	2.52	-38.4	-4.62
L04	222.30	23.90	317.40	60.95	374.88	68.31	169.29	927.21	0.34	7.8	2.43
L05	38.94	8.67	32.86	6.76	44.73	134.27	1.02	2.68	0.39	8.4	2.41
L06	52.90	6.34	54.54	16.91	66.07	42.32	12.93	218.72	0.04	-23.1	-3.19
L07	26.86	2.89	17.96	4.64	31.21	63.74	5.16	28.54	0.47	-26.2	-3.71
L08	10.56	6.83	12.46	3.15	14.95	46.41	2.44	1.32	0.11	-14.1	-1.87
L09	32.00	2.48	2.41	0.50	2.56	34.20	24.41	3.54	0.15	-33	-5.09
L10	11.16	2.34	7.67	2.01	13.16	25.78	9.02	3.04	0.00	-34.8	-5.23
L11	13.74	2.23	4.52	1.45	12.75	28.15	3.92	0.55	0.00	-38.2	-5.62
L12	27.59	11.66	33.75	11.25	35.77	52.93	21.85	72.16	0.08	-22.1	-2.64
L13	7.04	2.99	13.14	3.23	9.56	43.20	5.58	0.001	0.07	-18.1	-3.01
L14	15.06	3.13	11.58	3.14	19.63	46.15	7.37	0.001	0.04	-17.7	-2.75
L15	8.02	1.97	10.81	2.84	11.10	38.09	0.92	0.001	0.00	-19.5	-2.90
L16	8.64	2.48	5.38	1.67	12.39	25.36	0.97	0.001	0.13	-21.5	-3.45
L17	25.28	55.61	91.62	23.00	40.57	78.85	45.54	293.89	0.15	-24.4	-3.80
L18	30.81	3.08	6.96	2.10	14.83	62.46	7.87	0.00	0.16	-31	-4.48
L19	46.77	5.82	23.68	5.08	55.43	85.64	11.21	41.88	0.39	-32.6	-5.06
L20	13.82	3.03	4.78	1.16	14.52	24.71	4.73	0.001	0.32	-44.1	-6.15
L21	21.65	3.94	8.54	2.86	27.90	57.81	1.23	0.001	0.10	-27.3	-3.69
L22	6.78	2.24	9.80	2.54	9.40	35.74	0.68	0.001	0.07	-22.9	-3.08
L23	17.70	5.09	19.16	5.29	19.81	57.86	1.59	22.89	0.25	-25.2	-4.31
L24	50.62	4.70	41.02	7.23	101.12	23.56	13.17	101.80	0.15	-20.8	-3.24
L25	33.40	5.83	41.98	12.84	75.38	26.83	4.82	122.02	0.26	-25.6	-4.59

Major ions (mg/L) and stable isotopes (‰) during dry season.

Sample ID	Na	K	Ca	Mg	Cl	HCO_3	SO_4	NO_3	F	δ^2H	$\delta^{18}O$
L26	28.66	5.47	36.87	12.84	40.98	121.60	11.48	18.53	0.56	-24.8	-4.51
L27	51.66	25.72	102.40	6.49	73.85	101.37	82.10	123.46	0.41	-18.2	-3.18
L28	28.78	3.88	46.27	15.87	40.98	122.12	10.81	47.48	0.67	-24.9	-4.17
L29	13.66	4.25	39.71	6.31	18.54	95.65	6.17	28.84	0.32	-25	-4.49
L30	24.39	4.86	1.67	0.21	27.80	4.88	4.82	32.20	0.13	-26.6	-4.38
L31	247.20	9.33	168.50	25.42	354.78	103.22	89.54	407.33	0.48	-22.1	-3.77
L32	122.60	10.36	225.70	18.34	384.59	152.50	60.89	54.17	0.21	-13.1	-2.15
L33	5.52	4.26	2.58	0.56	6.36	7.49	0.44	8.22	0.04	-28.5	-4.87
L34	25.51	4.91	13.76	3.75	38.29	9.85	2.20	54.56	0.10	-27.1	-4.59
L35	19.15	5.36	14.37	4.17	24.43	45.40	6.78	7.69	0.21	-21.7	-3.31
L36	25.76	5.05	48.15	8.23	44.77	58.70	8.28	81.86	0.13	-30.6	-5.43
L37	169.30	172.90	399.40	68.72	645.14	69.67	225.99	900.34	0.63	-23.6	-4.04
L38	202.00	18.12	178.00	42.99	398.66	102.57	35.31	454.11	0.56	-16.1	-2.50
L39	13.27	1.60	17.23	3.48	13.47	16.94	38.84	2.52	0.23	-21.5	-3.34
L40	14.19	2.46	14.19	2.38	16.78	47.22	0.97	3.80	0.15	-21.4	-3.29
L41	25.85	3.54	28.24	12.20	36.00	116.78	1.94	9.25	0.43	-26.5	-4.50
L42	40.93	6.12	57.50	8.31	52.09	126.27	39.20	33.38	0.63	-15.2	-2.54
L43	24.65	1.68	41.41	3.70	15.71	102.91	15.88	0.001	0.33	-27.3	-4.68
L44	50.46	3.10	61.30	30.68	77.72	219.63	34.58	11.97	0.62	-26.9	-4.33
L45	21.40	2.32	37.75	4.34	27.97	96.60	4.71	20.01	0.38	-26	-4.26
L46	16.55	2.39	21.12	6.33	22.39	91.84	1.01	3.08	0.24	-29.7	-5.06
L47	33.93	9.43	53.23	8.42	51.47	107.94	20.63	37.32	0.30	-29.1	-4.96
L48	68.22	34.64	97.70	20.28	187.68	110.70	39.37	122.83	0.58	-21.5	-3.51
L49	14.13	4.29	10.04	1.56	19.52	10.72	0.56	35.77	0.24	-26.4	-4.44
L50	11.62	3.16	11.90	1.40	12.53	32.30	1.06	10.32	0.21	-25.6	-4.46

Major ions (mg/L) and stable isotopes (‰) during dry season.

Sample ID	Na	K	Ca	Mg	Cl	HCO_3	SO_4	NO_3	F	δ^2H	$\delta^{18}O$
L51	14.90	7.62	14.40	1.53	15.34	20.54	2.66	32.94	1.15	-26.4	-5.02
L52	27.21	4.12	22.42	7.17	58.22	46.69	8.61	1.83	0.29	-28	-4.79
L53	57.90	3.23	47.47	8.92	66.85	183.55	8.96	1.92	1.06	-17.1	-1.89
L54	26.30	6.70	45.72	13.80	37.19	153.05	4.91	17.00	0.31	-28.4	-4.72
L55	47.56	46.97	34.27	9.69	119.97	7.72	11.99	137.76	0.07	-26.4	-4.52
L56	12.13	1.14	1.92	0.65	18.45	6.90	5.61	3.75	0.13	-26.9	-4.66
L57	9.53	1.76	16.98	7.82	12.90	56.19	0.95	13.11	0.05	-27.2	-4.47
L58	28.93	7.58	63.82	24.85	104.87	91.99	23.42	55.51	0.12	-21.1	-3.24
L59	19.04	2.66	21.12	2.15	27.66	46.70	3.29	9.02	0.40	-27	-4.65
L60	17.32	3.54	19.11	4.14	23.18	35.29	7.91	25.46	0.23	-27.2	-4.57
L61	3.67	2.61	3.19	1.11	5.86	12.43	0.50	0.46	0.08	-29.5	-5.05
L62	69.23	10.64	47.97	6.04	104.18	49.86	29.77	81.75	0.23	-20.2	-3.35
L63	96.60	4.43	68.12	16.99	149.58	139.80	55.23	7.67	0.61	-11	-1.67
L64	21.71	2.08	40.35	11.13	73.72	31.28	5.22	51.02	0.18	-26.2	-4.55
L65	27.47	4.90	93.07	39.14	64.62	130.08	18.61	233.86	0.42	-24.9	-4.08
L66	22.15	60.31	14.24	4.25	29.52	30.34	21.20	79.04	0.13	-26.3	-4.35
L67	4.48	2.02	1.62	0.25	7.51	0.97	0.50	7.14	0.02	-26.1	-4.24
L68	45.28	7.17	132.80	29.80	119.63	107.79	24.78	230.98	0.16	-22.8	-3.89
L69	4.07	1.20	3.66	0.23	2.03	11.90	0.50	2.69	0.08	-24.8	-3.75
L70	6.66	1.73	12.14	4.18	8.39	45.61	2.00	0.00	0.31	-27.3	-4.54
L71	18.88	1.53	49.88	6.76	25.29	127.95	3.13	24.69	0.55	-25.5	-4.21
L72	21.81	33.32	27.73	6.91	36.44	48.50	18.84	70.13	0.36	-25.6	-4.23
L73	8.47	1.21	44.54	7.08	10.57	131.70	7.19	2.76	0.06	-27	-4.44
L74	90.32	8.04	158.10	32.91	254.71	39.30	54.73	467.31	0.07	-21.2	-3.47
L75	42.80	3.21	21.42	5.13	50.99	58.18	3.23	23.76	0.26	-24.3	-4.27

Major ions (mg/L) and stable isotopes (‰) during dry season.

Sample ID	Na	K	Ca	Mg	Cl	HCO_3	SO_4	NO_3	F	δ^2H	$\delta^{18}O$
L76	40.34	2.54	26.00	16.12	44.52	126.40	14.15	11.48	1.02	-19.7	-3.50
L77	36.12	2.93	44.98	17.69	90.02	59.70	15.26	54.83	0.05	-18.8	-3.64
L78	80.26	20.22	31.21	7.63	134.89	51.96	8.17	75.67	0.36	-16.5	-3.31
L79	33.80	2.30	82.41	28.86	85.21	104.85	24.90	127.23	0.49	-22.5	-4.13
L80	42.50	2.84	41.96	11.95	48.06	88.49	16.61	91.34	0.96	-20.4	-4.01
L81	30.52	17.11	27.92	4.64	33.73	45.77	19.55	56.94	0.41	-23.1	-4.08
L82	9.43	12.70	7.02	2.96	12.97	7.13	0.93	44.85	0.05	-26.3	-4.51
L83	6.71	1.06	4.14	0.62	9.02	4.77	0.50	6.81	0.13	-26.6	-4.48
L84	32.77	53.83	49.55	12.13	70.51	72.12	31.61	124.36	0.15	-25.7	-4.58
L85	20.58	2.73	33.26	15.39	24.86	127.03	2.43	28.93	0.35	-26.8	-4.54
L86	20.90	5.80	66.42	28.45	50.15	106.15	26.85	122.95	0.17	-29	-5.03
L87	5.44	1.30	33.46	3.25	3.13	91.32	0.50	43.18	0.05	-28.2	-4.52
L88	4.24	0.75	14.26	0.50	7.92	37.83	0.50	0.00	0.02	-35.2	-5.67
L89	15.36	0.67	24.99	0.54	22.93	57.43	0.50	24.67	0.02	-27.2	-4.44
L90	12.88	2.11	23.54	7.55	15.06	127.95	1.26	0.001	0.09	-26.7	-4.25
L91	20.53	3.71	15.28	4.18	28.90	65.22	1.71	0.001	0.04	-28.2	-3.79
L92	1.84	1.91	10.50	2.13	1.63	50.96	0.50	0.001	0.11	-31.8	-4.92
L93	31.83	0.89	19.26	4.59	35.30	103.50	0.50	21.82	0.01	-24	-3.74
L94	28.40	9.26	71.98	15.77	82.27	89.86	13.43	210.58	0.03	-12.8	-2.44
L95	31.22	6.36	23.67	6.54	49.88	45.22	9.97	84.72	0.04	-25	-4.01
L96	9.25	3.94	4.32	1.41	16.00	5.92	5.96	0.00	0.35	-28.1	-4.29
L97	6.15	3.18	2.86	1.24	10.90	4.48	2.02	2.19	0.09	-24.2	-4
L98	7.70	2.17	24.86	1.30	11.03	72.40	1.06	0.001	0.12	-26.8	-4.1
L99	33.53	2.57	53.32	5.23	38.40	85.02	13.89	7.98	0.44	-34	-4.94
L100	8.76	2.20	6.85	3.90	10.17	33.61	2.32	10.25	0.19	-32.3	-4.34

Major ions (mg/L) and stable isotopes (‰) during dry season.

Sample ID	Na	K	Ca	Mg	Cl	HCO_3	SO_4	NO_3	F	$\delta^{2}H$	$\delta^{18}O$
L101	44.51	13.63	84.49	18.93	103.17	132.51	25.46	102.25	0.24	-27.3	-4.12
L102	9.13	3.43	8.71	4.40	10.97	49.63	1.03	0.00	0.07	-3.5	0.50
L103	16.02	4.24	15.29	3.74	19.98	44.26	14.86	0.00	0.17	-17	-2.38
L104	31.15	3.89	42.42	9.15	39.56	147.73	5.40	3.17	0.44	-1.2	0.83
L105	13.94	2.80	8.98	2.24	16.53	40.58	1.44	0.00	0.12	-12	-0.87
L106	23.55	4.20	22.75	5.84	29.59	45.85	6.29	39.83	0.14	-28.6	-4.39
L107	10.18	3.75	15.19	3.75	15.01	20.12	3.75	32.31	0.05	-29.9	-4.63
L108	27.50	15.73	17.11	3.64	8.92	61.47	53.63	0.00	0.06	-26	-3.39
L109	24.09	2.66	15.26	3.24	29.72	65.05	3.22	7.47	0.23	-33.2	-4.91
L110	30.58	4.60	38.36	9.78	35.33	96.64	11.85	38.06	0.71	-26.2	-3.77
L111	21.43	3.90	15.99	4.84	28.11	57.21	10.57	0.00	0.53	-37.4	-4.83
L112	8.40	2.96	9.72	3.93	11.18	36.98	3.52	2.21	0.15	-32.9	-4.88
L113	2.83	4.80	24.96	6.51	3.05	4.84	4.74	0.00	0.05	-20.6	-2.56
L114	16.51	3.34	14.55	3.21	18.68	53.92	3.10	1.26	0.80	-32	-4.67
L115	39.46	10.92	46.50	13.85	108.38	21.91	5.32	112.20	0.03	-22.3	-3.21
L116	7.64	4.60	5.81	1.59	8.45	35.68	1.68	0.00	0.13	-14	-1.71
L117	2.13	1.09	2.14	0.58	3.43	4.88	0.13	6.76	0.01	-28.5	-4.53
L118	2.56	1.76	2.25	0.32	3.14	4.88	0.14	8.47	0.04	-26.3	-4.08
L119	24.95	3.65	26.99	8.45	33.40	52.81	5.85	49.88	0.17	-27.9	-4.60
L120	53.52	11.20	80.27	34.14	178.57	82.30	12.67	154.80	0.15	-21.5	-3.46

PTEs (µg/L) during wet season.

Sample ID	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
L01	5.0	1.0	13.5	2.0	4.0	754.0	744.7	19.6	14.8	6.4
L02	5.0	1.0	1.0	2.0	4.0	68.6	196.3	1.2	6.2	40.2
L03	5.0	1.0	1.0	2.0	4.0	13.9	1.8	1.0	21.0	108.0
L04	5.0	1.0	2.8	2.0	7.3	94.5	1223.0	1.0	5.3	1.5
L05	5.0	1.0	1.0	2.0	4.0	848.5	242.5	1.0	4.8	13.3
L06	5.0	1.0	2.2	2.0	4.0	694.6	185.5	1.3	4.0	24.9
L07	5.0	1.0	1.0	2.0	4.0	341.0	58.0	1.0	8.9	40.3
L08	5.0	1.0	1.0	5.5	6.4	105.6	2.3	1.0	4.0	8.7
L09	5.0	1.0	1.0	4.2	4.0	1.0	0.3	1.0	11.0	3.9
L10	5.0	1.0	1.0	2.6	7.5	624.5	5.7	1.0	7.8	36.9
L11	5.0	1.0	1.0	2.0	4.0	987.5	7.4	1.0	15.0	5.1
L12	5.0	1.0	1.0	2.0	5.5	56.9	4.5	1.0	4.0	37.4
L13	5.0	1.0	1.2	2.0	4.0	5498.0	810.9	1.0	4.6	9.8
L14	5.0	1.0	1.0	2.0	4.0	78.1	1.7	1.0	9.2	1.5
L15	5.0	1.0	1.0	3.8	4.0	750.0	0.3	1.0	7.2	1.3
L16	5.0	1.0	1.0	2.0	4.0	10410.0	402.7	1.0	4.6	4.9
L17	5.0	1.0	1.0	2.0	4.0	118.9	152.1	1.0	4.8	9.0
L18	5.0	1.0	1.0	5.2	4.0	8.0	2.3	1.0	10.1	8.9
L19	5.0	1.0	1.0	2.0	8.9	304.3	3.6	1.0	12.1	22.9
L20	5.0	1.0	1.0	2.0	4.0	1.0	0.3	1.0	12.3	9.9
L21	5.0	1.0	1.0	2.0	4.0	184.4	5.0	1.0	15.4	20.0
L22	5.0	1.0	1.0	2.0	12.4	40.2	0.7	1.0	13.4	9.8
L23	5.0	1.0	1.0	2.0	5.5	66.3	22.0	1.0	6.3	264.9
L24	5.0	1.0	1.0	2.0	17.3	147.1	3.8	1.0	4.5	7.4
L25	5.0	1.0	1.0	2.0	5.0	1004.0	10.0	4.9	13.1	108.5
L26	5.0	1.0	1.0	2.0	4.2	372.0	334.3	1.2	9.3	17.5
L27	5.0	1.0	1.0	2.0	4.8	3.3	3.7	1.0	5.2	12.0
L28	5.0	1.0	1.0	2.0	4.0	243.5	3.6	1.0	8.5	27.6
L29	5.0	1.0	1.0	2.0	46.8	0.1	1.5	1.1	19.0	62.2
L30	5.0	1.0	1.0	2.0	4.0	10.9	34.8	1.1	4.7	8.4
L31	5.0	1.0	1.0	2.0	19.3	19.9	35.7	1.4	5.3	27.2
L32	5.0	1.0	1.0	2.0	20.5	44.0	822.5	1.9	6.8	19.3
L33	5.0	1.0	1.0	2.0	10.0	1016.0	12.2	1.4	4.0	9.7
L34	5.0	1.0	1.0	2.0	47.1	10.7	6.0	1.9	8.6	10.1
L35	5.0	1.0	1.0	2.0	14.9	333.0	10.6	1.0	4.0	68.8
L36	5.0	1.0	1.0	2.0	5.9	144.1	3.0	1.0	13.0	11.5
L37	5.0	1.0	1.0	2.0	4.0	1.0	0.7	1.0	7.2	2.3
L38	5.0	1.0	1.0	2.0	4.2	1.0	24.5	1.0	11.5	8.8
L39	5.0	1.0	1.0	2.0	4.0	1.0	19.7	1.0	4.4	8.7
L40	5.0	1.0	1.0	2.0	4.0	1083.0	12.6	1.0	5.3	8.0

PTEs (µg/L) during wet season.

Sample ID	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
L41	5.0	1.0	1.0	2.0	4.0	1223.0	12.6	1.2	15.0	48.3
L42	5.0	1.0	1.0	2.0	4.0	503.6	2305.0	1.0	5.9	122.3
L43	5.0	1.0	1.0	2.0	4.0	1.0	8.8	1.0	4.0	9.8
L44	5.0	1.0	1.0	2.0	4.0	197.5	114.9	1.0	7.9	78.8
L45	5.0	1.0	1.0	2.0	4.0	1.0	2.0	1.0	4.0	6.7
L46	5.0	1.0	1.0	2.0	4.0	413.2	19.6	1.0	5.7	26.1
L47	5.0	1.0	1.0	2.0	4.0	344.5	90.3	1.0	6.1	4.0
L48	5.0	1.0	1.0	2.0	4.0	1.0	1.6	1.0	6.3	2.7
L49	5.0	1.0	1.0	2.0	10.2	303.8	11.5	1.0	8.8	16.8
L50	5.0	1.0	1.0	2.0	4.0	273.7	6.6	1.0	4.0	29.5
L51	5.0	1.0	1.0	2.0	4.0	34.4	2.1	1.0	5.2	8.5
L52	21.1	1.0	1.0	2.0	4.0	108.0	32.8	1.0	7.3	52.5
L53	46.5	1.0	1.0	2.0	5.7	524.0	9.5	1.0	9.1	13.1
L54	9.4	1.0	1.0	2.0	4.0	386.5	5.5	1.0	7.5	56.5
L55	5.0	1.0	1.0	2.0	4.0	1.0	9.5	3.7	11.2	7.4
L56	5.0	1.0	1.0	2.0	5.0	303.7	50.3	3.9	4.9	204.0
L57	5.0	1.0	1.0	2.0	10.6	6.2	1.2	1.8	7.6	5.6
L58	5.0	1.0	1.0	2.0	5.1	1.0	3.0	1.0	8.3	12.7
L59	5.0	1.0	1.0	2.0	4.0	2220.0	24.7	1.0	6.8	109.9
L60	5.0	1.0	1.0	2.0	4.0	1433.0	49.0	1.0	4.0	97.2
L61	5.0	1.0	1.0	2.0	4.0	19430.0	167.6	25.7	4.0	118.2
L62	5.0	1.0	1.0	2.0	4.0	1.0	1.9	1.0	4.0	6.7
L63	5.0	1.0	1.0	2.0	4.2	36.6	80.3	1.0	14.0	28.1
L64	5.0	1.0	1.0	2.0	4.0	2016.0	34.0	2.0	8.7	183.3
L65	5.0	1.0	1.0	2.0	5.4	277.5	6.0	2.1	4.7	27.6
L66	5.0	1.0	1.0	2.0	53.4	9.0	13.4	1.0	4.0	119.3
L67	5.0	1.0	1.0	2.0	25.4	102.9	3.0	1.0	4.9	46.5
L68	5.0	1.0	1.0	2.0	4.0	1265.0	14.0	1.0	14.2	12.5
L69	5.0	1.0	1.0	2.0	4.0	19.8	4.7	1.0	4.0	136.6
L70	5.0	1.0	1.0	2.0	4.0	1287.0	13.0	1.0	8.8	6.4
L71	5.0	8.4	1.0	2.0	4.0	10.6	25.0	1.0	4.6	18.8
L72	5.0	1.0	1.0	2.0	4.0	48.5	4.3	1.0	4.0	31.9
L73	5.0	1.0	1.0	2.0	4.0	1675.0	15.6	1.0	8.2	48.3
L74	5.0	1.0	1.0	2.0	6.1	74.2	147.5	1.0	11.1	13.3
L75	5.0	1.0	1.0	2.0	4.0	30.4	998.1	1.0	12.3	11.0
L76	5.0	1.0	1.0	2.0	41.7	5.9	5.2	1.0	7.1	36.7
L77	5.0	1.4	1.0	2.0	20.5	66.9	21.4	1.0	7.4	123.3
L78	5.0	2.6	1.0	2.0	4.0	8.5	964.1	5.0	4.2	28.3
L79	5.0	5.5	1.0	2.0	4.0	11.1	2.4	1.0	6.6	11.3
L80	5.0	1.0	1.0	2.0	4.0	21.8	129.0	1.0	8.7	30.9

PTEs (µg/L) during wet season.

Sample ID	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
L81	5.0	12.8	1.0	2.0	9.6	17.0	2.8	1.0	4.0	64.9
L82	5.0	2.1	2.2	2.0	5.3	6.8	56.3	4.6	4.0	11.3
L83	5.0	4.5	1.0	2.0	33.4	3717.0	37.1	1.3	32.1	44.4
L84	5.0	1.0	1.0	2.0	4.0	1.0	24.9	1.0	6.2	6.5
L85	5.0	1.0	1.0	2.0	4.0	1.0	0.5	1.0	4.8	7.4
L86	5.0	1.0	1.0	2.0	4.0	697.6	8.9	1.0	4.0	14.0
L87	5.0	12.7	1.0	2.0	4.0	49.3	21.1	2.2	4.3	49.0
L88	5.0	5.1	1.0	2.0	4.0	1339.0	223.5	1.0	9.1	11.8
L89	5.0	1.0	1.0	2.0	51.0	26.7	13.8	1.8	4.1	49.0
L90	5.0	1.0	1.0	2.0	4.0	4499.0	105.1	1.0	15.0	8.6
L91	5.0	8.9	1.0	2.0	19.9	21.4	1.3	1.0	24.1	18.1
L92	5.0	1.0	1.0	2.0	7.3	15790.0	158.9	1.8	4.0	26.6
L93	5.0	1.5	1.0	2.0	4.0	8.3	11.0	1.4	4.0	6.5
L94	5.0	8.6	1.0	2.0	6.6	18.2	6.3	1.0	4.5	26.9
L95	5.0	22.6	3.7	2.0	4.0	95.1	201.2	1.5	4.0	40.1
L96	5.0	3.7	1.0	2.0	4.0	387.5	1317.0	1.0	4.0	13.8
L97	5.0	1.0	1.0	2.0	4.0	530.5	141.9	1.0	4.9	8.3
L98	5.0	1.0	1.0	2.0	5.4	113.7	7.9	1.0	5.4	8.3
L99	5.0	7.6	1.0	2.0	4.0	6250.0	78.0	1.0	7.7	16.6
L100	5.0	4.4	1.0	2.0	7.0	249.7	15.9	1.0	15.2	141.4
L101	5.0	6.4	2.7	2.0	7.4	599.2	1711.0	1.0	7.9	48.7
L102	5.0	13.6	1.0	2.0	4.0	2552.0	25.9	1.0	7.1	34.5
L103	11.0	2.7	2.1	2.0	4.0	12160.0	431.2	1.9	6.2	35.9
L104	5.0	2.7	1.0	2.0	4.0	92.1	103.4	1.0	8.3	13.5
L105	5.0	2.3	1.0	2.0	4.0	264.8	7.3	1.0	8.1	31.7
L106	5.0	1.0	1.0	2.0	5.4	1789.0	32.7	1.0	11.5	71.5
L107	5.0	1.0	1.0	2.0	11.8	599.6	10.9	1.0	7.2	133.9
L108	5.0	1.0	1.0	2.0	6.9	5.9	244.0	1.0	13.2	14.0
L109	5.0	1.0	1.0	2.0	4.9	317.4	6.2	1.0	16.1	15.2
L110	5.0	1.0	1.0	2.0	4.0	161.6	16.8	1.0	8.9	71.0
L111	5.0	1.5	1.0	2.0	4.0	7.4	0.7	1.0	5.3	6.0
L112	5.0	1.0	1.0	2.0	4.0	645.6	12.7	1.0	5.6	51.3
L113	5.0	1.0	1.0	2.0	4.0	23.7	21.5	1.0	4.8	5.8
L114	5.0	8.6	1.0	2.0	4.1	391.6	20.7	1.0	6.9	139.9
L115	5.0	1.0	1.0	2.0	4.0	8.0	8.1	2.6	4.2	13.4
L116	5.0	1.0	1.0	2.0	4.0	2800.0	201.6	1.0	4.9	23.8
L117	5.0	1.0	1.0	2.0	24.9	85.2	10.3	2.8	4.0	16.4
L118	5.0	1.0	1.0	2.0	4.0	17.8	27.2	1.0	4.0	15.4
L119	5.0	1.0	1.0	2.0	4.0	8.4	14.8	1.0	9.9	12.5
L120	5.0	1.0	1.0	2.0	4.0	74.7	2.6	1.0	7.8	9.9

PTEs (μg/L) during dry season.

Sample ID	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
L01	5.0	1.0	9.6	2.0	4.0	5.4	2.1	9.3	13.2	10.9
L02	5.0	1.0	1.0	2.0	4.0	130.7	57.8	1.0	4.4	46.6
L03	5.0	1.0	1.0	2.0	4.0	9.9	1.1	1.0	10.0	12.9
L04	5.0	1.0	2.6	2.0	9.7	489.1	1251.0	1.0	6.7	10.5
L05	5.0	1.0	1.0	2.0	4.0	621.4	234.1	1.0	5.0	19.3
L06	5.0	1.0	19.0	2.0	4.0	283.8	174.6	1.0	4.0	14.1
L07	5.0	1.0	1.0	2.0	5.3	63.4	36.7	1.0	8.9	16.2
L08	5.0	1.0	1.0	6.4	4.0	65.3	2.8	1.0	4.2	12.7
L09	5.0	1.0	1.0	4.5	4.0	3.4	0.4	1.0	12.1	6.7
L10	5.0	1.0	1.0	2.8	4.0	10.9	1.1	1.0	8.9	120.7
L11	5.0	1.0	1.0	2.0	4.0	6.5	0.5	1.0	10.0	10.5
L12	5.0	1.0	1.0	2.0	4.0	197.7	14.4	1.0	4.0	38.6
L13	5.0	1.0	1.0	3.8	4.0	9364.0	799.0	1.0	4.4	16.1
L14	5.0	1.0	1.0	2.0	4.0	78.1	3.9	1.4	6.3	18.5
L15	5.0	1.0	1.0	4.7	4.0	5.4	0.4	1.9	10.1	7.2
L16	5.0	1.0	1.0	2.0	4.0	8149.0	344.9	1.0	4.6	12.5
L17	5.0	1.0	1.0	2.0	4.9	260.6	66.9	1.0	5.6	28.4
L18	5.0	1.0	1.0	2.0	4.0	19.5	2.7	1.0	11.6	15.6
L19	5.0	1.0	1.0	2.0	4.0	70.0	2.8	1.0	15.0	33.9
L20	5.0	1.0	1.0	2.0	4.0	2.3	0.3	1.0	12.3	8.3
L21	5.0	1.0	1.0	2.0	4.0	211.5	11.1	1.0	12.5	117.7
L22	5.0	1.0	1.0	2.0	14.1	32.1	1.2	1.0	12.3	27.2
L23	5.0	1.0	1.0	2.0	4.0	330.8	13.9	1.0	8.6	54.6
L24	5.0	1.0	1.0	2.0	18.5	297.4	5.0	1.0	4.8	22.0
L25	5.0	1.0	1.0	2.0	14.1	326.0	11.8	6.3	11.6	40.1
L26	5.0	1.0	1.0	2.0	4.0	409.3	7.2	1.0	8.2	17.4
L27	5.0	1.0	1.0	2.0	4.0	12.7	6.8	1.0	7.4	17.2
L28	5.0	1.0	1.0	2.0	4.0	493.9	4.7	1.0	6.3	39.5
L29	5.0	1.0	1.0	2.0	56.3	8.1	0.7	1.5	10.6	61.6
L30	5.0	1.0	1.0	2.0	4.0	112.2	15.6	2.4	4.4	11.2
L31	5.0	1.0	1.0	2.0	34.5	39.1	92.2	1.0	5.3	68.9
L32	5.0	1.0	1.6	2.0	18.2	105.8	570.0	3.5	8.8	32.6
L33	5.0	1.0	1.0	2.0	4.0	827.0	3.4	1.0	4.0	7.5
L34	5.0	1.0	1.0	2.0	29.9	12.8	5.3	1.6	7.7	19.6
L35	5.0	1.0	1.0	2.0	4.0	146.8	2.6	1.0	4.0	9.6
L36	5.0	1.0	1.0	2.0	11.3	372.8	4.3	1.0	9.7	37.4
L37	5.0	1.0	1.0	2.0	11.0	6.3	6.3	1.0	5.9	13.2
L38	5.0	1.0	1.0	2.0	9.2	245.7	87.4	1.0	11.5	14.0
L39	5.0	1.0	1.0	2.0	4.0	24.5	10.1	1.0	4.3	14.2
L40	5.0	1.0	1.0	2.0	4.0	27.4	2.6	1.0	5.3	11.1

PTEs (µg/L) during dry season.

Sample ID	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
L41	5.0	1.0	1.0	2.0	4.0	1087.0	8.2	1.8	8.6	11.3
L42	5.0	1.0	1.0	2.0	6.2	184.3	1597.0	1.0	5.9	67.4
L43	5.0	1.0	1.0	2.0	4.0	6.6	1.9	1.0	4.0	10.4
L44	5.0	1.0	1.0	2.0	4.0	85.1	176.2	1.0	7.6	23.6
L45	5.0	1.0	1.0	2.0	4.0	1.0	0.7	1.0	6.8	24.3
L46	5.0	1.0	1.0	2.0	4.0	347.6	20.3	1.0	6.9	111.7
L47	5.0	1.0	1.0	2.0	4.0	472.3	139.3	1.0	6.7	18.0
L48	5.0	1.0	1.0	2.0	4.0	1.0	0.3	1.0	6.3	5.7
L49	5.0	1.0	1.0	2.0	8.0	498.9	8.9	1.0	7.1	48.7
L50	5.0	1.0	1.0	2.0	4.0	13.2	33.9	1.0	4.9	14.1
L51	5.0	1.0	1.0	2.0	6.1	29.7	1.4	1.0	6.1	14.0
L52	8.4	1.0	1.0	2.0	4.0	11780.0	92.6	1.0	8.0	50.3
L53	5.0	4.5	1.0	2.0	4.0	131.8	8.0	1.0	9.7	90.2
L54	18.8	5.0	1.0	2.0	4.0	133.2	5.0	1.0	6.5	23.8
L55	6.8	1.0	1.0	2.0	25.0	23.4	28.0	6.2	16.1	302.8
L56	5.0	1.0	1.0	2.0	4.0	145.4	28.8	4.7	5.7	12.0
L57	5.0	1.0	1.0	2.0	4.0	5.5	0.9	1.0	6.6	17.1
L58	5.0	1.0	1.0	2.0	7.7	4.4	2.9	1.0	7.5	18.2
L59	5.0	1.0	1.0	2.0	4.0	1230.0	12.3	1.0	6.6	10.1
L60	5.0	1.0	1.0	2.0	4.0	584.3	7.2	1.0	4.9	23.1
L61	5.0	1.0	1.0	2.0	7.1	115.7	3.4	1.0	4.0	21.8
L62	5.0	1.0	1.0	2.0	4.0	14.2	109.8	1.0	4.0	17.7
L63	5.0	1.0	1.0	2.0	4.0	12.8	249.7	1.0	7.9	9.8
L64	5.0	1.0	1.0	2.0	4.0	579.5	14.0	1.0	8.1	36.9
L65	5.0	1.0	1.0	2.0	4.0	536.1	4.9	1.9	8.9	17.2
L66	5.0	1.0	1.0	2.0	52.3	9.9	9.0	1.0	4.0	120.0
L67	5.0	1.0	1.0	2.0	17.2	140.7	7.1	1.0	4.0	33.5
L68	5.0	1.0	1.0	2.0	6.6	251.4	5.4	1.0	6.6	51.6
L69	5.0	1.0	1.0	2.0	4.0	27.3	21.2	1.0	4.0	175.1
L70	5.0	1.0	1.0	2.0	4.0	164.1	5.7	1.0	7.5	28.9
L71	12.0	5.8	1.0	2.0	4.0	30.4	1.0	1.0	5.3	27.8
L72	5.0	1.0	1.0	2.0	4.0	15.1	3.0	1.0	4.0	10.1
L73	5.0	1.0	1.0	2.0	4.0	2507.0	20.4	1.0	6.0	35.6
L74	5.0	1.0	1.0	2.0	8.5	32.2	159.5	1.0	8.7	9.7
L75	5.0	1.0	1.0	2.0	4.8	296.0	772.5	1.0	8.3	27.8
L76	5.0	1.0	1.0	2.0	4.0	4.6	136.7	1.0	7.7	13.3
L77	5.0	1.0	1.0	2.0	12.1	11.0	17.5	1.0	8.6	58.0
L78	5.0	2.1	14.7	2.0	4.0	43.9	1667.0	1.0	4.0	73.9
L79	5.0	4.3	1.0	2.0	4.0	12.0	3.3	1.0	7.9	11.8
L80	5.0	1.0	1.0	2.0	4.0	3.0	113.8	1.0	8.0	294.8

PTEs (μg/L) during dry season.

Sample ID	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
L81	5.0	12.8	1.0	2.0	4.6	11.5	1.6	1.0	5.9	80.6
L82	5.0	1.0	2.5	2.0	4.0	13.9	51.3	3.8	4.0	13.8
L83	5.0	3.6	1.0	2.0	8.8	1064.0	12.8	1.0	28.8	34.8
L84	5.0	1.0	1.0	2.0	4.0	10.6	106.1	1.0	4.0	154.6
L85	5.0	1.0	1.0	2.0	4.0	13.9	1.1	1.0	5.9	16.8
L86	5.0	1.0	1.0	2.0	4.0	1390.0	31.5	1.0	9.2	43.4
L87	5.0	10.3	1.0	2.0	4.0	72.3	21.1	1.0	4.0	40.2
L88	5.0	6.8	1.0	2.0	4.0	297.7	122.6	2.1	4.0	8.3
L89	5.0	1.0	1.0	2.0	23.9	5.3	14.2	1.0	4.0	20.9
L90	5.0	1.0	1.0	2.0	4.0	531.1	64.0	1.0	6.9	11.1
L91	5.0	1.0	1.0	2.0	4.0	256.9	18.2	1.0	11.1	23.8
L92	5.0	1.0	1.0	2.0	14.6	17.4	0.7	1.0	4.0	16.7
L93	5.0	1.0	1.0	2.0	4.0	6.2	10.9	1.0	4.0	12.0
L94	5.0	5.1	1.0	2.0	5.8	15.5	6.1	1.0	4.0	15.8
L95	5.0	19.2	2.8	2.0	4.0	5.3	182.7	1.0	4.0	29.1
L96	5.0	2.6	1.0	2.0	4.0	57.5	1142.0	1.0	4.0	29.6
L97	5.0	1.0	1.0	2.0	4.0	578.0	201.3	1.0	4.0	14.9
L98	5.0	1.0	1.0	2.0	4.0	35.9	11.1	1.0	6.5	31.5
L99	5.0	8.2	1.0	2.0	4.0	1840.0	55.3	1.0	8.7	55.4
L100	5.0	3.8	1.0	2.0	7.0	248.9	7.9	1.0	10.8	60.9
L101	5.0	3.6	1.0	2.0	5.3	334.3	1846.0	1.0	6.3	22.0
L102	5.0	10.2	1.0	2.0	4.0	9618.0	75.1	1.0	6.9	47.6
L103	10.8	3.4	2.6	2.0	4.0	10220.0	388.7	1.0	6.2	21.5
L104	5.0	2.9	1.0	2.0	4.0	190.8	91.8	1.0	8.1	9.5
L105	5.0	3.1	1.0	2.0	4.0	1783.0	15.0	1.0	8.2	9.6
L106	5.0	1.0	1.0	2.0	4.0	461.9	3.2	1.0	7.5	8.8
L107	5.0	1.0	1.0	2.0	4.0	44.8	4.2	1.0	5.5	41.4
L108	5.0	1.0	1.0	2.0	4.0	9.1	1.9	1.0	10.1	4.9
L109	5.0	1.0	1.0	2.0	4.0	455.8	8.7	1.0	10.4	47.1
L110	5.0	1.0	1.0	2.0	4.0	426.5	17.1	1.0	8.9	55.3
L111	5.0	1.5	1.0	2.0	4.0	7.0	0.3	1.0	7.8	13.7
L112	5.0	1.0	1.0	2.0	4.0	187.8	6.7	1.0	6.9	11.7
L113	5.0	1.0	1.0	2.0	4.0	111.1	39.4	1.0	4.0	24.9
L114	5.0	7.2	1.0	2.0	4.0	229.7	12.7	1.0	6.4	54.5
L115	5.0	1.0	1.0	2.0	4.0	10.9	9.7	1.0	4.2	16.9
L116	5.0	1.0	1.0	2.0	4.0	2244.0	168.1	1.0	5.1	32.1
L117	5.0	1.0	1.0	2.0	13.6	145.7	9.2	2.3	4.0	19.0
L118	5.0	1.0	1.0	2.0	4.0	32.2	48.2	1.0	4.0	20.3
L119	5.0	1.0	1.0	2.0	4.0	21.6	1.5	1.0	8.1	26.9
L120	5.0	1.0	1.0	2.0	7.7	673.8	12.5	5.6	6.7	684.5