DEPARTMENT OF CIVIL & ENVIRONMENTAL ENGINEERING

University of Strathclyde Engineering

Isotope hydrology and hydrogeochemistry of surface water and groundwater in the Lake Malawi basin to support sustainable water resource management

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This thesis is submitted in partial fulfilment of the requirement for the degree of

DOCTOR OF PHILOSOPHY

The University of Strathclyde , SCOTLAND

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Limbikani Chitsundi Banda

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immeasurable support and friendship, enriched my PhD journey. Moreover, I have been fortunate to have emotional and moral support from a circle of friends who kept me balanced and focused. I sincerely thank Mr. Alphaeus Ngonga, Mr. Kennedy Chitsundi Banda, and Dr. Maxwell Mkondiwa for their enduring friendship and solidarity during my PhD pursuit.

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Thank you all!

TO GOD BE THE GLORY

ABSTRACT

This thesis presents groundbreaking body of research aimed at examining meteoric water inputs and their interactions with surface water and groundwater systems to enhance understanding of Lake Malawi basin's hydrological processes to provide transformative insights into the basin's water cycle. This was achieved through an innovative multi-method approach that integrated stable isotopic and hydrogeochemical tracers. The thesis adopted an integrated-holistic methodological framework that considered precipitation, groundwater and surface water as interconnected systems in the basin's water cycle. The aim and objectives of the research were achieved through a series of scientific publications, forming a significant body of research with critical-practical and policy implications. The thesis successfully established a baseline for stable isotopes in precipitation, a fundamental benchmark for future isotopic studies in Malawi and the wider region. This foundational isotopic baseline provided groundbreaking isotopic insights into Malawi's water cycle by establishing a pioneering Local Meteoric Water Line, consistent with the Global Meteoric Water Line. The thesis revealed predominant oceanic and continental influences marked by moisture recycling likely from the African Great Lakes' large scale evaporation effect and seasonal shifts in the Intertropical Convergence Zone. The thesis provides increased and unique insights into origin of groundwater and geochemical evolution dynamics within the Lake Malawi basin's aquifer systems. The thesis demonstrates primary influence of non-evaporated modern precipitation on groundwater recharge, initiating critical geochemical reactions with host rock minerals upon infiltration into the subsurface zone. The rock mineral-water reactions release essential ionic species and form secondary minerals, with sodium and calcium ions being predominant cations, thereby influencing groundwater chemistry. Through geochemical modelling insights, the thesis clarified that groundwater evolution is dominated by silicate dissolution reactions, highlighting critical

relationships between meteoric water inputs, evaporative processes, and spatial-seasonal variations in groundwater hydrochemistry. The thesis further revealed distinct hydrogeochemical signatures and widespread nitrate occurrence, the latter underscoring potential human impacts on groundwater quality. The thesis established a basin-scale isotopic and hydrochemical baseline characterization of surface water using isotopic and chemical tracers. It showed that surface water flows are primarily influenced by non-evaporated modern precipitation and groundwater baseflow inputs, with distinct seasonal variability. Riverine flows exhibited greater isotopic variability than lakes and reservoirs, with predominant wet season depleted signals at higher elevations and dry season enriched signals in lowlands. Convergence of highland-plateau and rift margin river systems resulted in isotopic depletion within rift valley escarpment zones and progressive enrichment through lakeshore flood plains. The thesis highlights significant contribution of local precipitation to surface water flows and retention of isotopic enrichment signals in lakes likely due to high residence time. The thesis aligns with Malawi's Water Policy, Sustainable Development Goal 6, Water Resources Act-2013, and 2063 Development Agenda, advocating for expanded monitoring networks, cross-disciplinary collaborations, and community engagement. It also supports the objectives of GloWAL Network, IWAVE, GNIP, and GNIR, emphasizing regional collaboration and comprehensive data collection and sharing. Overall, this thesis provides new and unique knowledge critical for advancing understanding of Lake Malawi basin's hydrological cycle. It serves as a call to action for evidence-based sustainable water management, underscoring the importance of innovative, interdisciplinary, and participatory approaches. The thesis outcomes are expected to inform and guide development of sustainable water resource management strategies that aligns with objectives of SDG 6 and IWRM practices. This thesis delivers a new and unique body of research with critical policy, practical and scholarly implications.

PREFACE

This thesis comprises nine chapters, with Chapters 4 through 7 dedicated to addressing specific research questions. Each question is explored via a series of research articles that have been published, are currently under review, or are in preparation for submission to peer-reviewed journals. The primary aim and objectives of the research were achieved through a series of research articles that formed a significant body of research, with policy and practical implications for water resources monitoring framework and water policy initiatives, critical for guiding integrated water resources management (IWRM) practices and achieving the objectives of Sustainable Development Goal (SDG) 6. The format of Chapters 4 to 7 features a preface, a research article, and a postface. The preface in each of these chapters introduces the correlating research article and outlines the research question being tackled. It explains how the chapter connects with the rest of the thesis, thus enhancing thesis coherence and readability. Following the research article, the postface discusses principal article findings and elaborates on how the research question was resolved. It further illustrates integration of the research article within the overall framework of the thesis. It should be noted that when incorporating published peer-reviewed journal articles, their respective journal formats and styles have been maintained for individual journal identity. Also, references have been presented based on individual chapters for ease of navigation and readability. The following section presents a summary of research articles included in the thesis. This summary specifies the chapter, title, author contributions and research funding details. It also includes supplementary research articles, produced just prior and within the PhD period, that either form a partial inclusion or are completely outside the scope of the PhD research. Comments from peer-review process of the published and under-review articles, along with the authors' responses, detailing how each comment was addressed, are presented in appendix section.

MAIN RESEARCH ARTICLES

Research Article 1: Chapter 4

water

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Article

National Stable Isotope Baseline for Precipitation in Malawi to Underpin Integrated Water Resources Management

Limbikani C. Banda [1,*], Michael O. Rivett [2], Anold S. K. Zavison [3], Sydney Kamtukule [3] and Robert M. Kalin [1]

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This research article was peer-reviewed and published in the *Water-MDPI journal*, and it can be accessible via the following web link: [https://doi.org/10.3390/w13141927]. Below are details regarding contributions of authors and research funders. Importantly, this research article constitutes a significant body of knowledge in Chapter 4 of this thesis entitled "Baseline Characterization of Stable Isotopes in Precipitation."

Author Contributions: Conceptualization, L.C.B., M.O.R. and R.M.K.; methodology, L.C.B. and M.O.R.; validation, L.C.B. and A.S.K.Z.; formal analysis, L.C.B. and M.O.R.; investigation, L.C.B.; resources, L.C.B. and A.S.K.Z.; data curation, L.C.B. and A.S.K.Z.; writing—original draft preparation, L.C.B. and M.O.R.; writing—review and editing, M.O.R., L.C.B. and R.M.K.; visualization, L.C.B.; supervision, R.M.K. and S.K.; project administration, R.M.K. and S.K.; funding acquisition, S.K., R.M.K. and L.C.B. All authors have read and agreed to the published version of the manuscript.

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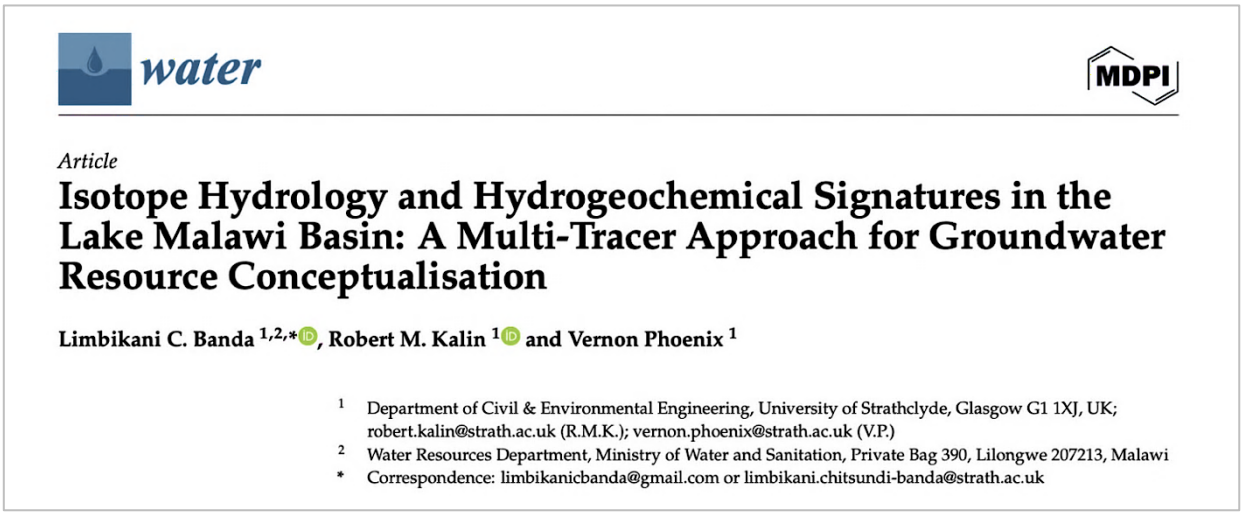
Research Article 2: Chapter 5



water

MDPI

Article

Isotope Hydrology and Hydrogeochemical Signatures in the Lake Malawi Basin: A Multi-Tracer Approach for Groundwater Resource Conceptualisation

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This research article was peer-reviewed and published in the *Water-MDPI journal*, and it can be accessed via the following web link: [https://doi.org/10.3390/w16111587]. Below are details regarding contributions of authors and research funders. Importantly, this research article constitutes a significant body of knowledge in Chapter 5 of this thesis entitled "Groundwater Resource Conceptualisation."

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Research Article 3: Chapter 6

Science of the Total Environment

Isotopic and Hydrochemical Tracers Reveal Surface Water Dynamics in the Lake Malawi Basin: A Mixed-Proxy Approach for Water Resource Conceptualization

--Manuscript Draft--

Manuscript Number:	STOTEN-D-24-44759
Article Type:	Research Paper
Keywords:	transboundary water resource; d-excess; stable isotope tracing; integrated water resource management; evaporation effect; conceptual model
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	Robert Michael Kalin, BSc MSc, PhD, CEnv, FICE, FRSC, FGS
	Vernon Phoenix

This research article was submitted to *Science of the Total Environment journal* for publication and is currently under peer-review consideration. The authorship contributions and funding details related to the research article are outlined below: Notably, the research article forms a significant body knowledge in Chapter 6 of this thesis entitled "Surface Water Resource Conceptualisation."

Research Article 4: Chapter 7 (7.1)

Constraining water-resource conceptualization through dual-stable isotope tracing of meteoric water inputs: Insights into surface and ground water dynamics in a Lake Malawi sub-basin

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This research article is in preparation for submission to *Journal of Hydrology, Regional Studies* for peer-review and publication. Below are details of authorship contributions and funding information associated with this research. This research article constitutes an important part of Chapter 7 of the thesis entitled "Groundwater and Surface Water Dynamics".

Author Contributions: Conceptualisation, L.C.B. and R.M.K.; methodology, L.C.B.; validation, L.C.B.; formal analysis, L.C.B. and R.M.K.; investigation, L.C.B.; resources, L.C.B. and R.M.K.; data curation, L.C.B.; writing—original draft preparation, L.C.B.; writing—review and editing, L.C.B., R.M.K. and V.P., visualisation, L.C.B. and R.M.K.; supervision, R.M.K. and V.P.; project administration, L.C.B., R.M.K. and V.P.; funding acquisition, L.C.B., R.M.K. and V.P. All authors have read and agreed to the published version of the manuscript.

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Research Article 5: Chapter 7 (7.2)

Seasonal and spatial dynamics of surface and ground water in South Rukuru River and Nkhata Bay lakeshore catchments: Implications for integrated water resource management.

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Author Contributions: Conceptualisation, L.C.B. and R.M.K.; methodology, L.C.B.; validation, L.C.B.; formal analysis, L.C.B. and R.M.K.; investigation, L.C.B.; resources, L.C.B. and R.M.K.; data curation, L.C.B.; writing—original draft preparation, L.C.B.; writing—review and editing, L.C.B., R.M.K. and V.P., visualisation, L.C.B. and R.M.K.; supervision, R.M.K. and V.P.; project administration, L.C.B., R.M.K. and V.P.; funding acquisition, L.C.B., R.M.K. and V.P. All authors have read and agreed to the published version of the manuscript.

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Research Article 6: Chapter 7 (7.3)

Groundwater and Surface Water Resource Conceptualisation using δD and $\delta^{18}O$ Tracers in the Songwe River/Lufira River, North Rukuru River and Karonga Lakeshore Catchments, a Transboundary Lake Malawi sub-Basin.

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SUPPLEMENTARY RESEARCH ARTICLES

Supplementary Research Article 1: Appendix

water

MDPI

Article

Water–Isotope Capacity Building and Demonstration in a Developing World Context: Isotopic Baseline and Conceptualization of a Lake Malawi Catchment

Limbikani C. Banda [1,*], Michael O. Rivett [2], Robert M. Kalin [2], Anold S.K. Zavison [1], Peaches Phiri [1], Laura Kelly [2], Geoffrey Chavula [3], Charles C. Kapachika [4], Macpherson Nkhata [1], Sydney Kamtukule [1], Prince Mleta [1] and Muthi Nhlema [5]

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This research article was peer-reviewed and is published in the *Water-MDPI journal*. It can be accessed at the following URL: [https://doi.org/10.3390/w11122600]. This study was conducted prior to the current research specifically to amass a significant body of data and information to inform the preliminary conceptualization of the ongoing research. This article is included as a supplementary article in the appendix section of the thesis. Below, details about the authors' contributions and funding sources are provided.

Author Contributions: Conceptualization, L.C.B., M.O.R., R.M.K., A.S.K.Z.; methodology, L.C.B., M.O.R. and R.M.K.; validation, L.C.B., A.S.K.Z.; formal analysis, L.C.B., M.O.R., L.K. and C.C.K.; investigation, L.C.B., M.O.R., L.K., A.S.K.Z.; resources, L.C.B., A.S.K.Z., P.P.; data curation, L.C.B., A.S.K.Z. and L.K.; writing—original draft preparation, L.C.B. and M.O.R.; writing—review and editing, M.O.R., L.C.B., L.K., R.M.K., G.C., P.P., M.N. (Macpherson Nkhata) and M.N. (Muthi Nhlema); visualization, L.C.B., M.O.R., C.K. and L.K.; supervision, R.M.K., M.O.R., P.P., P.M., S.K.; project administration, R.M.K., S.K., P.P. and M.N. (Muthi Nhlema); funding acquisition, R.M.K., S.K., P.M. and P.P.

Funding: We gratefully acknowledge the funding by the International Atomic Energy Agency (IAEA) under the Malawi Technical Cooperation (TC) Projects' grants (MLW/7/001: MLW/7/002/MLW/7/003), awarded to the Government of Malawi (Department of Water Resources in the Ministry of Agriculture, Irrigation and Water Development). We also acknowledge the financial contribution we received from the Government of Malawi and the Scottish Government Climate Justice Fund-Water Futures Programme research grant HN-CJF-03 awarded to the University of Strathclyde.

Supplementary Research Article 2: Appendix

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journal homepage: www.elsevier.com/locate/scitotenv

Mixed method analysis of anthropogenic groundwater contamination of drinking water sources in Malawi

Rebekah G.K. Hinton [a,b,*], Robert M. Kalin [a], Limbikani C. Banda [a,c], Modesta B. Kanjaye [d], Christopher J.A. Macleod [b], Mads Troldborg [b], Peaches Phiri [c], Sydney Kamtukule [c]

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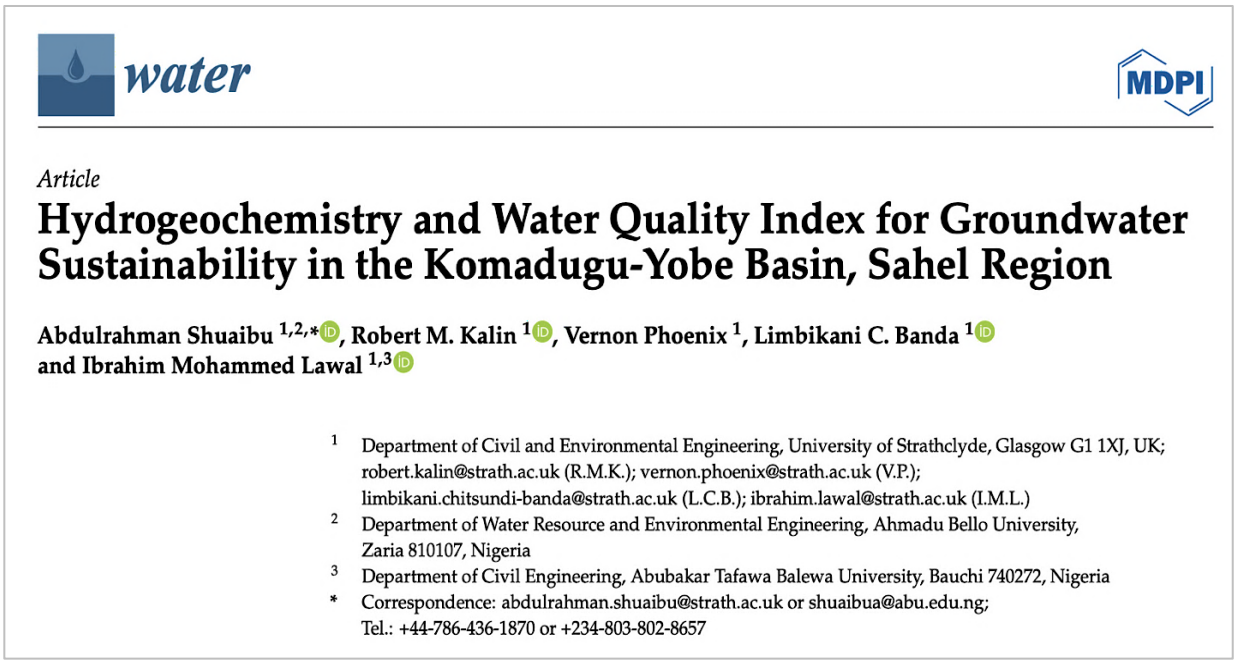
This co-authored research article was peer-reviewed and published in the *Science of the Total Environment journal*, and it can be accessed via the following URL: [https://doi.org/10.1016/j.scitotenv.2024.177418]. In this study, my primary contribution involved application of nitrogen-related isotopes (^{15}N) to trace the origins of nitrate in groundwater supplies throughout Malawi. This research article was prompted by findings from the thesis's principal paper, referred to here as research article 2 in Chapter 5 on conceptualization of groundwater resources and highlighted widespread presence of nitrate in groundwater across the Lake Malawi basin. Outline below are individual contributions of each author to the article.

Rebekah G.K. Hinton: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Robert M. Kalin: Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Formal analysis, Conceptualization. **Limbikani C. Banda:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Formal analysis, Data curation, Conceptualization. Modesta B. Kanjaye: Writing – review & editing, Conceptualization. Christopher J.A. Macleod: Writing – review & editing, Conceptualization. Mads Troldborg: Writing – review & editing, Conceptualization. Peaches Phiri: Writing – review & editing, Conceptualization. Sydney Kamtukule: Writing – review & editing, Conceptualization. This research article presented alongside its supplementary materials in the appendix section.

Supplementary research article 3: Appendix



water

MDPI

Article

Hydrogeochemistry and Water Quality Index for Groundwater Sustainability in the Komadugu-Yobe Basin, Sahel Region

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linked to the correct research but demonstrates my progress on research professional development through research engagement, collaboration and networking. This research article is presented alongside its supplementary materials in the appendix section.

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Science of the Total Environment

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the correct research. However, it demonstrates my strong research engagement and collaboration to foster researcher professional development and research engagement to foster collaboration, networking and sound skills and knowledge sharing. This research article is presented alongside its supplementary materials in the appendix section.

CRediT authorship contribution statement

Abdulrahman Shuaibu: Conceptualization, methodology, software, validation, formal analysis, investigation, resources, data curation, writing—original draft preparation, writing—review and editing, project administration, funding acquisition. **Robert M Kalin:** Conceptualization, validation, writing—review and editing, supervision, funding acquisition. **Vernon Phoenix:** validation, writing—review and editing, supervision, funding acquisition. **Limbikani C. Banda:** validation, writing—review and editing, visualization. **Rebekkah G. Hinton:** writing-editing. All authors have read and agreed to the published version of the manuscript.

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List of Abbreviations and Acronyms

‰	Permil
° C	degree Celsius
^{16}O	Oxygen-16
^{17}O	Oxygen-17
^{18}O	Oxygen-18
^{1}H	Protium
^{2}H	Deuterium
^{3}H	Tritium
CJF	Climate Justice Fund
cm	Centimetre
CWL	Central Water Laboratory
d	Deuterium excess (d-excess)
EARS	East African Rift System
EC	Electrical Conductivity
EIV-LMWL	Error in variables—Local Meteoric Water Line
GIS	Geographical Information System
GMWL	Global Meteoric Water Line
GNIP	Global Network of Isotopes in Precipitation
DCCMS	Department of Climate Change and Meteorological Services
GoM	Government of Malawi
GPS	Global Positioning System
H_2O	Water Molecule

IRMS	Isotope Ratio Mass Spectrometer
ISP	International Standard Procedure
ITCZ	Intertropical Convergence Zone
IWA	Isotopic Water Analyser
IWRM	Integrated Water Resources Management
Km	Kilometre
LEL	Local Evaporation Line
LIMS	Laboratory Information Management System
LMWL	Local Meteoric Water Line
m	Metre
masl	Metres above sea level
MDG	Millennium Development Goal
mg/L	Milligrams per litre
mm	Millimetre
MNIP	Malawi Network of Isotopes in Precipitation
MoAIWD	Ministry of Agriculture Irrigation and Water Development
MRPLP	Malawi Resilient Productive Landscapes Project
MWL	Meteoric Water Line
pH	power of Hydrogen ions
PI	Principal Investigator
RMWL	Regional Meteoric Water Line
RO	Research Objective
RQ	Research Question
SADC	Southern African Development Community

SDG	Sustainable Development Goal
SM	Supplementary Material
SVTP	Shire Valley Transformation Project
TBA	Trans-Boundary Aquifer
TDS	Total Dissolved Salts
UN	United Nations
UNEP	United Nations Environment Programme
IPCC	Intergovernmental Panel on Climate Change
IAEA	International Atomic Energy Agency
IWAVE	IAEA-Water Availability Enhancement
VSMOW	Vienna Standard Mean Ocean Water
WHO	World Health Organization
WMO	World Meteorological Organization
WRD	Water Resources Department
WRA	Water Resource Area
ZAMCOM	Zambezi Watercourse Commission
α	Fractionation factor
δ	Delta value in permil
ε	Enrichment factor
μS/cm	Micro siemens per centimetre
GloWAL	Global Water Analysis Network

CHAPTER 1: INTRODUCTION

1.1. Background

Malawi, a least developed country in Southeastern Africa, boasts a wealth of water resources, including Lake Malawi, several smaller lakes, reservoirs, and an extensive river network (GoM, 2014; Kalin et al., 2022). These resources are crucial for the country's socio-economic development, supporting vital sectors such as hydropower generation, irrigation, and transportation. These sectors are essential for the country's energy security and agricultural productivity (Bhave et al., 2022; Hurford et al., 2014; Kalin et al., 2022; Kelly et al., 2019; Kumambala., 2010, 2021; Kumambala et al., 2024; Mtilatila et al., 2020a., 2020b). Despite these abundant water resources, Malawi faces significant water management challenges, including seasonal variability, increasing water scarcity, and pollution (Hurford et al., 2014; Kalin et al., 2022). These challenges compromise sustainability and quality of the country's water resources. Furthermore, Malawi's susceptibility to extreme weather events exacerbates these management challenges, posing serious risks (Haddeland et al., 2014; UNEP., 2021; IPCC., 2014; Hipsey., 2013). This situation underscores the critical link between water management and broader environmental and economic policies, emphasizing the urgent need for comprehensive research in these areas to develop strategies that effectively manage water resources, ensuring their sustainability for future generations. However, a fundamental problem is the lack of comprehensive monitoring of the country's water resources, which is essential for generating data and information to guide sustainable management practices.

Central to Malawi's water resources is the Lake Malawi basin's water resource, playing an essential role in water, energy, and food (WEF) security nexus. This significant water body profoundly influences the socio-economic fabric of Malawi, supporting hydropower generation

through its sustenance of the Shire River's flow rates, particularly during the dry season. It is crucial for local economies and livelihoods of rural communities (Bhave et al., 2022; Hurford et al., 2014; Kalin et al., 2022; Kelly et al., 2019; Kumambala, 2010, 2021; Kumambala et al., 2024; Mtilatila et al., 2020a, 2020b). The water levels in Lake Malawi are influenced by runoff from surrounding mountainous regions in Malawi, Tanzania, and Mozambique, accounting for approximately 55%, 41%, and 4% to the lake's inflow, respectively (Bhave et al., 2022). Moreover, Lake Malawi serves as a vital source of both animal and overall protein supplies, significantly contributing to nutritional security and economic stability (Hara et al., 2016). Given its importance, there is a pressing need for comprehensive research aimed at better understanding and managing the dynamics of water levels and runoff contributions in Lake Malawi. Such knowledge is crucial for ensuring sustainable hydropower generation and effective water resource management in Malawi.

Management of the Lake Malawi basin is further complicated by impacts of climate change, such as altered precipitation patterns and rising temperatures. These changes threaten stability of water levels in Lake Malawi and, consequently, flow rates of the Shire River due to increased evaporation and vulnerability to climatic fluctuations (Lyons et al., 2011). The transboundary nature of the Lake Malawi basin, which it shares with Tanzania, Mozambique, and Zambia, necessitates strong international cooperation to ensure equitable water distribution and to mitigate conflicts, especially during periods of water deficits (Fraser et al., 2020; Liu et al., 2024; Yuan et al., 2019). Such international collaborations are critical given the shared nature of the basin’s water resources. However, there is a pressing need for robust water resource data to better inform transboundary water management policies. Enhanced data collection and sharing mechanisms could significantly improve decision-making processes and promote sustainable water use within the basin. Compounding these challenges, environmental degradation, including

siltation and declining river flows, continues to pose additional risks, particularly noticeable during dry seasons. Addressing these issues through robust policy measures and cooperative regional efforts requires a sustainable management approach grounded in high resolution scientific data and information to guide water policy. Despite the crucial role of Lake Malawi and its water systems, there has been a serious lack of investment in comprehensive water-resource monitoring and research aimed at better understanding the country's water resources in a transformative manner that informs water policy (Banda et al., 2024; Hinton et al., 2024; Kalin et al., 2022). Moreover, current scientific literature lacks comprehensive and high-resolution empirical data on isotope hydrology and hydro-geochemistry baselines for a better conceptualisation of the Lake Malawi basin's water resource systems, critical gaps this research seeks to address.

1.2 Research Aim

The research aims to examine meteoric water inputs and their interactions with surface water and groundwater systems to enhance transformative understanding of hydrological processes in the Lake Malawi basin. To achieve the research aim, an innovative multi-method approach that integrates stable isotopic and hydrogeochemical tracers was applied. Findings of this research are expected to contribute to a new body of scientific data, information, and knowledge, providing groundbreaking isotopic insights into the Lake Malawi basin's water cycle. These critical insights are expected to significantly support the framework for monitoring water resources and inform water policy initiatives, which are crucial for guiding integrated water resources management (IWRM) practices and achieving objectives of Sustainable Development Goal (SDG) 6.

1.3 Research Questions and Objectives

The research aim is supported by a set of research questions (RQs), each strategically aligned with a set of research objectives (ROs) to achieve the stated aim. The following are research questions and their associated specific research objectives:

1.3.1 Research Question 1

How can application of water isotope tracing contribute to enhanced understanding of local precipitation system in support for integrated water resource management (IWRM)?

1.3.1.1 Research Objectives

- **RO 1.1:** To establish a national-scale isotopic baseline characterisation for precipitation and develop a local meteoric water line using deuterium (δ^2H) and oxygen ($\delta^{18}O$) signatures.

- **RO 1.2:** To identify moisture sources that influence local precipitation using deuterium (δ^2H) and oxygen ($\delta^{18}O$) and deuterium excess (d-excess) tracer method.

1.3.2 Research Question 2

How can application of an isotopic and hydrochemical multi-tracer approach enhance groundwater resource conceptualisation in support for groundwater sustainability?

1.3.2.1 Research Objectives

- **RO 2.1:** To establish a basin-scale isotopic and hydrochemical baseline characterisation for groundwater system using deuterium (δ^2H) and oxygen ($\delta^{18}O$) and major ionic tracers.

- **RO 2.2:** To delineate groundwater recharge inputs and geochemical reactions controlling groundwater chemistry and evolution along the flow paths using deuterium ($\delta^{2}H$) and oxygen ($\delta^{18}O$) and major ionic tracers.

1.3.3 Research Question 3

How can application of an isotopic and hydrochemical mixed-proxy approach inform surface water resource conceptualisation in support for integrated water resources management (IWRM)?

1.3.3.1 Research Objectives

- **RO 3.1:** To establish a basin-scale isotopic and hydrochemical baseline characterisation for surface water system using deuterium ($\delta^{2}H$), oxygen-18 ($\delta^{18}O$) and major ionic tracers.

- **RO 3.2:** To identify surface water flow inputs and mechanisms controlling surface water hydrochemistry and input isotopic signal attenuation.

- **RO 3.3:** To build an improved basin-scale conceptual understanding for the Lake Malawi basin's water resource, using enhanced understanding of precipitation, groundwater and surface water systems, to inform sustainable water resource management.

1.3.4 Research Question 4

How can integration of isotopic and hydrochemical tracers at sub-basin scale underpin holistic basin-wide water resource system conceptualisation to improve understanding of the Lake Malawi basin's hydrological cycle?

1.3.4.1 Research Objectives

- **RO 4.1:** To identify spatial and seasonal changes and trends in isotopic and hydrochemical signatures of groundwater and surface water.

- **RO 4.2:** To clarify evidence of groundwater and surface water dynamics and examine implications of potential hydraulic interactions.

1.4 Thesis Structure

This thesis is a comprehensive compilation consisting of nine well-organized chapters. The first three chapters (Chapters 1 to 3) establish a foundational framework for the thesis, comprising an introduction, a literature review, and a detailed methodology, respectively. This setup paves way for analytical segments that follow. Chapters 4 through 7 are specifically designed to address research questions and their corresponding objectives. These chapters detail the research results, featuring a series of peer-reviewed journal articles, some already published, others under review, and some prepared for submission. The final two chapters (Chapters 8 and 9) focus on discussion, and conclusion and recommendations, respectively. These chapters synthesize key research findings and discuss their implications for sustainable management of water resources in Malawi and the wider region. This structured method ensures a thorough and cohesive investigation of the research aims and amplifies scholarly impact of the thesis. Below is a detailed description of each chapter in the thesis structure (Figure 1).

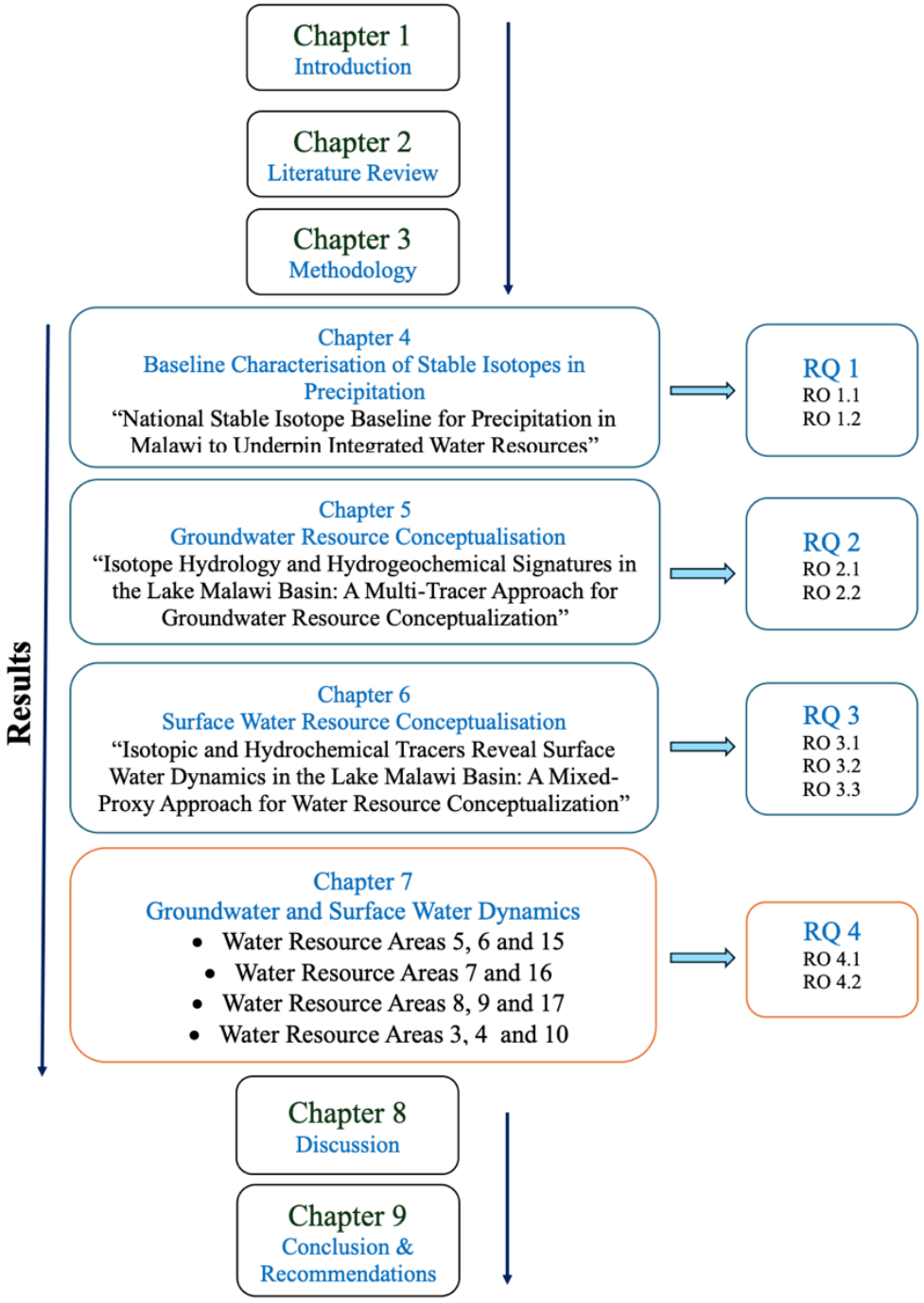

Figure 1. Summary of thesis structure flow chart

1.4.1 Chapter 1: Introduction

This chapter offers a thorough introduction to the research topic, highlighting the importance of the study area while clearly stating the main research aim. It also specifies the research questions that guided the investigation and lists the research objectives intended to fulfil the research aim. By providing this essential background, Chapter 1 lays the groundwork for an in-depth examination of the interconnected hydrologic and hydrogeologic systems of the Lake Malawi basin, creating the necessary context and framework for the critical analysis that follows.

1.4.2 Chapter 2: Literature Review

This chapter provides an in-depth review of existing literature related to the research topic, pointing out key challenges and important gaps in knowledge within the field. It emphasizes the changing nature of research in the Lake Malawi basin and sets the stage for the thesis by identifying crucial areas that require focussed investigation. In a way, Chapter 2 serves as the central part of the study, informing formulation of research questions and ultimately improving preliminary understanding of the hydrologic and hydrogeologic systems in the Lake Malawi basin.

1.4.3 Chapter 3: Methodology

This chapter describes the methodology used in the research to achieve the thesis aim and objectives. It explains the overall strategy and the innovative techniques applied during the study, ensuring a thorough and organized examination of the hydrologic and hydrogeologic systems of the Lake Malawi basin. By clearly and thoroughly detailing these methods, the chapter provides a strong foundation for the research, increasing the credibility and reproducibility of the findings.

1.4.5 Chapter 4: Results – Baseline Characterisation of Stable Isotopes in Precipitation

This chapter constitutes first segment of the thesis results section, featuring a published research article titled “National Stable Isotope Baseline for Precipitation in Malawi to Underpin Integrated Water Resources Management.” This chapter delivers a critical foundational water stable isotopic characterisation of precipitation, significantly enhancing our understanding of influence of meteoric water inputs into groundwater and surface water systems in the Lake Malawi basin.

1.4.6 Chapter 5: Results – Groundwater Resource Conceptualisation

This chapter represents second segment of the thesis results section, showcasing a peer-reviewed and published research article titled “Isotope Hydrology and Hydrogeochemical Signatures in the Lake Malawi Basin: A Multi- Tracer Approach for Groundwater Resource Conceptualization.” This chapter delivers an enhanced conceptualization of the aquifer systems within the Lake Malawi basin, achieved through seamless integration of water stable isotopic and hydrogeochemical evidence. By synthesizing these diverse lines of investigation, Chapter 5 establishes a robust foundation for understanding hydrology of the Lake Malawi basin, thereby refining the overarching water resource system. Overall, this chapter provides critical insights into the meteoric water inputs in Chapter 4 influence groundwater system following groundwater recharge in the Lake Malawi basin.

1.4.7 Chapter 6: Results – Surface Water Resource Conceptualisation

This chapter constitutes third segment of the thesis results section and features a research article titled “Isotopic and Hydrochemical Tracers Reveal Surface Water Dynamics in the Lake Malawi Basin: A Mixed-Proxy Approach for Water Resource Conceptualization.” This chapter is

largely informed by findings obtained in Chapter 4 and 5 to significantly enhance understanding of the Lake Malawi basin's hydrology by employing a synergistic application of water stable isotopic and hydrochemical methods. Through this innovative mixed-proxy approach, Chapter 6 offers an improved conceptualization of surface water dynamics, thereby enriching the overall understanding of the Lake Malawi basin's water cycle.

1.4.8 Chapter 7: Results – Groundwater and Surface Water Dynamics

This chapter comprises fourth segment of the thesis results section, presenting comprehensive water stable isotopic and hydrochemical baseline characterization of four Lake Malawi sub-basins grouped based on water resource areas (WRAs). Section 7.1 examines a Lake Malawi sub-basin that constitutes Water Resource Areas (WRAs) 5, 6, and 15, providing valuable insights into their unique hydrological profiles. Following this, Section 7.2 offers a detailed research article focusing on the water stable isotopic and hydrochemical baseline characterization of a Lake Malawi sub- basin encompassing WRAs 7 and 16. This section is complemented by another article on water stable isotopic and hydrochemical baseline characterization of a Lake Malawi sub-basin covering WRAs 8, 9, and 17, further enriching understanding of the area's hydrological dynamics. The chapter is supplemented by a research article, covering WRAs 3, 4, and 10 of the Lake Malawi basin, that was published prior to the current research. Thus, Chapter 7 provides critical insights into the intricate nature of the hydrological and hydrogeological interrelationships within the Lake Malawi basin, significantly improving the conceptualisation of the Lake Malawi basin's water resource system.

1.4.9 Chapter 8: Thesis Discussion

This chapter presents a critical discussion of the key research findings, emphasizing ways in which the newly acquired data and unique insights contribute to refining of the Lake Malawi basin's water resource system, critical for sustainable water resource management. This chapter situates the thesis within the broader framework of sustainable development goals (SDGs) and Integrated Water Resources Management (IWRM), highlighting relevance and implications of the current research in informing comprehensive water resources monitoring and contributing to addressing pressing water challenges. Furthermore, it elucidates significant contributions of the thesis to existing scientific body of knowledge while also illuminating future trajectories of isotope hydrology research in Malawi and the wider region, particularly through the GloWAL and IWAVE initiatives. By synthesizing these insights, Chapter 8 underscores the vital role that this research plays in fostering sustainable practices and guiding policy formulation and implementation for effective water management in the Lake Malawi basin and beyond.

1.4.10 Chapter 9: Conclusion and Recommendations

This chapter offers a comprehensive concluding summary of the thesis, synthesizing the key insights and overarching themes that emerged from the research. This chapter not only encapsulates the significant contributions of the research but also articulates forward-thinking recommendations for future research endeavours.

1.5 Summary

Chapter 1 laid the groundwork for an in-depth, systematic examination of the hydrological and hydrogeological systems within the Lake Malawi basin. It highlighted the critical importance

and timeliness of this research, given the basin's significant impact on regional water, energy, and food security. The framework of the study is defined through a series of well-defined questions designed to dissect the complex mechanisms governing the basin's water resource systems. This chapter outlined the specific research aim, objectives and the methodological approach, setting the stage for the detailed investigations to follow. It also forecasts potential implications of the research outcomes on sustainable water management. The following Chapter 2 describes the review and synthesis of existing data and literature in order to identify gaps in data and knowledge to inform formulation of research primary aim, questions, and specific objectives.

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CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Chapter 2 establishes a foundational framework for the thesis, drawing upon a review of existing knowledge, data, and literature relevant to the thesis topic. It underscores key challenges and identifies gaps in the existing data and knowledge. Specifically, the chapter establishes essential groundwork for the thesis, identifying key research areas that support the argument of the thesis. In that way, this chapter guides development of the thesis, informing formulation of research aims, questions, and objectives. The literature was reviewed continually throughout development of the thesis, culminating in the final phase. The significant body of research presented in this thesis is grounded in a series of research publication articles; hence, each article underscores reviewed literature specific to its focus, showcasing critical examination undertaken in each segment.

2.2 Water Resources

2.2.1 Water Resources Availability

The Lake Malawi basin, shared between Malawi and neighbouring countries, is distinguished by its transboundary surface and groundwater resources. Lake Malawi, which significantly serves Malawi, Mozambique, and Tanzania, is a predominant feature of this basin. The Songwe River is another transboundary water body, traversing the Malawi-Tanzania border. The Lake Malawi basin also has transboundary aquifers, which require international water cooperation for efficient water management; this is vital for achieving Sustainable Development Goal (SDG) target 6.5.2 (Fraser et al., 2020). Precipitation during the wet season predominantly replenishes these water resources, with a noticeable decline in water levels during the dry period

(Atkins., 2011a; BGS., 1996; Kalin et al., 2022). Several water reservoirs along major rivers cater for domestic, industrial, agricultural needs, with potential for hydropower generation (Banda et al., 2024). Notable surface water reservoirs include the Kamuzu (I and II) and the Lunyangwa reservoirs, with capacities of 125,000 m^3/day and 25,900 m^3/day and supply water to the cities of Lilongwe and Mzuzu, respectively (Banda et al., 2024). Groundwater plays a crucial role as a drinking water source, mainly in rural areas, with approximately 49,032 groundwater abstraction points, consisting of community boreholes and protected shallow wells, ca. 85.8% of which are defined as either fully or partially functional (Kalin et al., 2022). The basin boasts various artesian systems and springs discharges, the latter holding potential for geothermal energy production and sustaining localised riverine flows, critical during the dry season (Banda et al., 2024; Dávalos-Elizondo et al., 2021; Kalebe., 2017). The Lake Malawi basin is faced with numerous management challenges due to lack of scientific data and information systematically and continuously collected to inform better understanding of water resource systems, critical for sustainable water resource management. Other notable challenges include declining water quality attributed to geogenic and anthropogenic sources (Banda et al., 2024; Hinton et al., 2024; Monjerezi et al., 2011; Addison et al., 2020), and prolonged dry season that lower groundwater table below the depths of wells, thereby affecting water supplies, particularly for the marginalised rural population (Smith-Carrington and Chilton, 1983; Kumambala et al., 2010; Kalin et al., 2022). Water quality and infrastructural degradation escalate during extreme flooding events, particularly along the lakeshore flood-prone areas. The water quality situation is exacerbated by illegal waste disposal, unauthorized effluent discharges, and inadequate enforcement of water and environmental regulations, posing serious management problems. Furthermore, inefficient operation of municipal sewage systems, which often discharge untreated or poorly treated waste into water bodies, significantly degrades water quality (Owen et al., 2005). Compounding these

issues is sedimentation due to deforestation, small-scale irrigation from rapid urbanization, rampant sand mining, and unchecked growth of aquatic weeds, induced by siltation and agricultural runoff. These factors severely impact water quality, hydropower generation, transportation on waterways, and biodiversity (GoM., 2010).These different challenges underline the critical need for a more investment towards comprehensive water resources monitoring and research to inform science-led decision-making process that underpins sustainable water resource management.

2.2.2 Natural Water Balance

An evaluation of water resources conducted in Malawi provided substantial insights into the country's hydrological balance and the challenges associated with water resources management. By analysing 30 years of hydro-meteorological data through an advanced simulation model, it was just how clarified that precipitation plays a critical role in water availability, with the national mean annual rainfall of 980 mm (Figure 3) (GoM., 2014). However, it was observed that only a small portion of the mean annual rainfall contributed directly to replenishment of both surface water and groundwater reserves. This highlights the complex relationship between the meteoric water input and actual surface water and groundwater resources availability. According to Figure 3, approximately 23% of the meteoric water input, which is about 225 mm, contributes to surface runoff, and just 5%, or roughly 53 mm, effectively recharges groundwater. It also indicates that a substantial 72% of the meteoric water input is lost through evapotranspiration, highlighting a significant challenge in Malawi's water cycle as high rates of evapotranspiration greatly diminish the available water resources that are crucial for the social economic development of the country.

The dynamics of surface water add complexity to the overall water balance. Lake Malawi plays a crucial role, capturing 63% of the country's surface water flow, while the remaining 37% drains into the Shire River and Lake Chilwa (GoM., 2014). The geographical features at the lake's outlet and operations at the Liwonde barrage are key factors in regulating the Shire River's flow rates. As a major storage facility, the lake has the capacity to stabilize variations in the Shire River flow rates, thus ensuring a reliable water supply throughout the year. This is especially beneficial for hydropower generation, which constitutes 98% of Malawi's electricity production, exploiting the river's gradients. Despite the apparent adequacy of current water resources, estimated to be 20 times the annual demand of approximately 1.1 billion m^3 (as of 2012), with irrigation and domestic usage accounting for 87% and 13%, respectively, the future outlook remains very uncertain (Figure 4). Water demand is projected to increase by 2.5 times by the year 2035 (GoM., 2014). Although the current water resources appear to surpass present and anticipated future demands, the seasonal variability in water availability presents a significant challenge (Figure 4; 5). This issue becomes particularly severe during dry seasons when water shortages intensify. This disparity underscores the necessity for comprehensive water resources monitoring and research to inform sustainable water management strategies to ensure a sustainable water supply year-round. Addressing these variations with measures such as dedicated financial investment for comprehensive water resources monitoring, enhanced water conservation practices, improved storage infrastructure, and optimized water allocation is crucial in averting potential shortages. Furthermore, adopting efficient irrigation methods and seeking alternative water sources are vital to meet the growing needs of the agricultural and domestic sectors (Kalin eta l., 2022; GoM., 2014).

In conclusion, despite Malawi's considerable endowment of water resources, which currently surpasses both existing and projected demands, there is an urgent need for sustainable

management and adoption of innovative strategies which largely hinge on robust and high-resolution water resources monitoring data and information. These are critical in addressing seasonal fluctuations and ensuring the long-term stability of the country's water resources. The future of water security in Malawi will crucially depend on strategic planning and implementation of advanced solutions to optimize management of water resources monitoring and management assets.

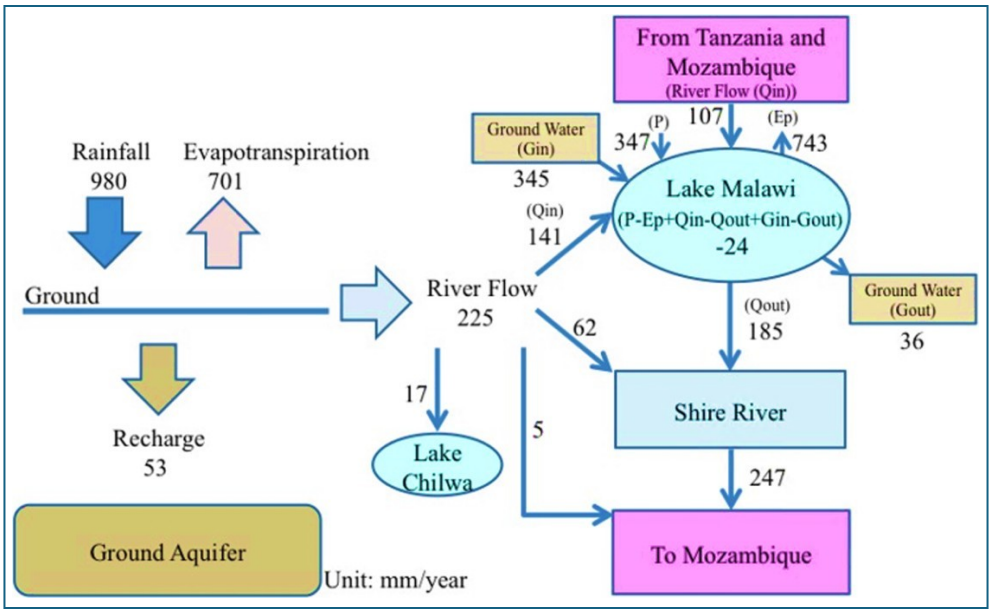

Figure 3. Natural Water Balance in Malawi (GoM., 2014).

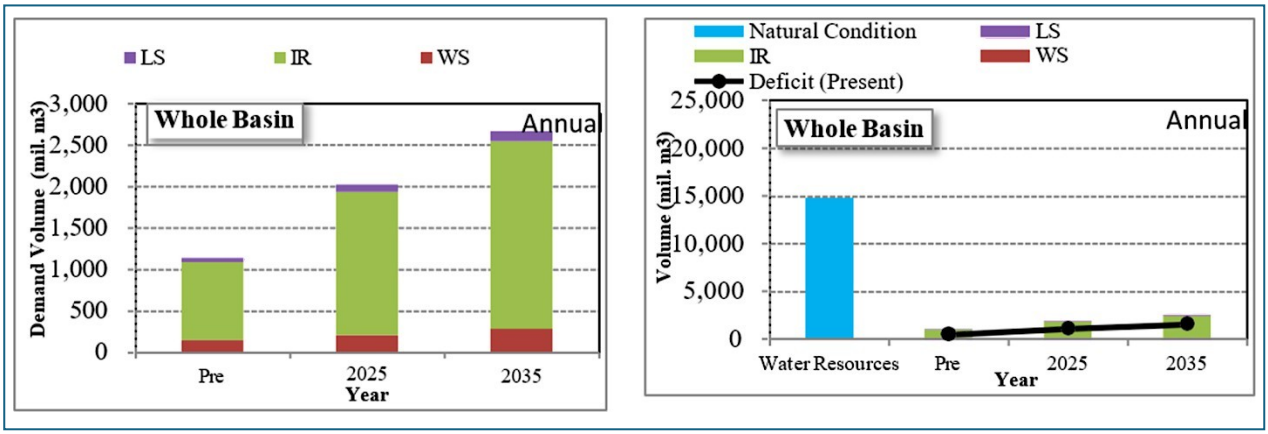

Figure 4. Transition of Water Demand (Left) and Comparison between Annual Water Demand and Water Resources (Right) (GoM., 2014).

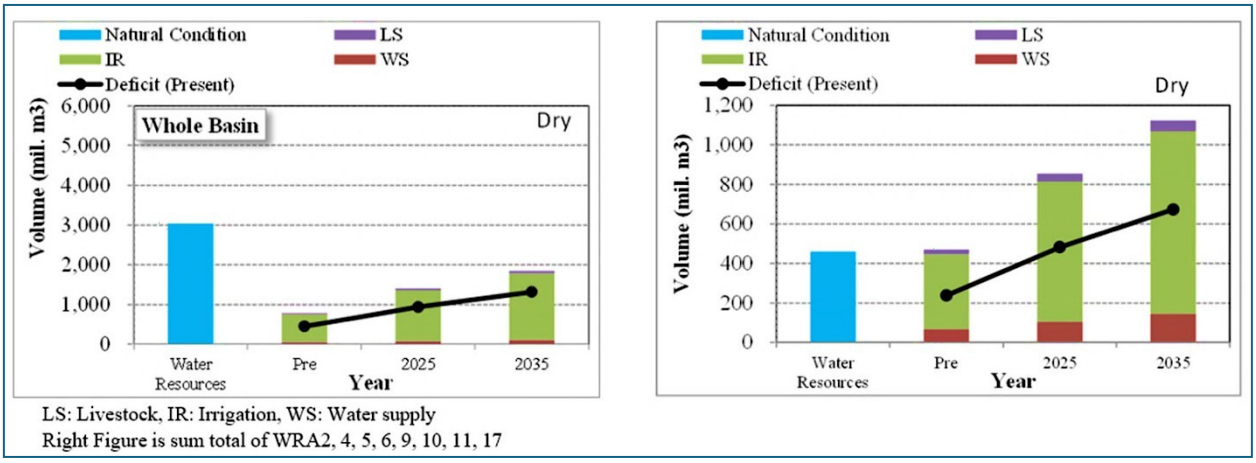

Figure 5. Comparison between Water Demand and Water Resources (Left: Dry Season, Right: Driest Month) (GoM., 2014).

2.3 Water Resource Management and Development Challenges

In Malawi, strategic management and development of water resources are crucial, underpinning key sectors such as agriculture, energy, and broader socio-economic advancements (Kalin et al., 2022: GoM., 2014; GoM., 2005; GoM., 2014). Despite the legislative framework provided by the Water Resources Act of 2013, persistent systemic constraints exacerbate the difficulties in managing these vital resources effectively (GoM., 2014). These challenges jeopardize not only the sustainable supply of water but also threaten the health of aquatic ecosystems. One of the foremost obstacles in this domain is the ambiguous distribution of roles and responsibilities among various governmental water-related agencies, leading to fragmented governance and inefficient policy enforcement (MoIWD., 2010). This uncertainty complicates integration of efforts across sectors, including allocating sufficient attention to the impacts of hydropower developments on water resources. Such integration is further stymied by chronic budgetary constraints and a scarcity of skilled personnel, hindering effective regulatory enforcement and fulfilling agency mandates. Moreover, Malawi's capability to gauge and analyse hydrological data is hampered by

inadequate infrastructure and mismanagement, particularly evidenced by a decrease in hydrological monitoring stations and inconsistent data validation practices (Foster et al., 2010; MoIWD., 2011; GoM., 2017). This scenario leads to gaps in critical data, impeding timely and informed decision-making. Despite support from Official Development Assistance (ODA) partners, significant improvements in resource allocation and compliance with measurement standards remain necessary.

The country also faces severe challenges in monitoring water quality and pollution control, mostly due to sporadic and poorly coordinated monitoring efforts (MoIWD., 2011; GoM., 2014). The lack of comprehensive water quality monitoring standards and critical deficiencies in data management severely limits effective pollution assessment and control, compromising public health and ecological integrity. Additionally, existing environmental laboratories suffer from a lack of essential resources and staffing, particularly in Northern Malawi, thus undermining extensive monitoring endeavours (MoIWD., 2011; GoM., 2014). Environmental degradation, notably from deforestation and subsequent soil erosion, poses further risks to the sustainability of water resources. Research that explores connections between water quality, ecosystem health, and agricultural productivity is critically lacking, neglecting essential aspects of resource sustainability. Enforcement of protective measures for water sources within forest reserves is lax, thereby posing risks to the longevity of these vital water resources. The challenges extend into the realm of infrastructure development within the water supply sector, crucial for achieving Sustainable Development Goals (MoIWD., 2011; GoM., 2017; Joshua et al., 2022). The water supply sector's growth is plagued by high levels of non-revenue water, aging infrastructure, and inadequate capacity to meet growing demand (MoIWD., 2011; GoM., 2017; Akpabio et al., 2021). Moreover, lack of transparency in reporting water quality status to consumers diminishes public trust in water

supply services. In energy sector, the intersection of hydropower development with water resource management remains inadequately addressed. The absence of rigorous water budget evaluations for different sectors presents sustainability risks for new hydropower projects, particularly without adequate assessments of water balance. Furthermore, the overlooked implication of sediment loading in rivers on aquatic ecosystems and water quality require urgent attention. Addressing these multifaceted challenges necessitates a cohesive strategy that clarifies institutional roles, enhances data management, and strengthens water quality oversight (MoIWD., 2011; GoM., 2014). It is imperative to prioritize environmental protection, foster stakeholder collaboration, and support sustainable infrastructure development to advance sustainable water resource management in Malawi. Adopting such a systematic and inclusive approach will be pivotal in achieving sustainable and equitable water resource management, ultimately supporting the country's broader developmental and environmental conservation goals (MoIWD., 2010).

2.4 Evolution of Water Legislation and Implications on Water Governance

Water governance in Malawi has undergone significant transformations, influenced heavily by evolving legislative and institutional frameworks. The journey through various legislations and policies provides insight into the country's efforts to ensure effective management and sustainable use of its water resources. The foundational legislative change came with enactment of the Water Resources Act of 1969 (GoM., 1969; Kumambala., 2010; Ng'ong'ola., 1999). This crucial piece of legislation established a comprehensive basis for the management, conservation, and allocation of water resources in Malawi. It delineated rights and responsibilities concerning water usage, setting the stage for subsequent regulations and policies focused on sustainability and equitable distribution. Building upon this foundation, Malawi saw further refinement of its water

management strategies through introduction of the Water Works Act (WWA) of 1995. This act replaced earlier fragmented legislations with a unified framework governing the operations of all Water Boards (Kumambala., 2010; Ng'ong'ola., 1999). One of the significant outcomes of this act was the restructuring of the institutional framework, transferring responsibilities from the Ministry of Water Development to regional water boards as part of decentralization policy. This decentralization was strategically aimed at enhancing community-focused management, which is better aligned with local needs and conditions, thus promoting efficiency and accountability in water service provision. The implementation of the 1994 Water Resources Management Policy and Strategy (WRMPS) marked a renewed commitment to improving water supply and sanitation services, emphasizing stakeholder engagement and inclusive decision-making. This strategy endorsed a commercialized approach to water management, seeking to balance regulation with economic sustainability. As Malawi faced the growing demands of urbanization and population growth, securing financial resources for maintenance and expansion of water infrastructure and supply services became paramount.

Despite these legislative advancements, Malawi's water management sector faces ongoing challenges. The effectiveness of the Water Resources Act (WRA) is often hampered by issues such as weak enforcement, limited institutional capacity, and low public awareness. These factors collectively undermine the WRA's ability to facilitate sustainable water management. Similarly, the Water Works Act, while pivotal in regulating water service provision and maintaining safety standards, continues to encounter financial and technical constraints that diminish its operational success. Furthermore, Malawi's strategic water policies aim to foster comprehensive management and align with a cohesive vision. Unfortunately, challenges in integration across vital sectors like agriculture and urban development, along with infrastructural and budgetary limitations, frequently

hinder effective policy implementation. This necessitates a heightened focus on investing in infrastructure, enhancing institutional capacities, and increasing public awareness to support robust policy enforcement and adaptation.

As Malawi continues to refine its approach to water governance, accumulated experiences and insights from legislative and policy improvements remain crucial. Complementing legislative efforts, emerging research in fields such as isotope hydrology and hydrogeochemistry promises to fill existing knowledge gaps and improve understanding of water resource dynamics, essential for ongoing sustainable management. In conclusion, while Malawi possesses a comprehensive legislative and policy framework for water resource management, addressing implementation bottlenecks through robust investments, educational initiatives, and strengthened institutional support is essential. Only by overcoming these challenges can Malawi ensure sustainable management and equitable distribution of water resources, securing a healthier future for all its citizens.

2.5 Isotope Hydrology

Isotope hydrology combines principles from both hydrology and nuclear physics to trace water movement and understand the water cycle through application of isotopic techniques. This branch of science reveals invaluable and unique insights into the age, origin, and history of water bodies by analysing variations in the abundance of isotopes such as deuterium (^{2}H) and oxygen-18 (^{18}O). It has advanced capabilities in water and environmental monitoring, paleoclimatology, and climate impact assessment by elucidating the interrelationships within water cycles under diverse climatic and geographical conditions.

2.5.1 Fundamental Principles of Isotope Hydrology

2.5.1.1 Environmental Isotopes

Environmental isotope tracers have become indispensable in hydrology and environmental sciences, providing critical insights into subsurface water dynamics that conventional hydrometric techniques often miss. The use of stable isotopes such as carbon-13 (^{13}C), oxygen-18 (^{18}O), deuterium (^{2}H), sulfur-34 (^{34}S), and nitrogen-15 (^{15}N), as well as radioactive isotopes like tritium (^{3}H), carbon-14 (^{14}C), and strontium-87 (^{87}Sr), plays a crucial role in deciphering the complexities of hydrological systems (Ivanovich & Harmon, 1992). These isotopes are introduced into the hydrosphere via natural phenomena, such as cosmic ray interactions that produce cosmogenic nuclides, as well as through human activities. They provide consistent metrics crucial for understanding issues like groundwater recharge rates, land use changes, and historical climate conditions.

Stable isotopes of oxygen and hydrogen serve as key indicators of water molecule dynamics across various environmental contexts. Isotopic tracers have become indispensable for revealing complex subsurface interactions, such as identifying groundwater flow patterns, evaluating solute exchange kinetics across geochemical phases, and assessing subterranean chemical reactions (Salem et al., 2004; Cox & Wilson., 2005). The significant concentration differences between environmental tracers in surface and groundwater enable researchers to effectively delineate recharge and discharge zones (Kalbus et al., 2006).

Environmental isotope techniques are critically valuable in arid and semi-arid regions, where groundwater resources are limited and under increasing stress. These advanced tools not only assist in locating ancient groundwater reserves but also facilitate in-depth quantitative analyses of

groundwater systems, proving essential for contemporary water resource management (Verhagen et al., 1991). Additionally, geochemical tracers enhance the functionality of isotopes by marking distinct water segments navigating through complex subsurface pathways. Essential chemical metrics, such as sodium and nitrate concentrations, together with trace elements like strontium, elucidate dynamics of water movement through various soil and rock strata (Kalbus et al., 2006). Furthermore, stable isotopes of oxygen and hydrogen distinguish between water flows following rainfall and pre-existing water stocks, enriching our understanding of hydrological processes within watershed areas. The fluctuating isotopic composition between newly fallen rain and existing environmental water is crucial for effective water management and for evaluating hydrological responses to climatic variability (Kendall & Caldwell, 1998). Therefore, integration of environmental isotope tracers in hydrological research provides profound insights into the intricate interactions and mechanisms governing groundwater flow and recharge. By enhancing comprehensive water resources monitoring and understanding of water systems that support development of improved strategies for water resource management, these techniques are invaluable in addressing the hydrological challenges of changing climates and evolving land-use practices.

2.5.1.2 Stable Isotopes in Hydrology

In environmental studies, atoms that naturally vary due to differences in neutron counts yet maintain the same proton count (isotopes) are utilized as traceable markers. Specifically, isotopes ^{2}H and ^{18}O are extensively analysed, as their fractionation yields unique patterns indicative of environmental processes including evaporation, condensation, and precipitation. The application of stable water isotopes of hydrogen (H) and oxygen (O) offers critical insights into the dynamics of

water sources and their movement within diverse hydrological systems. This is primarily facilitated by the use of stable isotopes such as oxygen isotopes (^{16}O, ^{17}O, and ^{18}O) and hydrogen isotopes (^{1}H) and deuterium (^{2}H or D), which operate as effective tracers, being integral constituents of water molecules (Kendall & Caldwell, 1998). In contrast to other environmental tracers like chloride (Cl^-), which may dissolve in water influencing concentrations, hydrogen and oxygen isotopes are intrinsic to the water molecule itself, providing a direct means for assessing hydrological processes across various environments including the atmosphere, hydrosphere, biosphere, and the Earth's upper crust.

The isotopic composition of water within a catchment area is shaped largely by two primary factors: phase changes at the ground surface (such as evaporation, condensation, and melting) and mixing processes occurring above and below the surface. Faure (1986) detailed how various factors, including altitude, temperature, biological processes, and key hydrological events such as evaporation and precipitation, influence heavy isotope fractionation (Faure., 1986). This results in isotopic fractionation, the partitioning of elements into lighter and heavier isotopic ratios. There exist two stable hydrogen isotopes, ^{1}H and the heavier ^{2}H, along with three stable oxygen isotopes (^{16}O, ^{17}O, and ^{18}O) (Fetter., 1994). These isotopes combine in water molecules in multiple configurations, providing stable molecular forms with atomic weights ranging from 18 to 22. Notably, the predominant water molecule, $^{1}H_2{}^{16}O$, displays higher vapor pressure compared to its heavier equivalents such as $^{2}H_2{}^{18}O$. As water shifts between its liquid and vapor phases, the heavier isotopes tend to accumulate in the liquid state, leading to isotopic fractionation that changes the ratio of hydrogen to oxygen isotopes (Fetter, 1994). Consequently, oceanic evaporation yields isotopically lighter water vapor relative to the residual seawater, culminating in precipitation that carries a heavier isotopic signature owing to the enriched presence of ^{2}H and ^{18}O. The isotope ratios

of deuterium-to-hydrogen ($^{2}H/^{1}H$) and oxygen-18 to oxygen-16 ($^{18}O/^{16}O$) are generally expressed as dimensionless δ values, indicating deviation from a standard reference known as the Vienna Standard Mean Ocean Water (V-SMOW). These δ values are calculated using Equation 1 (Craig., 1961):

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) x\ 1000\ ‰ \quad \ldots(1)$$

where (R) represents either the D/H or $^{18}O/^{16}O$ ratios. Positive δ values denote enrichment in ^{18}O or D relative to the V-SMOW standard, while negative values reflect depletion. The δD and $\delta^{18}O$ measurements are crucial for comparing isotopic characteristics of various water sources and are typically plotted on a δD versus $\delta^{18}O$ diagram to assess their positions relative to the Global Meteoric Water Line (GMWL), which is defined by Equation 2:

$$\delta D = 8\delta^{18}O + 10 \quad \ldots(2)$$

The GMWL is a crucial benchmark for determining origins and pathways of local groundwater. Isotopic signatures in water samples that fall below this line typically indicate secondary processes, such as evaporation prior to infiltration or the presence of ancient waters affected by varying climatic conditions (Fritz et al., 1979). On the other hand, groundwater that aligns closely with the GMWL often suggests minimal alteration by such processes, reinforcing the idea that these waters have undergone limited isotopic interaction with surrounding geologies (Mazor, 2004). In practical applications, stable isotopes of oxygen and deuterium play a crucial role in effective groundwater resource management. These isotopes serve as reliable tracers, enabling the assessment of natural water cycles and tracking groundwater movements, significantly improving understanding of hydrological dynamics (Subyani, 2004). Furthermore, isotope tracers have been instrumental in

investigating mixing between unconfined and confined aquifer systems and in determining mean residence times of groundwater. These applications highlight their critical importance in contemporary hydrological studies (Rapti-Caputo & Martinelli, 2008). Overall, stable isotopes of hydrogen and oxygen are invaluable tools for elucidating water dynamics across various landscapes. Their ability to illuminate both historical and contemporary hydrological processes underscores their significance in both academic research and practical groundwater management. This knowledge facilitates development of effective strategies for sustainable water usage, which is especially vital in the context of changing environmental conditions.

2.5.1.3 Deuterium Excess

Deuterium excess (*d*-excess) calculated using formula ($d = \delta D - 8\delta^{18}O$), has been recognized as a crucial tracer for unravelling complexities of climatic interactions and hydrological processes (Dansgaard, 1964). As an analytical tool, it not only facilitates differentiation of isotopic compositions but also significantly contributes to clarification of the climatic determinants influencing precipitation patterns. The construct of the Meteoric Water Line (MWL) offers a robust framework for analysing the isotopic ratios of hydrogen and oxygen in precipitation. This line, illustrating the relationship between δD and $\delta^{18}O$, allows researchers to juxtapose local precipitation isotopes against global benchmarks, thereby illuminating impacts of climatic factors and secondary moisture sources (Froehlich et al., 2002). Shifts in deuterium excess can signal alterations in moisture origins or variations in climatic conditions that affect the water cycle within specific regions (Merlivat and Jouzel, 1979). Previous research has shown that deuterium excess correlates strongly with several environmental parameters, such as humidity, air temperature, and sea surface temperature, particularly in ocean regions that act as moisture reservoirs (Natali et al., 2022).

Research has also revealed that when meteorological stations are subjected to high temperatures and low vapor pressures, they typically exhibit decreases in *d*-excess values (Cui et al., 2017). Furthermore, kinetic isotopic fractionation, prompted by partial evaporation of raindrops, markedly alters the isotopic composition of collected precipitation (Stewart, 1975). This finding highlights the necessity to account for local climatic conditions in isotopic assessments. Additionally, re-evaporation of raindrops introduces further complexity; as raindrops re-evaporate, they become enriched in heavier isotopes, thereby modifying the isotopic signature of precipitation and reflecting the intricate interplay of meteorological patterns (Risi et al., 2008). Other factors, such as the origin of air masses and the altitude at which condensation occurs, also significantly influence this isotopic signature. At higher altitudes, the prevailing conditions often lead to vapour depletion following earlier condensation events, resulting in precipitation that is isotopically lighter (Celle-Jeanton et al., 2004). Moreover, diffusive exchanges between lower-level vapor and raindrops can significantly impact the isotopic composition, particularly under conditions of high relative humidity (Gedzelman et al., 2003; Fudeyasu et al., 2008).

The practical applications of *d*-excess extend into areas beyond mere isotopic analysis. As Meyer et al. (2002), Stenni et al. (2007), and Fisher et al. (2004) found, deuterium excess affords valuable insights into origins of subsurface ice and elucidates secondary precipitation processes. These studies underscore the potential of *d*-excess as an indicator of environmental shifts, enabling researchers to document not only current meteorological conditions but also historical climatic trends. In conclusion, deuterium excess serves as a pivotal metric in the examination of hydrological and climatic processes. Its capacity to reflect variations in isotopic ratios and its correlation with critical environmental factors secures its place as an indispensable tool in the arsenal of climatologists and hydrologists.

2.5.1.4 Isotope Fractionation

Understanding isotope ratios necessitates an appreciation of two primary forms of fractionation: equilibrium and kinetic. Equilibrium fractionation occurs during phase transitions under stable conditions, whereas kinetic fractionation arises from irreversible processes. The landmark contributions by Harmon Craig in establishing the Standard Mean Ocean Water (SMOW) have provided a vital benchmark for comparative studies in hydrological isotopic analysis (Craig, 1961). Isotope fractionation refers to t alterations in isotopic composition of water during phase transitions, such as the transformation of liquid water into vapour during evaporation or the change from ice to liquid during melting (Hiscock, 2005). These changes are attributed to mass differences between isotopes, which consequently influence their physical properties.

A significant consequence of isotope fractionation is that heavier isotopes typically exhibit decreased mobility, characterized by slower diffusion rates, lower collision frequencies, and reduced reaction velocities. Additionally, they display increased binding energy (Schwarzbauer et al., 2024). For example, water molecules containing heavier isotopes such as ($^{1}H_{2}{}^{18}O$) or ($^{1}H_{2}H^{16}O$) have lower vapour pressures compared to those with lighter isotopes ($^{1}H_{2}{}^{16}O$), rendering them less likely to transition from liquid to vapour during evaporation. On the contrary, these heavier molecules are more likely to make the transition from vapour to liquid during condensation, a process termed mass-dependent isotope fractionation (Albarède, 2011; Sharp, 2007; Thiemens, 2006). Isotope fractionation is primarily categorized into equilibrium and kinetic types. Equilibrium fractionation transpires in contexts where reactants and products are in close proximity, allowing for thorough mixing and enabling back reactions. This type of fractionation can be quantitatively characterized by equilibrium fractionation factor, represented by the symbol α.

$$\alpha_{R-P} = \left(\frac{R_{Reactant}}{R_{Product}}\right) \quad \ldots(3)$$

In Equation 3, R is reactant and P is product. This results in a fractionation factor α for a phase transition in an evaporation process between liquid water and water vapor:

$$\alpha^{18}O_{L-G} = \left(\frac{{}^{18}O/_{16}O_{Liquid}}{{}^{18}O/_{16}O_{Vapour}}\right) = 1.0093 \text{ @ } 25\ ^{\circ}C \quad \ldots(4)$$

In equation 4, when α values exceed 1, the isotopic ratio of the product (P) will be lower than that of the reactant (R). In the context of evaporation, this means that the water vapor generated (P) will be less heavy than the liquid water from which it originates (R) (Equation 5).

$$18RVapour = \left(\frac{{}^{18}O/_{16}O_{Liquid}}{{}^{18}O/_{16}O_{Vapour}}\right) = 1.0093 \text{ @ } 25\ ^{\circ}C \quad \ldots(5)$$

Isotope fractionation, along with the fractionation factor α, is highly sensitive to temperature (O'Neil., 1986). The extent of fractionation is significantly greater at lower temperatures compared to higher temperatures. Specifically, the fractionation factor α for ^{18}O in the exchange between water and water vapor is affected by temperature (T) (Majoube., 1971). The isotopic distinction between the reactant and the product can be expressed using the enrichment factor ε (‰).

$$\varepsilon^{18}O_{Liquid\leftrightarrow Vapour} = \left(\frac{{}^{18}O/_{16}O_{Water}}{{}^{18}O/_{16}O_{Vapour}}\right) \times 1000\ ‰ = 9.3 \text{ @ } 25\ ^{\circ}C \quad \ldots(6)$$

In Equation 6, the evaporation process occurring at 25°C, δ value of the generated water vapor

(product) differs from that of the liquid water (reactant) by 9.3 ‰. Fractionation factors are commonly represented as $10^3 \ln\alpha$ because this expression provides an approximation of the equilibrium fractionation expressed in ‰ (Equation 7).

$$\varepsilon^{18}\mathrm{O}_{\mathrm{Liquid}\leftrightarrow\mathrm{Vapour}} \approx \varepsilon^{18}\mathrm{O}_{\mathrm{Liquid}} - \varepsilon^{18}\mathrm{O}_{\mathrm{Vapour}} \approx 1000 \times \mathrm{In}\,\alpha\,{}^{18}\mathrm{O}_{\mathrm{Liquid-Vapour}} \quad \ldots(7)$$

Isotopic equilibrium often is not achieved due to temperature fluctuations or the extraction of water vapor, which requires us to consider kinetic fractionation. This process is irreversible and involves continuous removal of the product formed. When it comes to evaporation, the effect of kinetic fractionation depends on relative humidity (h) of the atmosphere. Gonfiantini (1986) outlined the principles of kinetic fractionation based on Equations 8 and 9 (Clark and Fritz 1997).

$$\Delta\varepsilon^{18}\mathrm{O}_{\mathrm{Liquid}\rightarrow\mathrm{Vapour}} = 14.2 \times (1-\mathrm{h})\ ‰ \quad \ldots(8)$$

$$\Delta\varepsilon^{2}\mathrm{H}_{\mathrm{Liquid}\rightarrow\mathrm{Vapour}} = 12.5 \times (1-\mathrm{h})\ ‰ \quad \ldots(9)$$

One approach to explaining variation in isotopic composition during phase changes is the Rayleigh distillation process. This process is described by Rayleigh distillation equation that depicts fractionation of isotopes between two reservoirs, where one reservoir is reduced in volume. As evaporation takes place, the remaining liquid water becomes more enriched in heavier isotopes. This effect is defined by Equation 10.

$$R = R_0 \times f^{(\alpha-1)} \quad \ldots(10)$$

In Equation 10, R is resulting isotope ratio, R0 is initial isotope ratio, f is fraction of water remaining, while α is e equilibrium fractionation factor. The Rayleigh equation is applicable to open systems where the equilibrium fractionation factor remains constant, and the product is

continuously removed. However, evaporation typically occurs under non-equilibrium conditions, making air humidity a crucial factor (Kendall and McDonnell., 1998; Cappa et al., 2003; Sun et al., 2021). When the humidity is > 100%, it becomes necessary to account for kinetic fractionation. As a result, the total fractionation occurring between liquid water and water vapor is the sum of equilibrium fractionation (εLiquid $\leftrightarrow$ vapour) and kinetic fractionation ($\Delta\varepsilon$Liquid $\rightarrow$ vapour) (Kendall and McDonnell., 1998) (Equation 11):

$$\delta^{18}O_{Liquid} - \delta^{18}O_{Vapour} = s^{18}O_{Liquid-Vapour} + \Delta s^{18}O_{Liquid \rightarrow Vapour} \quad \ldots(11)$$

2.5.2 Application of Isotope Hydrology to Water Resource Management

Isotope hydrology has emerged as a pivotal scientific tool within the framework of Integrated Water Resources Management (IWRM), particularly crucial in unravelling the intricate dynamics between groundwater and surface water systems. The infusion of isotopic data into water resource management enriches the scientific foundation upon which decisions are made, providing profound insights pivotal for the sustainable stewardship of hydrological assets, particularly in environments confronting developmental challenges such as Malawi. The inclusion of isotope hydrology techniques can substantially refine water resource characterization and management as has been demonstrated in various studies across Africa (Banda et al., 2019). These investigations have delineated water source provenance, evaluated modern and historical recharge rates, mapped flow regimes, and elucidated interactions between groundwater and surface waters, thereby highlighting the transformative potential of isotope hydrology in fortifying IWRM practices.

Despite this progress, a notable gap remains in the accessibility to robust isotope hydrology facilities in developing nations, a limitation that curtails their capability to fully harness these advanced scientific tools. In Malawi, recent developments signal a shift from dependency on

international isotopic analyses toward cultivating local expertise and infrastructure. A landmark in this endeavour was the establishment of a national Isotope Hydrology laboratory in collaboration with the International Atomic Energy Agency (IAEA). This initiative represents a significant stride towards empowering Malawi with the necessary resources to conduct localized isotope studies that are essential for an in-depth understanding of its unique hydrological cycles and the effective management of its water resources. Despite these advancements, challenges persist, including limited infrastructure and a scarcity of technical expertise in isotope hydrology. For IWRM to reach its full potential in developing contexts like Malawi, enhancement of access to isotopic analysis tools and a concerted focus on cultivating local expertise are imperative. This encompasses not merely the establishment of facilities but also comprehensive training of personnel to generate, analyse, and interpret isotopic data effectively. The current over-reliance on international resources for data generation notably restricts the capacity of local authorities to make informed, timely decisions that resonate with their specific hydrological realities.

Looking forward, to realize the full potential of isotope hydrology in Malawi and similar settings, addressing several research gaps remains essential. Robust isotopic studies need to be undertaken at both local and national scales, with a particular emphasis on understanding precipitation patterns and their contributions to hydrological models. Establishing a Local Meteoric Water Line (LMWL) for Malawi would offer a critical benchmark for future research. Moreover, integrating isotope studies with hydrogeochemistry would facilitate a more nuanced understanding of groundwater-surface water (GW-SW) interactions, thereby enhancing the sophistication of water management strategies. Basin-wide studies that incorporate proxy indicators like water isotopes are quintessential for crafting efficacious water management strategies. Identifying key catchments that

reflect Malawi's diverse hydrological contexts will enable focused research and ensure that findings have broader applicational value across the region.

Overall, enhancing the capabilities in isotope hydrology transcends mere academic pursuit; it is a strategic imperative for achieving sustainable development goals and ensuring the long-term viability of water resources in developing regions. Intertwining isotope data into water management protocols promises to endow policymakers and water managers with invaluable insights, fostering informed decision-making and promoting sustainable practices in water resource management. The following chapter outlines the methodologies employed in this thesis to explore these themes and aims to contribute meaningful strategies toward effective and sustainable management of vital water resources in Malawi and beyond.

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CHAPTER 3: METHODOLOGY

3.1 Introduction

Chapter 3 outlines a general methodological framework used to address research aims and objectives, with specific methods described in each research publication article specific to its focus, presented in results Chapters (Chapters 4, 5, 6 and 7). The general methodological framework is categorised into five key phases: identifying data and knowledge gaps, establishing baseline for stable isotopes in precipitation, conceptualising groundwater resource system, conceptualising surface water resource system, and examining groundwater and surface water dynamics. This chapter details research materials and methods used to achieve research aims and objectives. The first phase involved identifying knowledge gaps through exhaustive literature review and synthesis, presented in preceding chapter, Chapter 2. The second phase involved feasibility study of the Lake Malawi basin's water resource systems. That preliminary conceptualisation of the study area informed formulation of research aim, questions and specific objectives. The third phase involved designing and formulation of overarching research plan. These critical steps laid a concrete base for execution of the research study. The research plan was executed in four phases. The first phase established a baseline for stable isotopes in precipitation, presented in results Chapter 4. The second phase conceptualised groundwater resource system, presented in results Chapter 5. The third phase conceptualised surface water resource system, presented in results Chapter 6. The final phase explored groundwater and surface water dynamics, presented in Chapter 7. During the last phase, the study area, Lake Malawi basin, was segmented into four sub-basins based on river and lakeshore catchments, also referred to as Water Resource Areas (WRAs) (Figure 6 and Table 1).

The preceding section presents descriptions of materials and methods used during the research to achieve the set research aim and objectives.

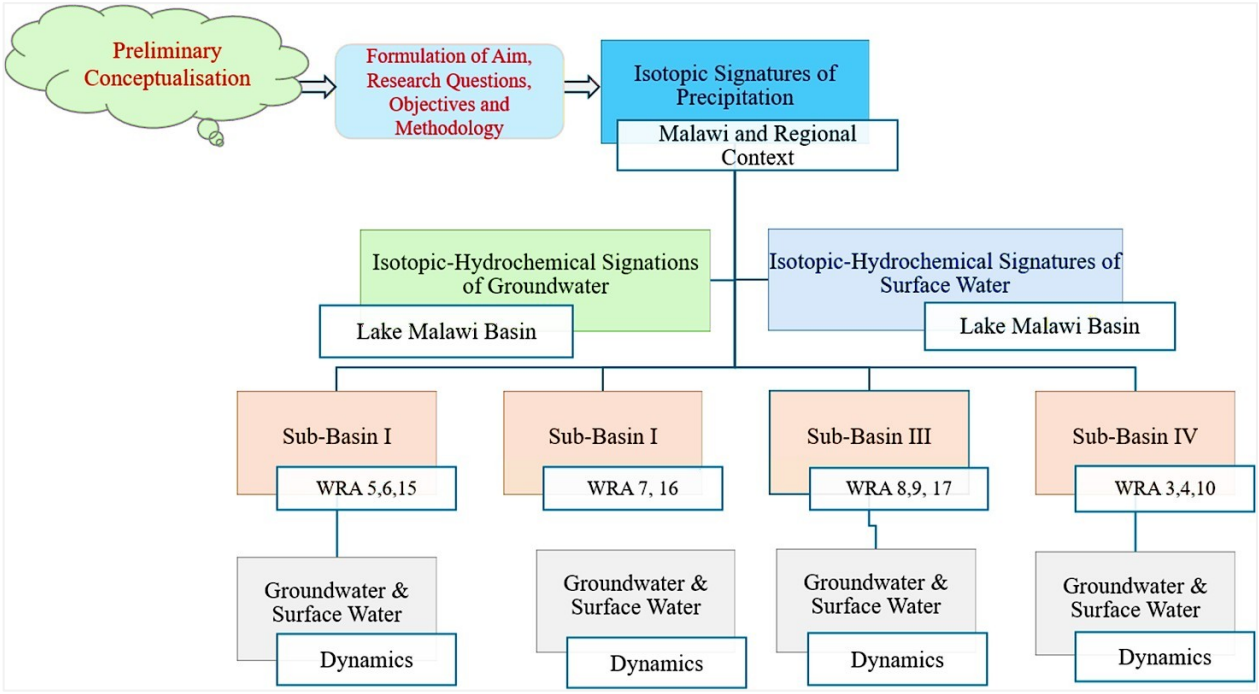

Figure 2. Methodological approach for Lake Malawi basin conceptualisation.

Table 1. Water resources areas (WRA) and corresponding catchments in LMB

Sub-basin No.	**WRA**	**River/Lakeshore Catchment**
Sub-basin I	WRA 5	Bua River catchment
	WRA 6	Dwangwa River catchment
	WRA 15	Nkhotakota Lakeshore catchment
Sub-basin II	WRA 7	South Rukuru and North Rumphi River catchments
	WRA 16	Nkhata Bay Lakeshore catchment
Sub-basin III	WRA 8	North Rukuru River catchments
	WRA 9	Songwe and Lufira River catchments
	WRA 17	Karonga Lakeshore catchment
Sub-basin V	WRA 3	Southwest Lake Malawi catchment
	WRA 4	Linthipe River catchment
	WRA 10	Southeast Lake Malawi catchment

3.2 Research Materials

This section provides a detailed description of materials used in planning and execution of this research study to achieve the primary aim and specified objectives. These research materials included both new and existing data/information, and software applications used throughout the research study.

3.2.1 Data and Information

Primary data used in this research study included the following: precipitation data (Isotopic and hydro-meteorological data), groundwater data (Isotopic and hydro-geochemical data), and surface water data (Isotopic and hydrochemical data). These datasets were grouped into two main categories: existing and/ or old data and current and /or new data. In this thesis, existing data is defined as data and information that was collected and generated prior to this research study; whereas new data is defined as data or information collected and generated during this research study.

Existing data and information was sourced primarily from published peer-reviewed articles, published and unpublished official reports (from governmental and non-governmental organizations (NGOs)) and included notable documents such as Water Resources Masterplan of 2014, Water Resources Act of 2013, National Water Policy, and 2063 National Development Agenda. The existing data was also sourced from published and unpublished academic MSc. and PhD theses. The existing data and information were also retrieved from Global Network of Isotopes in Precipitation (GNIP) online database, Malawi Network of Isotopes in Precipitation (MNIP) data repository, and Department of Climate Change and Meteorological Services (DCCMS) database. This robust body of data and literature resource was instrumental in guiding this research study, informing knowledge

gaps identification process, and shaping formulation of research aims, questions and objectives.

New data were generated during field surveys, field measurements, stable isotopic and hydro-geochemical analyses in laboratories at Central Water Laboratory in Lilongwe, Malawi, University of Strathclyde in Glasgow, Scotland and IAEA in Vienna, Austria. The new data were also retrieved from GNIP online database, MNIP data repository, and DCCMS database. The new data and information were also accessed from newly published peer-reviewed articles and official reports from government and NGOs. Overall, these distinct data sources provided a robust foundation for conducting this research study and addressing the stated aims and objectives.

3.2.1.1 Exiting Data

Primary existing data used in this research study included the following datasets: stable isotopic and hydro-meteorological data from the MNIP data repository and GNIP database, stable isotopic-hydrochemical data for groundwater and surface water sources from a peer-reviewed journal article on a Lake Malawi sub-basin IV (Figure 2; Table 1) published by the author prior to this research study (Banda et al, 2019). The existing stable isotopic data for local precipitation was collected or generated from the MNIP between 2014 and 2020 under Technical Cooperation Projects (MLW7001-7004), supported by the IAEA. This data was provided by the Water Resources Department (WRD) of the Ministry of Water and Sanitation in Malawi. Furthermore, the existing stable isotopic (oxygen ($^{18}O/^{16}O$); hydrogen ($^{2}H/^{1}H$)) and hydro-meteorological (air temperature; precipitation amount) datasets generated, from surrounding GNIP stations in Tanzania, Mozambique, Zambia, and Zimbabwe, between 1969 and 2019 were retrieved from the GNIP database of the IAEA. The hydro-meteorological data collected from meteorological monitoring network in Malawi for parameters such as air temperature and precipitation amount was obtained

from DCCMS of the Ministry of Natural Resources and Climate Change. The primary geospatial data in form of raster and shapefiles delineating international, national, and hydrological boundaries, land use patterns, groundwater contours, geological faults, river drainage networks, lakes, and other geographical features were sourced from the Water Resources Department (WRD) and Geological Survey Department (GSD) of the Government of Malawi. The digital elevation model (DEM) used in this research study was sourced from the United States Geological Survey (USGS). Quality control measures guaranteeing existing data reliability included re-checking ion balance error (IBE) for hydrochemical data, verification of sampling and analysis protocol employed in generating the data and comparison with new dataset for consistency.

Existing data quality control and validation measures included verifying sources and lineage of each dataset to ensure they originated from credible and reliable repositories. This process involved checking metadata accompanying each dataset for detailed information on data collection methods, instruments used, resolution, and any processing steps undertaken. Other aspects considered included assessing completeness and consistency of datasets, identifying any missing values or outliers that could affect analysis, and examining temporal and spatial coverage representativeness in datasets such as GNIP to ensure alignment with the study's geographical and temporal scope. Isotopic and hydro-meteorological datasets were cross-checked against independent sources or similar datasets to identify discrepancies. Quality control measures guaranteeing existing data reliability included re-checking ion balance error (IBE) (for hydrochemical data) and verification of sampling and analysis protocols employed in generating the data and comparison with new dataset for consistency. The data was normalized and standardized to resolve discrepancies in units and scales to ensure uniformity. By systematically

addressing these quality control steps, the reliability and validity of the data were enhanced, thereby strengthening the foundation of the research study.

3.2.1.2 New Data

New data generated and collected as part of this research study include the following datasets: stable isotopic and hydro-meteorological data from MNIP and GNIP stations, alongside stable isotopic and hydro-geochemical data for groundwater and surface water sampling points across the Lake Malawi basin. This data was collected and generated through field surveys and laboratory analyses between 2021 and 2023. The data collection and generation process involved collecting water samples from the MNIP stations throughout Malawi for isotope analysis and water samples from groundwater and surface water sampling points across the Lake Malawi basin for stable isotopic and hydro-geochemical analysis. The water samples were analysed concurrently from 2021 to 2023 at three different laboratory facilities: the Central Water Laboratory (CWL) of the Ministry of Water and Sanitation in Lilongwe, Malawi; the Environmental Analytical Laboratory at the University of Strathclyde in Glasgow, Scotland; and the IAEA Isotope Hydrology Laboratory in Vienna, Austria. Supplementary metadata including GPS coordinates, elevation, and other related onsite observation details were compiled during the field surveys. Where necessary, the new datasets were augmented with the existing datasets to effectively achieve the stated aims and objectives of the research study.

3.2.2 Software Applications

This section details software applications and packages that were used during the research study to help conduct tasks such as: literature search and referencing, data collection, manipulation,

statistical analysis, geochemical modelling, geospatial computation and mapping and publication of research findings. The following are software applications and packages used during the research study:

3.2.2.1 Mendeley

This software was used as a multifaceted reference management platform, facilitating efficient management of research literature, providing an organizational framework for extensive collections of academic papers. It was also used to automatically generate bibliographies and citations, which supported scholarly writing and publications. This software application was chosen to reduce potential for citation errors and saved considerable time during drafting of this thesis and associated research articles.

3.2.2.2 Quantum Geographic Information System (QGIS) (Version 3.22.1)

This GIS software developed by Gary Sherman, as an open-source GIS tool was used for geospatial mapping and analysis. This software was chosen for its open-source nature, with potential for GIS skills and knowledge transfer and exchange post PhD, considering Malawi is a least developed country where licensing technology is significantly challenging. The software was sourced from the following web-link: https://qgis.org.

3.2.2.3 PHREEQC Interactive (Version 3.7.3 (15968))

This software, developed by Parkhurst et al. in 1980, was used for simulating geochemical reactions and calculate Saturation Indices (SI). The software was sourced from the following US Geological Survey web-link: https://www.usgs.gov/software/phreeqc-version-3.

3.2.2.4 Origin Pro 2022 (Academic)

This software, developed by OriginLab Corporation, was primarily used to conduct advanced data analysis and visualization. This software is licensed to the University of Strathclyde.

3.2.2.5 Minitab 21

This software was mainly used to conduct descriptive statistical analysis. It was developed by Minitab LLC and licensed to the university of Strathclyde.

3.2.2.6 DataGraph (Version 5.4)

This software was primarily used for creating advanced graphs. It was developed by David Adalsteinsson at Visual Data Tools, Inc., between 2006 and 2024, and licensed to the researcher. This software was sourced at: http://www.visualdatatools.com/DataGraph](http://www.visualdatatools.com/DataGrap.

3.2.2.7 Microsoft Excel (Version 16.91 (24111020))

Microsoft Excel was mainly used for organizing, storing, viewing, analysing, and modelling research data. It was also used for basic plotting and statistical computations. Microsoft Excel was developed by Microsoft and licensed to the University of Strathclyde.

3.2.2.8 Microsoft Word (Version 16.91 (24111020))

Microsoft Word was used for writing and editing thesis and publications. The Microsoft Word was developed by Microsoft licensed to the University of Strathclyde.

3.2.2.9 Microsoft PowerPoint (Version 16.91 (24111020))

Microsoft PowerPoint was used for organising and formatting this thesis and its associated publications figures. and editing thesis and publications. Microsoft PowerPoint was developed by Microsoft licensed to the University of Strathclyde.

3.3 Research Methods

This section describes methods that were used to collect and generate existing and new datasets in this research study. It also describes methods used for analysis and interpretation of the collected and generated datasets to achieve the stated aims and objectives. The section outlines details of the overall research planning, including the following: selection of sampling points, sampling methods, and analysis methods. It further details field and laboratory equipment used for sample collection and analysis and approaches and techniques employed for data and information interpretation. The following is a comprehensive description of sampling strategy employed for the research study to effectively meet the set aims and objectives

3.3.1 Sampling Strategy

A carefully designed sampling strategy was employed to achieve comprehensive and representative datasets. The following key consideration informed the designing of sampling strategy for this research study: representative sampling, temporal resolution, spatial coverage, interdisciplinary integration, and isotopic and hydro-geochemical characterisation. The following is a detailed description of the sampling strategy for the research study.

3.3.1.1 Precipitation

First phase of this research study focused on establishing a baseline for stable isotopes in precipitation in Malawi in context of the surrounding region. For that to be achieved, five MNIP stations were selected for data collection of existing data and generation of new data (Figure 3a; Table 2). Additionally, four provisional stations (stations established for the purposes of this research study) were established to enhance spatial coverage, and these included the following; Bvumbwe Research Station in Blantyre, Chinyonga Area in Blantyre City, Mwanza Agricultural Development District (ADD) in Mwanza District, and Chiputula Area in Mzuzu City (Table 3). For regional precipitation analysis, surrounding GNIP stations including Gorongosa and Chitengo in Mozambique, Ndola in Zambia, Harare in Zimbabwe, and Dar es Salaam in Tanzania were selected for regional date collection (Figure 1b; Table 4). All existing and new data from the local and regional precipitation sampling stations were standardised to the internationally required monthly average format that allowed calculation of meteoric water lines (IAEA., 2019). The local dataset, collected between 2014 to 2022, was temporally lacking, hence was augmented by the temporally high-resolution regional GNIP dataset collected between 1969 to 2022. This integration produced a more representative and high-resolution dataset that offered a comprehensive local and regional perspective. This integration also allowed an enhanced spatial and temporal characterisation of meteoric water in precipitation at both local and regional scales (IAEA/WMO 2019).

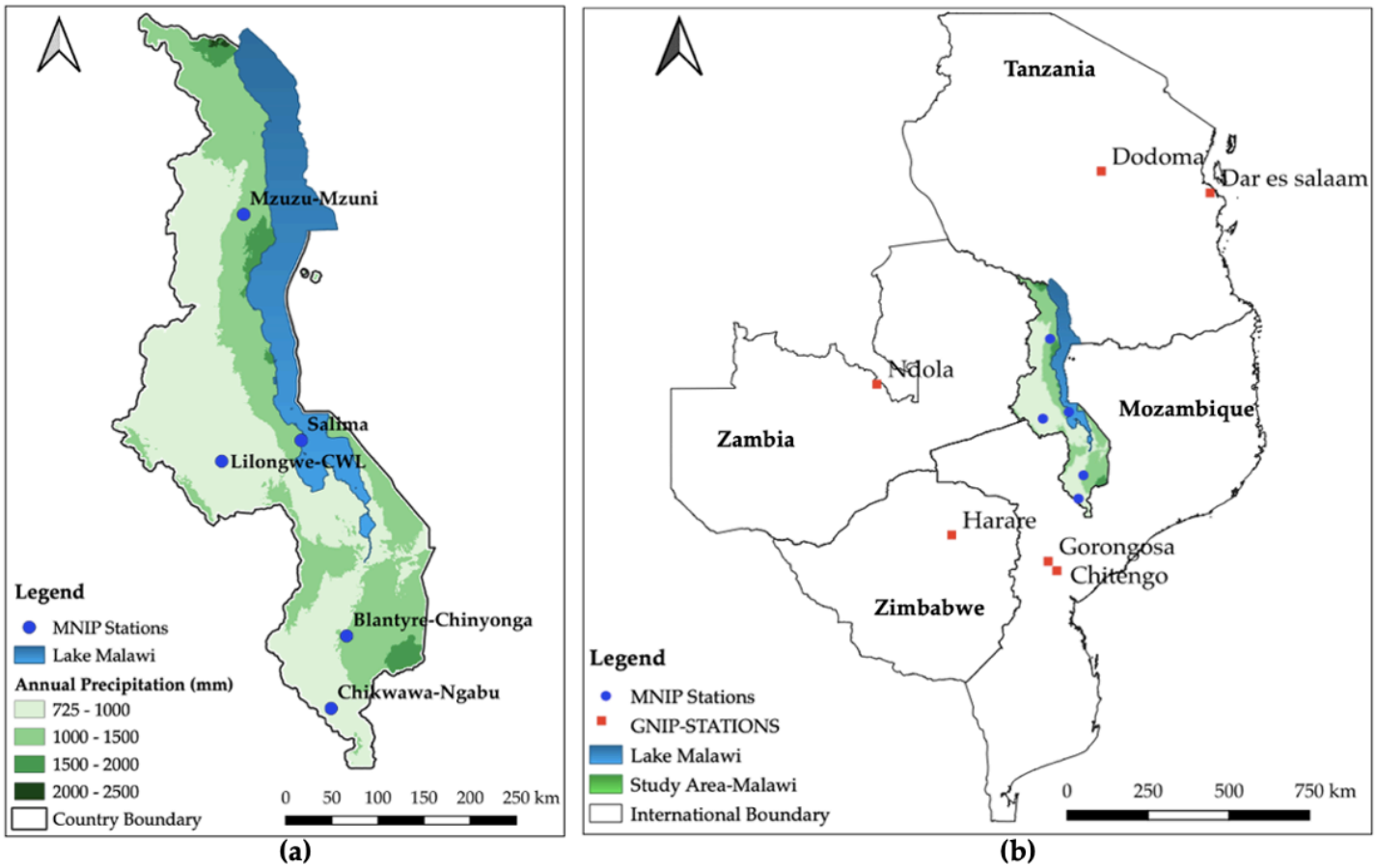

Figure 3. Malawi network of isotopes in precipitation (MNIP) stations (a) and global network of isotopes in precipitation (GNIP) stations (b).

Table 2. Malawi network of isotopes in precipitation (MNIP) stations within LMB

*Meteorological Services Stations	MNIP Stations	Decimal Degrees		Altitude (m a.s.l)
		Latitude	Longitude	
Mzuni	Mzuni	-11.41977	33.9952843	1287
Chitedze	Chitedze	-13.97662	33.7686897	1046
Salima	Salima	-13.75402	34.5892292	512
Ngabu	Ngabu	-16.53686	34.8912164	80

Table 3. Malawi network of isotopes in precipitation (provisional) stations across LMB

*Meteorological Services Stations	Provisional Stations	Decimal Degrees		Altitude (m a.s.l)
		Latitude	Longitude	
Mzuni Met Station	Chiputula	-12.89406	34.267595	1292
Bvumbwe Research Station	Chitedze	-15.920	35.070	1182
Chichiri Met Station	Chinyonga Area	-15.81392	35.0397	1127
Mwanza ADD Met Station	Mwanza ADD	-15.620	34.520	682

Table 4. Global network of isotopes in precipitation (GNIP) stations surrounding Malawi.

GNIP Stations	WMO Codes	Country	Decimal Degrees		Altitude (m a.s.l)
			Latitude	Longitude	
Harare	6777400	Zimbabwe	-17.83	31.02	417
Dodoma	6386200	Tanzania	-16.1852	35.7533	1157
Dar es salaam	6389400	Tanzania	-6.88	39.2	55
Ndola	6756100	Zambia	-13	28.65	1331
Chitengo	6729501	Mozambique	-18.9751	34.34842	34
Gorongosa	6729502	Mozambique	-18.6717	34.07239	346

3.3.1.2 Groundwater

Second research phase focussed on groundwater resource conceptualisation within the Lake Malawi basin's aquifer systems. Groundwater sampling points were selected near surface water sampling points allow evaluation of groundwater and surface water interactions in Chapter 7. Groundwater sampling points were strategically chosen from upper, middle, and lower reaches of the Lake Malawi basin to ensure spatial coverage. The selected groundwater sampling points included, dug-wells, springs, and production boreholes equipped with hand pumps. The groundwater sampling was conducted during wet and dry season for temporal resolution which allowed delineation of inter/intra-seasonal variability. Also, spatial high-resolution sampling was conducted at catchment scale that allowed more detailed investigation.

3.3.1.3 Surface Water

Third phase of this research study involved conceptualisation of the surface water resource system in the Lake Malawi basin. Thus, designing of surface water sampling strategy considered both technical and administrative factors which included the following: number of sampling points which translated into sample size, dual-seasonal sampling, time allocated for sampling and analysis to ensure timely delivery of research findings, accessibility of sampling points excess during wet (rainy) season, and more importantly health and safety of the research team. To achieve the primary aim and objective of this phase, surface water sources including rivers, water reservoirs, a lagoon, and lakes, were selected for both isotope and hydrochemical sampling. This allowed characterisation of different surface water bodies across the Lake Malawi basin. Specifically, major river systems targeted for sampling included Songwe and Lufira Rivers, North Rukuru River, South Rukuru and Kasitu Rivers, Linthipe, Lilongwe and Diamphwe Rivers, Bua River, and Dwangwa River systems. These river systems were selected for sampling, alongside an extensive network of tributaries across the Lake Malawi basin. Lakes selected for sampling included Lake Malawi, Lake Kazuni, and Lake Chiwondo. Chia Lagoon was also selected for sampling, alongside major water reservoirs in the basin that included Kamuzu Reservoirs (I & II) along Lilongwe River, Lunyangwa Reservoir along Lunyangwa River, Ruvuo Reservoir along Ruvuo River, Chikangawa Compound Reservoir along Chikangawa River, Chitete Reservoir along Chitete River, and Lusa Reservoir along Lusa River.

River sampling points were primarily selected from upper river reaches, middle river reaches, and lower river reaches. This approach allowed examination of isotopic-hydrochemical input and output signals along the river flow paths, identifying factors influencing input signal attenuation and their implications on the Lake Malawi basin's hydrology. Reservoir sampling

points were primarily selected at inflow and outflow points, and at midpoints where it was feasible. This approach allowed assessment of input and out signals, increasing understand of isotopic and hydrochemical signal attenuation and retention by the water reservoirs and implications on the corresponding riverine outflows. Lake Malawi is elongated, stretching from far northern Malawi through central to Southern Malawi. Therefore, lake sampling points were established to cover the upper, middle, and lower sections of the lake for enhanced spatial coverage. Lake Kazuni, a swollen lake along the South Rukuru River, was sampled from lower section just before it drains into the South Rukuru River. For Lake Chiwondo, one sampling point was established considering accessibility logistics at the time of sampling. Chiya Lagoon was sampled at the lower reach, before it discharges into Lake Malawi, thereby capturing the lagoon's input signals contribution to the lake.

Timings of the surface water field surveys accounted for the dual-season nature of the Lake Malawi basin; thus, sampling was conducted during both wet and dry seasons for temporal resolution. Most sampling points were established near hydrometric and surface water (quality) monitoring stations for the Water Resources Department (WRD. Notably, access to certain sites was limited, especially during the wet season when traveling to remote and flood-prone areas proved difficult. This logistical challenge influenced designing of the sampling strategy and overall coverage, but efforts were made to mitigate the constraints.

3.3.2 Field Sampling Methods

3.3.2.1 Isotope Sampling

Water samples for stable isotopes analysis were collected using 50-ml High-Density Polyethylene (HDPE) bottles, filled to the brim to prevent any airspace, sealed with paraffin film, and further secured with waterproof tape. This rigorous protocol was essential to prevent any

interferences that could alter original isotopic signatures of the water samples through leakage, evaporation, or chemical and biological processes. To maintain sample integrity, all the water samples were stored at a constant temperature of 4°C and away from direct sunlight during both transport and storage at the analysing laboratory. Precipitation samples were collected using dip-in samplers installed at MNIP stations and using standard rain gauges at provisional sampling stations. The dip-in samplers are designed to minimize evaporation effects, thus reliably preserving representativeness of the water samples. Where standard rain gauges were used, water samples were promptly covered with paraffin film to mitigate evaporation. Primarily, monthly aggregate water samples were collected from the MNIP stations. In some cases, water samples were collected weekly and aggregated into monthly composite samples. Rivers were sampled from main flow channels to ensure homogeneous mixed samples were collected. As for smaller rivers, standard grab water samples were collected and deemed representative, as these are deemed well-mixed due to narrow channels. In larger rivers, where mixing might not always be homogenous, water samples were collected at specific intervals across rivers to achieve aggregate-composite water samples, aided largely by convenient access from road/railway bridges. Before collecting the water samples, sampling bottles were thoroughly rinsed three times with sample water to avoid cross-contamination and then filled with no headspace. Lake water samples were primarily collected remotely from estuaries 1 km off the shoreline using boats and specialized depth samplers. Grab sampling was used to collect water samples from water reservoirs at their main inflow and outflow of reservoirs where they are deemed homogenously mixed. Adjustments were made for water samples from the middle sections of reservoirs, hence more representative composite samples were collected other than grab samples. Groundwater sampling focused on community water supply production boreholes which were regularly used, hence effectively purged prior to sampling. Where

boreholes were not in regular use, they were purged for at least five minutes to expunge stagnant water column and ensure more representative samples were collected. Springs were sampled at or near primary discharge points, avoiding sampling stagnant pools prone to isotopic modification through evaporation and atmospheric exchanges.

3.3.2.2 Hydrochemical Sampling

Water samples for hydrochemical analysis and isotope samples were collected simultaneously, using the same methodology. For hydrochemical water samples, two acid-washed HDPE 1-liter bottles were used at each sampling point. Concentrated Hydrochloric acid (HCl) was added to one of the bottles (with an acid to water sample ratio of 2 ml:1000ml), labelled acidified or + acid, to maintain sample stability for cation analysis by reducing pH to 2. Water sample acidification prevent s suppresses microbial activities and keeps cationic species from precipitating by keeping them dissolved during transportation and storage (APHA, 2005). Prior to water sample collection, the non-acidified sampling bottles were rinsed three times with water from the sampled point to prevent cross-contamination. The samples were collected with no headspace to eliminate any gas exchange with atmospheric air, which could alter the water sample hydrochemical composition. Like isotope samples, river samples were collected from main flow channels to ensure proper mixing, while spring samples were collected at primary discharge points. The water samples were properly labelled and stored at 4°C during transportation and storage. Regulated temperature helps to prevent chemical or biological changes, thus preserving integrity of water samples. The water samples were filtered through Whatman glass fibre filters with a 0.45 μm retention. Water sample filtration is crucial for removing insoluble particles that could obstruct or damage the sensitive analysis equipment. Overall, hydrochemical water sampling adhered to APHA (2005).

3.3.3 Water Analysis Methods

3.3.3.1 Field Analysis

Field surveys involved direct measurements of unstable water parameters including temperature, electrical conductivity (EC), total dissolved solids (TDS), and power of hydrogen ions (pH) at sampling points to ascertain the basic hydrochemical conditions and physical characteristics of the water. The field measurements were taken onsite and, where feasible, in- situ using portable multi-meter (Model: HI-98194, Hanna Instruments, Woonsocket, RI, USA). The multi-meter was carefully calibrated before taking any measures and was allowed to stabilise for 2 to 5 minutes before recording any readings. For surface water, the portable multi-meter's probe was submerged at least 100 mm into consistently flowing water channel, avoiding stagnant pools. At springs, measurements were recorded at the primary discharge points. For pumped or bailed groundwater samples, the temperature was immediately measured with the multi-meter probe immersed in a 250-ml polyethylene beaker for representative readings. Overall, the onsite measurements provided initial data on conditions of the sampled water sources at the time of sampling, helping to assess potential changes that might have occurred during water sample transportation and storage.

3.3.3.2 Laboratory Analysis

3.3.3.2.1 Isotope Analysis

Water isotope samples were analysed using a Picarro laser spectrometer (Model: L2110-i, Picarro Inc., Santa Clara, CA, USA) at Ministry of Water and Sanitation isotope hydrology laboratory in Lilongwe, Malawi. To mitigate time constraints and ensure quality assurance and control, a subset of the isotope samples was analysed using a laser spectroscopy-based technique

on a Picarro laser spectrometer (Model: L2140-i, Picarro Inc., Santa Clara, CA, USA) at the IAEA isotope hydrology laboratory in Vienna, Austria. Inter-laboratory samples were analysed between the two laboratories and produced comparable results. The sample analysis procedure involved creating a sample list in batches of 10 using Laboratory Information Management System (LIMS). Each batch included calibration and control standards to ensure robust analysis. A 1 ml sample was filtered through a 0.45 μm filter into a 2 ml glass vial and transferred to an autosampler unit for the Picarro Water Isotope Analyzer (IWA). The sample analysis was performed in high-precision mode, featuring three autoruns with dry synthetic air as a carrier gas. To prepare the IWA, first, two vials of deionized water were analysed, mostly achieving concentration peaks between 19,000 – 21,000 ppm, which were acceptable for quality control and assurance. The sample analysis was initiated after a 60-minute IWA equilibration period. Each sample was injected six times into IWA vaporiser to ensure high accuracy. Reference materials including Lake Kyoga (enriched) and Standard-09 (Greenland Ice (depleted)), were used to cover expected concentration range of stable isotope compositions. Control standards included Standard-11 (Monaco Lagoon) and Standard-06 (Heidelberg tap water), ensuring stringent quality assurance and control practices. Upon completion of the sample analysis, data files from individual analytical runs were combined and assigned identifiers before being exported to LIMS for normalization and validation. The initial three injections from each water sample were disregarded to mitigate potential memory effects, while remaining injections were processed as raw data using residual memory correction technique. Normalization was achieved by referencing the Vienna Standard Mean Ocean Water (VSMOW) and Standard Light Antarctic Precipitation (SLAP) scales, using two reference points to ensure accuracy. The finalized data underwent integration, with additional identifiers added before being exported to LIMS for further processing, normalization, and validation. The water sample chain of

custody, including sample collection, onsite measurements, sample transportation, sample holding, sample preparation, and sample analysis, adhered to International Standard Procedures (ISP) (IAEA, 2009). The water isotope analysis results were reported as delta (δ) values, representing relative difference in isotopic ratios between a sample and a standard (Coplen, 2011) (Equation 12).

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) x\ 1000\ ‰ \quad \ldots(12)$$

Where R represents a unitless isotopic ratio and where R_{sample} and $R_{standard}$ are isotopic ratios ($R = {}^{2}H/{}^{1}H$ and $R = {}^{18}O/{}^{16}O$) of sample and standard, respectively. The delta notation (δ) measures deviation of a sample from a standard. These deviations are relatively small and are thus expressed in parts per thousand (‰) to account for the minor isotopic variations (Rozanski et al., 1993; Coplen, 2011; IAEA, 1981). A positive δ value indicates enrichment in heavy isotopes compared to the VSMOW standard, while a negative δ value indicates depletion in that respect, where the VSMOW values for $\delta^{2}H$ and $\delta^{18}O$ are set to zero. Deuterium excess (*d*-excess or *d*), defined in Equation (2) (Dansgaard, 1964), is used as a proxy indicator for meteorological conditions in source regions where precipitation-bearing moisture originates (Rozanski et al., 1993; Merlivat and Jouzel, 1979; Gat et al., 1970). The *d*-excess is primarily influenced by atmospheric relative humidity over the ocean surface (Clark and Fritz, 1997). When mean global humidity is approximately 85%, resulting mean global d-excess value for precipitation is *ca.*10 ‰ (Merlivat and Jouzel, 1979; Gonfiantini, 1986).

$$d = \delta^{2}H - 8\delta^{18}O\ ‰\ \text{VSMOW} \quad \ldots(13)$$

A *d* value of approximately 10 ‰ suggests that precipitation originated from oceanic moisture, with

no or insignificant evaporation effects. In contrast, a *d* value greater than 10 ‰ may indicate influence of moisture recycling through large-scale evaporation which correspond to low atmospheric humidity at its source region (IAEA, 2005). The *d* value can also be affected by secondary processes like raindrop evaporation beneath clouds and evaporation of water bodies on land (Rozanski, 1993; Froehlich et al., 2002). These processes can either decrease or increase *d* values, respectively, allowing *d*-excess to be used as a reliable proxy indicator for moisture source and evaporation effects.

3.3.3.2.2 Hydrochemical Analysis

Hydrochemical analyses were performed both at the Environmental Analytical Laboratory of the University of Strathclyde in Glasgow, Scotland, and at the Central Water Laboratory of the Ministry of Water and Sanitation in Lilongwe, Malawi. The hydrochemical analyses included measurements of dissolved anionic and cationic species following International Standard Procedures (ISP) (APHA, 2005). Collaboration between the two labs facilitated timely analysis and inter-laboratory quality controls. Ion chromatography (Model: 850 Professional IC, Metrohm, Switzerland) quantified fluoride, chloride, nitrate, and sulphate ions. An inductively coupled plasma spectrometer (Model: iCAP 6000 Series, Thermo Scientific, Waltham, MA, USA) measured cations including iron, sodium, potassium, magnesium, calcium, and manganese. Carbonate and bicarbonate concentrations were determined using standard titration method (standard hydrochloric acid method), while alkalinity was measured using a photometric analyser (Model: KONE Aquakem V.7.2.AQ2, Skalar, Brenda, Netherlands). To verify accuracy of the hydrochemical analysis results, an ionic balance error (IBE) was calculated for analysis of each sample and achieved an acceptable range of ± 5% in all the samples. All field measurements and

laboratory analyses were conducted in strict adherence with ISP (APHA., 2005).

3.3.4 Data Analysis and Interpretation

3.3.4.1 Descriptive Statistical Analysis of Stable Isotopic and Hydrochemical Data

Data analysis and interpretation of stable isotopic and hydrochemical data involved use of various descriptive statistical treatment methods. These methods included distribution statistics to ascertain frequency of different values among the measured parameters, represented visually in histograms. The mean, mode, and median were computed to depict central tendency of the datasets, with box plots and interquartile range plots providing additional visualization. Further, the range, standard deviation, and interquartile range were employed to assess the variability or dispersion of the measured concentrations. These measures helped illustrate the extent of spread within the data, using visual aids such as box plots, interquartile plots, and scatter plots. Collectively, these descriptive statistics offered crucial insights into the measured hydrochemical parameters and facilitated identification of potential relationships among them. By utilizing these statistical tools, the data was presented in a clearer and more interpretable manner.

3.3.4.2 Stable Isotope Data

3.3.4.2.1 Precipitation Data

The first phase of data analysis aimed to identify key input signals from local precipitation. A descriptive statistical analysis was conducted to detect any spatial or temporal trends or patterns in the data. The locally measured $\delta^{18}O$ and $\delta^{2}H$ data for precipitation from MNIP stations were used

to establish the first-ever Local Meteoric Water Line (LMWL) through an error-in-variable regression analysis (Boschetti et al., 2019). The precipitation data was subsequently plotted and compared against the Global Meteoric Water Line (GMWL) to assess any influence of evaporation. In addition to the LMWL, a Regional Meteoric Water Line (RMWL) was calculated using $\delta^{18}O$ and $\delta^{2}H$ data from the MNIP and regional GNIP stations, providing insights into isotopic characteristics of meteoric water across the surrounding region. Deuterium excess was calculated using Equation 13 (Dansgaard, 1964) to delineate primary sources of air moisture affecting local and regional precipitation and to explore implications for isotopic signal attenuation along groundwater and surface water flow paths across the Lake Malawi basin. Correlations were drawn between isotopic data and factors such as precipitation amount, air temperature, and elevation to determine potential isotopic effects. Generally, when precipitation data aligns with the GMWL, it indicates that the original moisture source bearing that precipitation originated from an oceanic source and has not been significantly evaporated (Woodcock et al., 1963; Craig et al., 1965). Further, precipitation data plotting below the GMWL suggest excess oxygen-18 ascribed to secondary evaporation of raindrops during precipitation events (Craig et al., 1961). When precipitation data plot above the GMWL, it indicate excess deuterium higher than 10‰ of the GMWL, often associated with localised moisture recycling effect (Yurtsever et al., 1980).

3.3.4.2.2 Groundwater and Surface Water Data

The second stage of data analysis involved examining stable isotope signatures of groundwater and surface water to identify any spatial or temporal trends across the Lake Malawi basin. The $\delta^{18}O$ and $\delta^{2}H$ data were analysed alongside the Local Meteoric Water Line (LMWL), which was calculated in the first phase of data analysis (Banda et al., 2021), the Global Meteoric

Water Line (GMWL) (Craig, 1961), and a local deuterium excess line determined during this current phase of data analysis (Banda et al., 2024). This comparison was conducted to provide insights into the origins and fractionation (enrichment/depletion) processes of groundwater and surface water. The $\delta^{18}O$ and $\delta^{2}H$ data were categorized according to seasons, hydrological catchments (also known as Water Resource Areas, or WRAs), physiographic zones, and elevation levels (upland or lowland) to facilitate detailed data analyses across different spatial and temporal scales. Deuterium excess was calculated for individual samples to investigate influence of evaporation and identify origins of recharging inputs to groundwater and surface water systems. The use of spatial maps in conjunction with diverse graphical data representations, including delta space plots, box plots, piper plots, and histograms, significantly improved analysis and interpretation of the stable isotopic data. Typically, when $\delta^{18}O$ and $\delta^{2}H$ data for groundwater and surface water align with LMWL or the Global Meteoric Water Line (GMWL), it indicates that the water originates from meteoric sources without substantial evaporative alterations. However, deviations from these lines may indicate a variety of isotopic fractionation processes including interaction of water with aquifer rocks, hydrogen sulphide exchange reactions, and open-surface evaporation and condensation.

3.3.4.2 Hydrochemical Data

This section describes methodologies and techniques applied in analysing and interpreting hydrochemical data. Various methodological approaches were used for data analysis and interpretation. Graphing and visualization techniques were employed to illustrate data patterns and trends visually. Geospatial analysis was conducted using QGIS software to analyse spatial distributions and relationships. A Piper diagram was used to categorise and compare different water

types. Similarly, a Gibbs diagram was applied to delineate geochemical reactions controlling water chemistry and evolution. Chloro-Alkaline Indices were used to evaluate ion exchange reactions within the groundwater system. Bivariate and multivariate ionic weight ratios were used to identify geochemical reactions influencing water chemistry. Lastly, geochemical modelling was conducted using PHREEQC software to predict mineral solubility and chemical reactions.

3.3.4.2.1 Piper Plots: Classification of Hydrochemical Facies to Group Water Types

A Piper plot was employed to analyse hydro-geochemistry of both groundwater and surface water, facilitating identification of distinct hydrochemical facies (Piper, 1944). This method enhanced understanding of the hydro-geochemical characteristics in the Lake Malawi basin and illustrated how surrounding rock minerals impact chemical signatures of groundwater along its flow paths. In the process of crafting a Piper plot, concentrations of key cations (calcium, magnesium, and the aggregate of sodium and potassium) as well as anions (bicarbonate, sulphate, and chloride) were initially converted from mg/L to meq/L. These concentrations were subsequently normalized to ensure their combined total approached 100%. After normalization, the values of cations and anions were plotted on a triangular diagram, where each point's position indicated relative proportions of these ions in a water sample. These data points were then projected onto a diamond-shaped plot, offering a clearer visual depiction of the chemistry of groundwater and surface water. The position of each point relative to the axes revealed the compositional type of water across the Lake Malawi basin. By classifying water samples into distinct types, this technique provided deeper insights into the factors driving the chemical evolution of both ground and surface water along their flow paths.

3.3.4.2.2 Gibbs Diagram: Geochemical Evolution

The Gibbs diagram was used to identify geochemical reactions controlling groundwater chemical evolution in the Lake Malawi basin, including rock weathering, precipitation, and evaporation. In this diagram, log-transformed TDS (mg/L) is plotted along the horizontal axis to reflect overall dissolved ion species concentration (Gibbs, 1970), while the vertical axis depicts ionic weight ratios of major ions: either the ratio of sodium to the sum of sodium and calcium (Na^+/ ($Na^+ + Ca^{2+}$)), or the ratio of chloride to the sum of chloride and bicarbonate (Cl^- / ($Cl^- + HCO_3^-$)). These ratios are used to evaluate influence of rock-water reactions relative to those of evaporation and precipitation. A typical Gibbs diagram is divided into three distinct zones, each representing a dominant mechanism controlling water chemistry: Rock Dominance, where chemistry is primarily influenced by reactions with rock minerals; Evaporation or Crystallization Dominance, characterized by evaporation exceeding precipitation, leading to higher TDS concentrations; and Precipitation Dominance, where rainwater, typically low in TDS, predominantly affects the water chemistry. The dominant control process is determined by where most samples plot on the diagram.

3.3.4.2.3 Chloro-Alkaline Indices: Ion Exchange Reactions

Schoeller chloro-alkaline indices were used to refine evidence of ion exchange reactions and determine how these reactions affect groundwater chemistry in the Lake Malawi basin. Equation 14 and 15 define computation of the Schoeller chloro-alkaline indices.

$$\text{CAI (I)} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{(\text{Cl}^-)} \quad \ldots(14)$$

$$\text{CAI (II)} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{(\text{HCO}_3^- + \text{CO}_3^{2-} + \text{SO}_4^{2-} + \text{NO}_3^-)} \quad \ldots(15)$$

When values of CAI-I and CAI- II are less than zero, it indicates that cation exchange is happening in a forward reaction. If the values are greater than zero, it means the exchange is occurring in a reverse direction (Schoeller., 2005).

3.3.4.2.3 Saturation Index Method: Geochemical Modelling

The Saturation Index (SI) was used to determine equilibrium state of groundwater in relation to rock minerals (Merkel et al., 2008.; Singh et al., 2017; Srinivasamoorthy et al., 2008). Defined by Equation (16) and computed using PHREEQC software (version 3.7.3), SI measures the balance between groundwater and rock minerals (Parkhurst & Appelo, 1999).

$$\text{SI} = \log\left(\frac{\text{IAP}}{\text{K}_{\text{sp}}}\right) \quad \ldots(16)$$

In Equation (16), 'IAP' denotes ion activity product, and 'K_{sp}' denotes solubility product. The PHREEQC software computes SI by logging ratio of Ion Activity Product (IAP) to Solubility Product (K_{sp}). An SI value of zero indicate that the system is in equilibrium, while a negative SI value indicate that groundwater is undersaturated with minerals, a condition that potentially leads to mineral dissolution. A positive SI value suggest that groundwater is oversaturated, implying an excess in mineral content that could cause precipitation.

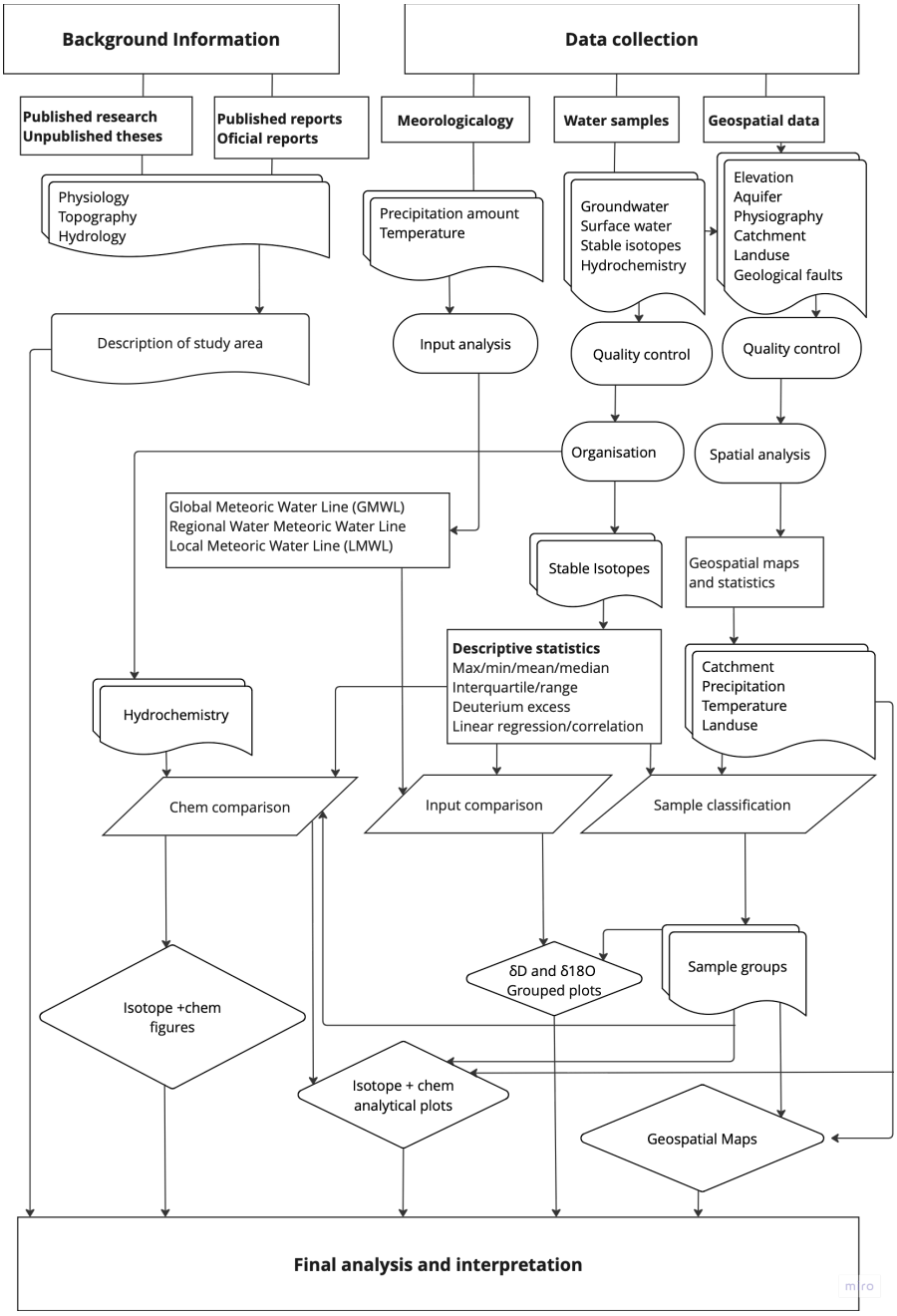

Figure 4. Methodological flow chart: data collection, analysis, interpretation.

3.4 Summary

This chapter described the materials and methods employed to meet the set primary aim and objectives of this research study. It explored applicability of a novel mixed-methods approach

(primarily integrating isotopic and hydrochemical tracers) to water-resource conceptualisation in a developing world context, where data scarcity and limited resources hinder comprehensive monitoring and analysis of water resource systems. The outlined methodology effectively supported achievement of the research's primary aim and objectives through this designed innovative, stepwise process. The methodology segmented implementation of the study into five distinct phases. The initial phase involved identifying knowledge gaps through a systematic review and analysis of existing data and literature. The second phase focused on establishing a stable isotopic baseline for precipitation within the study area. In the third and fourth phases, the methodology facilitated a detailed conceptualization of groundwater and surface water resources, respectively. The final phase integrated insights from the earlier phases and explored interactions between groundwater and surface water at a sub-basin level. Each phase employed specific methodological approaches, detailed within this chapter, that significantly contributed to meeting the research aims and objectives. These methodologies were further validated and elaborated upon a series of peer-reviewed articles, some of which are published, others under review, and some prepared for submission, underscoring the rigor and scholarly contribution of this research study. Figure 3 in this chapter summaries the comprehensive flow process of the research study, condensing the sequential and interconnected nature of the employed methodologies. Building upon this detailed methodological framework, the subsequent chapter (Chapter 4) delves into establishment of a baseline characterization of stable isotopes in precipitation. This analysis proved crucial for decoding the isotope hydrology and hydrogeochemistry of the Lake Malawi basin. The findings anticipated from Chapter 4 significantly enhanced understanding and interpretation of origins and interactions of surface water and groundwater within the basin, providing a critical scientific basis for sustainable water resource management in the region.

3.5 References

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CHAPTER 4: BASELINE CHARACTERISATION OF STABLE ISOTOPES IN PRECIPITATION

4.1 Preface

Chapter 3 of this thesis detailed the research methodology used to fulfil the aim and objectives of the PhD research in this thesis. Chapter 4, the current chapter, presents results from the first phase of the thesis, that was conducted in the Lake Malawi basin, quite key to this thesis. The primary goal of this phase was to conduct a thorough characterisation of stable isotopic composition of precipitation in Malawi and to establish a Local Meteoric Water Line (LMWL) to support Integrated Water Resource Management (IWRM). This phase addressed research question (RQ) 1: "How can application of water isotope tracing enhance understanding of local precipitation to support IWRM?" The research objectives tackled were: (RO 1.1) to establish a national-scale isotopic baseline characterization for precipitation using oxygen ($^{18}O/^{16}O$) and deuterium ($^{2}H/^{1}H$) ratios; (RO 1.2) to develop LMWL for Malawi in the context of the wider region, and (RO 1.3) to identify and delineate moisture sources that influence local precipitation using deuterium excess tracer method, for predictive modelling of how changes in global climate trends might impact regional local and regional hydrology. The findings from this phase were published in a peer-reviewed journal and form the main content of this chapter.

The initial motivation for the first phase of the thesis was ignited by the author's preliminary isotope studies in Malawi, which specifically examined the Linthipe River and Southwest Lake Malawi catchments (Banda et al., 2019), as well as the Shire River and Ruo River catchments (Banda et al., 2020). The earlier study focusing on the Lake Malawi catchment (Banda

et al., 2019) investigated the suitability and applicability of isotopic techniques for water resource management in Malawi. This research critically evaluated the in-country capacities and access to isotope hydrology technology from the perspective of the developing world. Significant shortcomings in technical capacity and access to isotope hydrology technology were uncovered. Moreover, the study underscored a profound deficiency in water-related research in Malawi, emphasizing the critical need for comprehensive research into surface water and groundwater management at both catchment and basin levels. One of the primary findings highlighted the lack of local baseline isotopic data for precipitation, surface water, and groundwater. Establishing a baseline for precipitation is crucial for the accurate interpretation of isotopic data from groundwater and surface water within the hydrological cycle. Prior to this PhD study, local research predominantly relied on stable isotopic benchmarks derived from precipitation data obtained from nearby stations in the Global Network of Isotopes in Precipitation (GNIP), accessed through the International Atomic Energy Agency (IAEA) GNIP database. These preliminary findings highlighted the urgent necessity to develop a local stable isotopic baseline for precipitation and a Local Meteoric Water Line (LMWL). Establishing these would provide a locally-specific isotopic reference that accurately reflects the unique atmospheric, hydrological, and geographical conditions of the area, which are not fully represented by the Global Meteoric Water Line or regional meteoric water lines from neighbouring GNIP stations.

This first phase of the thesis represents a groundbreaking advance in the contribution to scientific knowledge by providing robust, new datasets of stable isotopes and delivering unique insights into the characteristics of meteoric water in local and regional precipitation. The key outcomes of the first phase of the thesis, which are discussed in this chapter, include establishment of the first baseline data of stable isotopes in precipitation and the Local Meteoric Water Line

(LMWL) for Malawi. This milestone was facilitated by leveraging stable isotopic data collected from local MNIP stations from 2014 to 2019 and regional GNIP stations from 1969 to 2019. Another significant outcome from this phase of the thesis is the delineation of moisture sources influencing local-meteoric water isotopic signals. The following is a peer-reviewed journal article that outlines the key findings of the initial phase of the thesis.

4.2 Research Article 1: Main Paper

water

IMPACT FACTOR 3.0

CITESCORE 5.8

Article

National Stable Isotope Baseline for Precipitation in Malawi to Underpin Integrated Water Resources Management

Limbikani C. Banda, Michael O. Rivett, Anold S. K. Zavison, Sydney Kamtukule and Robert M. Kalin

MDPI

https://doi.org/10.3390/w13141927

water

MDPI

Article

National Stable Isotope Baseline for Precipitation in Malawi to Underpin Integrated Water Resources Management

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Abstract: With the resurgence of water-isotope tracing applications for Integrated Water Resource Management in developing countries, establishing a stable isotopic baseline is necessary. Developing countries, including Malawi, continue to struggle with the generation of consistent and long-term isotopic datasets due to non-existent or inadequate in-country water-isotope capacity. Malawi has made significant advances in its quest to establish a stable isotopic baseline through the establishment of the Malawi Network of Isotope in Precipitation. This study provides the first results for the isotopic characterization of precipitation in Malawi with a view to reinforcing understanding of the country's hydrological cycle. Error-in-variables regression defined a Local Meteoric Water Line as δ^2H = 8.0 (±0.3) $\delta^{18}O$ + 13.0 (±2.0) using stable isotopic records of 37 monthly samples from 5 stations between 2014 and 2019. Local precipitation (isotopic composition) is consistent with global precipitation expectations, its condensation-forming process occurring under equilibrium conditions and a higher intercept (d-excess) above the 10‰ for Global Meteoric Water Line, implying that air moisture recycling significantly influences local precipitation. Wider variations observed in local precipitation isotopic signatures are largely attributed to different moisture-bearing systems and diverse geographic factors across the country. Additional stations are recommended to improve spatial coverage that, together with longer temporal records, may help understanding and resolving uncertainties such as the altitude effect. This pioneering study is expected to facilitate Malawi's ambition to achieve integrated use and improved protection of its surface water and groundwater resources in response to mounting climate change, growing population and land-development concerns.

Keywords: precipitation; Stable Isotope Baseline; Local Meteoric Water Line; Integrated Water Resources Management; deuterium excess; Malawi

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1. Introduction

Integrated Water Resource Management (IWRM) requires an understanding of the provenance of the various water sources contributing to a resource that may enable their protection. Establishing the stable-isotopic signature of these waters and mixed waters subsequently occurring within water resources provides diagnostic insight into the physical processes the water has been subjected to over time, the identification of possible water sources and the improved understanding and conceptualization of the local or regional hydrological cycle; all which underpin IWRM [1–5].

The diagnostic value of surface water and groundwater resource stable-isotope signatures is predicated upon the characterization of isotopic signatures present in meteoric (precipitation) inputs [6–9]. It is important to the national-scale implementation of IWRM that countries establish stable-isotopic baseline signatures in local precipitation. In developing countries such as Malawi and across Sub-Saharan Africa (SSA), baseline development and wider isotopic tool use have been hindered by poor socioeconomic conditions, little

investment in the science and a lack of in-house isotope analytical facilities. Reliance to date has been on samples collected and exported by researchers in developed countries leading to sporadic isotope studies in Malawi [10–17].

Malawi has a complex land-locked hydrology. The north–south-oriented country spans significant latitude from 9° S to 17° S. Its location at a southern extremity of the East African Rift System (EARS) results in significant topographic variation, from *c.* 30 to 3000 m asl. Lake Malawi covers 23% of the surface area of the country and its setting within the larger African Great Lakes region (incl. Malawi, Victoria and Tanganyika) results in a predominant great-lake influence (a significant source of moisture) on its East African regional climate [18]. It experiences a sub-tropical climate influenced by altitude, relief and Lake Malawi. It is generally cool in plateau areas but hot in the rift valley, becoming increasingly semi-arid from the north to the southern lowlands. Seasonal contrasts are significant with distinct wet (November–April) and dry (May–October) seasons driven by north-easterly winds (Mpoto) in the former and strong south-easterly winds (Mwera) in the latter seasons. Topographically influenced mean temperatures range from 17 to 37 °C in the hot–dry season. Precipitation is influenced by the migration of the Inter Tropical Convergence Zone (ITCZ), Congo Air Boundary (CAB) and Tropical Cyclones [19]. Given the above complexities, spatial–seasonal characterization of variations in precipitation stable-isotope signature across Malawi is vital to assess the expected depletion of heavier isotopes from increased latitude, closeness to the continental interior and increased altitude due to temperature variations and 'rainout' effects [18]. To date, Malawi has relied upon stable isotopic data records from Global Network of Isotopes in Precipitation (GNIP) stations located outside the country [10–17]. Malawi represents a gap in SSA's regularly monitored network.

The country is vulnerable to several 'global issues'. Although there are substantial surface water resources within Lake Malawi and its Shire River outflow, these only provide pipeline supplies to its urban centers. Most of Malawi's population is the rural poor, in common with around half a billion people in SSA [20], almost exclusively reliant on groundwater [21]. Such supplies are affected by functionality concerns, a global issue, with many of Malawi's circa 120,000 water points vulnerable to 'asset stranding', driving the consideration of IWRM alternatives [22,23]. Malawi's water resources are also vulnerable to a host of development pressures, including irrigated agriculture, urbanization, rapidly increasing population (*c.* 3% annually), increasing (hydroelectric) energy needs and deforestation; each disturbing hydrological systems and disrupting the sensitive balances between runoff and recharge [24–29]. Malawi has a significant vulnerability to climate change and associated intensification of drought and flood events. Although influence is already probable, evidenced by a series of climatic perturbations in SSA [30–32] and in Malawi [30,33–35], the priority remains to establish current baselines (including stable isotopes) to benchmark further change. Finally, as a landlocked country neighboring Mozambique, Tanzania and Zambia, and its main Shire River draining into the Zambezi River also influencing Angola, Botswana, Namibia and Zimbabwe, Malawi has significant transboundary aquifer and surface water obligations [36].

Malawi is one of the world's most physically vulnerable places to repercussions resulting from climate change [37,38]. The country has recorded climatic evidence of significant temperature variability and increased intensity and frequency of occurrence of floods and drought [29–35]. Climate-change-induced perturbations in the Sub-Saharan precipitation regime causing a rise in numerous severe weather incidents are also asserted [30–32].

Our research is an outcome of the partnership between the International Atomic Energy Agency (IAEA) and Malawi's Ministry of Forestry and Natural Resources that enabled the 2018 commissioning of an isotope hydrology national facility. This specifically comprises the operationalization of an Isotope Hydrology Laboratory (IHL) and the establishment of the Malawi Network of Isotopes in Precipitation (MNIP). The data collected to date from the MNIP form our focus herein. The objectives set were to establish a stable isotopic baseline for precipitation at national scale for Malawi, to understand the factors

that may influence spatial and temporal (intra-seasonal) isotopic signature variability and to develop a Local Meteoric Water Line (LMWL) for Malawi that will act as a benchmark for future isotopic studies assessing water-resource status. The overarching goal was to provide a foundational characterization of precipitation that will reinforce understanding of Malawi's hydrological cycle and thereby underpin future IWRM and policy decision making. This study represents the first-ever characterization of the stable isotope precipitation baseline for Malawi and hence provides a pivotal step to achieving the long-held ambition to provide isotope-informed IWRM for the country. Study findings have already helped underpin our companion catchment [39] and basin-scale [40], stable-isotope studies in Malawi and ongoing studies of other catchments.

2. Materials and Methods

2.1. Study Area Setting

Malawi occurs as an elongate plateau towards the south-western extreme of the lower EARS that structurally dominates its landform (Figure 1). Its diverse physiography ranges from highlands reaching 3000 m asl, plateau occurring at 750–1300 m covering much of the country, rift valley scarp and the rift valley and associated plains that decline to around 30–100 m asl in the Lower Shire Valley–Mozambique border. The highland and plateau comprise normal-faulted blocks of Precambrian and Lower Palaeozoic Basement gneiss and granulite rock (the pan-African 'basement rock') with Quaternary colluvium, alluvium and lacustrine basins forming the rift valley plains. These form Malawi's three main aquifer types; the weathered basement rock, the often-underlying fractured basement rock and the valley alluvial aquifer systems upon which rural Malawians extensively rely upon for water supply [21,22,41].

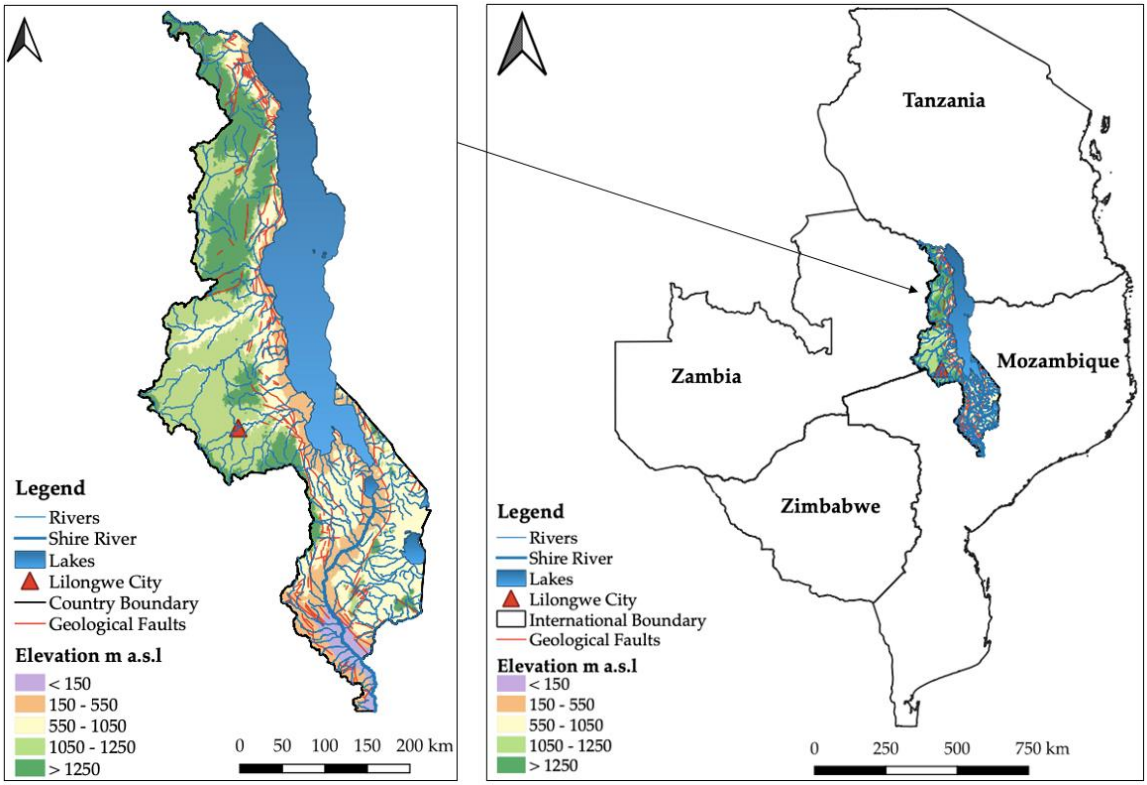

Figure 1. Study area showing topography (various colored zones), major rivers, lakes, fault lines and neighboring coun–tries.

Malawi's drainage system is dominated by the Lake Malawi–Shire River system, into which a vast network of many of its rivers drain (e.g., Ruo, Linthipe, Rukuru and Dwangwa). A few rivers drain to the endorheic Lake Chilwa basin to the east of the rift valley. Other moderately large lakes (Chiuta and Malombe) also exist, as well as many

dams (reservoirs) constructed for water supply. Malawi is a water-stressed nation, and in particular, groundwater and surface water resources during the dry season are significantly stressed, especially in severe drought years [21].

Climate and Precipitation Derivation in Malawi

Malawi's climate is sub-tropical, with generally cool conditions experienced in the plateau and hot, dry conditions in the rift valley. A distinct wet season from November to April and dry season from May to October occurs throughout the country. Based on the revised Köppen-Geiger system, Malawi's climate may be classified as Aw or Savannah, with the following defining criteria; 'Not (Af) and Pdry < 100 − MAP/25', where Af is rainforest, MAP is mean annual precipitation and Pdry is precipitation of the driest month [35]. ITCZ migration southwards between December and January, and northwards between February and March, accounts for the moisture for most of Malawi's precipitation. South-east trade winds blowing across the Indian Ocean from east to west along the Mozambique Channel occasionally bring widespread heavy precipitation in April extending into May in northern Malawi, and infrequent tropical storms that vary in impact and intensity. Due to its proximity to the East African Coast, Malawi experiences rather light precipitation and drizzles (locally known as Chiperoni) mainly during early month of July, particularly in highlands facing south-east [29].

Malawi's precipitation regime has two distinct features: a region with a strong precipitation maximum in austral autumn along Lake Malawi's western shoreline and a brief period of reduced precipitation in mid-February ascribed to a shift in prevailing precipitation and circulation regime [42]. The precipitation regime is characterized by strong seasonality, inter-annual fluctuations and intra-annual spatial and temporal distribution and variability, which are critical to water resources planning and management [43]. Inter-annual monthly precipitation is influenced by Indian Ocean Sea Surface Temperature (SST) attributed to the El Niño Southern Oscillation Phenomenon [43]. Annual precipitation ranges from 725 mm to 2500 mm and the country's precipitation is largely influenced by diverse topography and proximity to Lake Malawi [44,45]. Generally, highlands receive the highest and lowlands the lowest precipitation amount. Most of the precipitation (*c.* 90%) occurs between November and April [46]. Within this period, precipitation is concentrated between December and March, with maxima occurring in January in most of the country but delayed until March, close to Lake Malawi's western shoreline [42].

2.2. Malawi Network of Isotopes in Precipitation (MNIP): Design, Sampling and Analysis

The Government of Malawi, with funding from International Atomic Energy Agency (IAEA) established a monitoring network of isotopes in precipitation at national scale through the Water Resources Department (WRD) in the Ministry of Forestry and Natural Resources between 2014 and 2018. The monitoring network is known as the '*Malawi Network of Isotopes in Precipitation*' (MNIP), and Figure 2a locates the MNIP stations. The MNIP was commissioned for collection of systematic data on isotopic signatures of precipitation for the establishment of a stable isotopic baseline for precipitation at national scale. Currently, it comprises five (5) stations (sited at (3) and near (2) meteorological service stations) equipped with a rain collector 'dip-in sampler' and access to meteorological equipment for measuring meteorological parameters (e.g., rain gauge for measuring precipitation amount). The siting rationale of the MNIP stations aimed at providing balanced national coverage and capturing influences of different weather systems affecting precipitation across the country. This was a fledgling starter network meant to be expanded (by geostatistical tools to achieve an optimal network design) with additional stations for spatial and temporal enhancement of the isotopic data records [47].

Between 2014 and 2019, a total of 40 monthly water stable-isotope samples were collected from the MNIP stations (Table 1) using dip-in samplers designed to prevent evaporation (and eliminate the need for paraffin) [48]. The water stable-isotope samples were collected on a daily and a weekly basis and thereafter mixed to provide integrated

monthly samples. Samples were contained in 25 mL brown (light-proof) bottles with air-tight caps and no headspace and kept at 4 °C during transportation and holding. Laboratory analysis involved daily, weekly and monthly precipitation samples, with monthly samples being the focus of this study. A sub-dataset (n = 37) (from stations with precipitation amount data) generated from monthly precipitation amount weighted samples were then used to derive a national Local Meteoric Water Line (LMWL) using error-in-variables regression analysis denoted EIV-LMWLw. The EIV-LMWLw equation included standard errors (representing mean deviation of isotopic values from the EIV-LMWLw) for its slope and intercept [39,49]. The weighted EIV-LMWLw equation was then compared with a non-EIV-LMWLw equation derived from a regressed entire non-weighted dataset (n = 40) to check any variations in extent of slope and intercept that were found to be insignificant. Summary statistics of precipitation isotopic data were computed based on the entire dataset (weighted and non-weighted), but the LMWL and other isotope-related graphs focused only on the precipitation amounts weighted dataset.

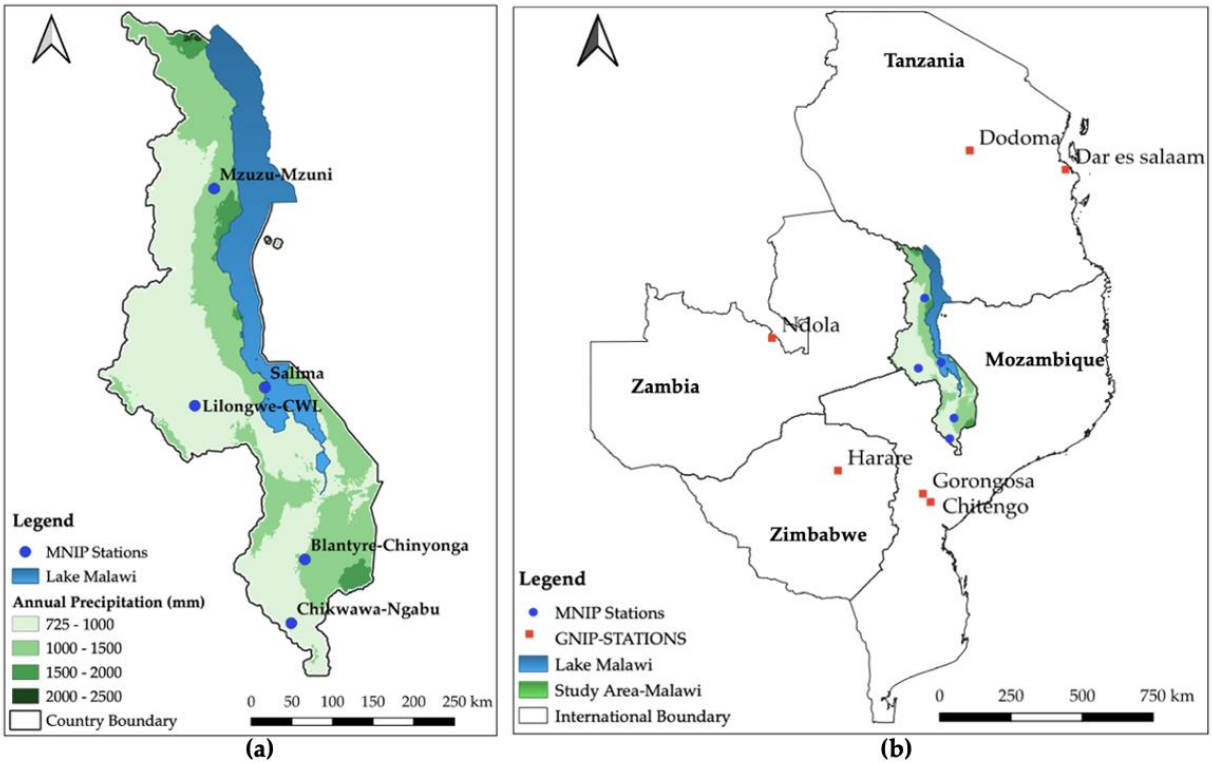

Figure 2. Malawi–network of isotopes in precipitation (MNIP) stations (**a**) and global network of isotopes in precipitation (GNIP) stations (**b**).

Analysis of oxygen ($^{18}O/^{16}O$) and deuterium ($^{2}H/^{1}H$) ratios was undertaken using an automated cavity ring-down spectrometer, specifically a Picarro isotopic water analyzer (Model: L2110-I, Picarro, Santa Clara, CA, USA) at Ministry of Forestry and Natural Resources Isotope Hydrology Laboratory (IHL). Daily calibration of light and heavy standards encompassing the expected ranges of isotopic signatures in the samples was undertaken, alongside the use of a daily control mid-range intermediate standard. The Picarro isotopic water analyzer was prepared by running two vials of deionized water, and accuracy of measurement was checked by inspecting concentration peaks, with adherence to an acceptable range of 19,000–21,000 ppm for abundance of isotope ratios for both deuterium ($\delta^{2}H$) and oxygen-18 ($\delta^{18}O$). The isotopic analysis precision (2σ) was set at ±0.2‰ for oxygen-18 and ±2.0‰ for deuterium, while quantification and validation of results were accomplished via dedicated Laboratory Information Management System (LIMS) software. The processed isotopic analysis results were reported in delta values ($\delta^{2}H$ and $\delta^{18}O$) representing parts

per thousand (‰) deviations from the international Vienna-Standard Meteoric Ocean Water (V-SMOW) [50,51] with precision (2σ) of ±0.2 permil for $\delta^{18}O$ and ±2.0 permil for $\delta^{2}H$. The deuterium excess parameter was calculated from Dansgaard's equation relating $\delta^{18}O$ and $\delta^{2}H$ of water, defined as $d = \delta^{2}H – 8\ \delta^{18}O$ [52]. The water stable-isotope chain-of-custody (onsite measurements, sample collection, transportation, holding, preparation and analysis) adhered to International Standard Methods [53].

Table 1. Summary of isotopic sampling undertaken from Malawi Network of Iso–topes in Precipitation (MNIP) Stations (1914–2019).

* Meteorological Services Stations	MNIP Stations	Decimal Degrees		Altitude (m a.s.l)	Monthly Samples
		Latitude	Longitude		
Mzuni	Mzuni	−11.41977	33.9952843	1287	6
Chitedze	Chitedze	−13.976628	33.7686897	1046	18
Salima	Salima	−13.75	34.5892292	512	4
Ngabu	Ngabu	−16.536863	34.8912164	80	7
Chichiri	Chinyonga	−15.813924	35.0397645	1127	5

* Meteorological services stations associated with MNIP stations; CWL: Central Water Laboratory.

The study focused on the only available stable isotopic data generated during wet season as Malawi's precipitation is largely received during this time of the year. Hence, only intra-seasonal variability of isotopic signatures of local precipitation was investigated, not inter-seasonal variability. Thus, the intra-seasonal variability in stable isotopic signatures of local precipitation has been displayed in Supplementary Material (SM) Figure S1 by way of averaging weighted monthly isotopic values of precipitation for each month of the wet season over the period 2014–2019. The upcoming phase of our work will largely focus on generating seasonal isotopic data for investigating inter-seasonal variability in isotopic signatures of local precipitation.

The local precipitation data were augmented by precipitation isotopic data obtained from neighboring international Global Network of Isotopes in Precipitation (GNIP) stations in Mozambique at Gorongosa (8 monthly samples) and Chitengo (4 monthly samples), Zambia at Ndola (154 monthly samples), Zimbabwe in Harare (188 monthly samples) and in Tanzania in Dar es Salaam (117 monthly samples) to reinforce the national meteoric water characterization and to capture regional status of isotopic signatures (spatially and temporally) thereby allowing a more complete regional meteoric characterization [48] (Figure 2b; Table 2). It was deemed vital to have this surrounding boundary defined for a landlocked country (and expected as standard to do so). The MNIP is spatially lacking and needs infilling, and the temporal earlier isotopic data records are useful to provide some way of extrapolating time series. Above all, the MNIP was designed to fit into the wider international network contribution. The resultant Regional Meteoric Water Line (RMWL) derived from a sub-dataset of precipitation amounts weighted stable isotopic samples (n = 449) (from stations with precipitation amount data) from MNIP, and the surrounding GNIP stations were also calculated by error-in-variables regression, denoted EIV-RMWLw.

Table 2. Summary of isotopic sampling undertaken from Global Network of Isotopes in Precipitation (GNIP) Stations (1969–2019).

GNIP Stations	WMO Codes	Country	Decimal Degrees		Altitude (m a.s.l)	Monthly Samples
			Latitude	Longitude		
Harare	6777400	Zimbabwe	−17.83	31.02	417	188
Dodoma	6386200	Tanzania	−16.1852	35.7533	1157	18
Dar es salaam	6389400	Tanzania	−6.88	39.2	55	117
Ndola	6756100	Zambia	−13	28.65	1331	154
Chitengo	6729501	Mozambique	−18.9751	34.34842	34	4
Gorongosa	6729502	Mozambique	−18.6717	34.07239	346	8

3. Results and Discussion

Stable isotopes data obtained from the local (MNIP) and regional (GNIP) precipitation stations have permitted comprehensive characterization of Malawi's current local meteoric system.

3.1. Co-Isotopic Relationships of Local Precipitation

Error-in-variables (EIV) regression was applied to the stable isotopic dataset collected from the MNIP stations to calculate a Local Meteoric Water Line (LMWL) that describes Malawi's local meteoric characteristics. The local meteoric water line (EIV-LMWL) is defined as: $\delta^2H = 8.0 \pm (0.3)\ \delta^{18}O + 13.0\ (\pm 2.0)$ (Figure 3). The EIV-LMWL shows a strong positive correlation between δ^2H and $\delta^{18}O$ values of local precipitation of slope consistent with the Global Meteoric Water Line (GMWL), defined as: $\delta^2H = 8\delta^{18}O + 10$ [50]. The stable isotopic signatures of local precipitation from the MNIP stations registered a mean deuterium excess value of 13.3‰, slightly above the GMWL intercept of 10‰. This is characteristic of local vapor recycling contribution to the local precipitation isotopic signatures [54]. A subset of the MNIP samples that plotted below the GMWL is indicative of the re-evaporation of raindrops during precipitation events (Figure 4) [55,56]. Most of the local precipitation samples scattered along the EIV-LMWL, with almost all the samples plotting within the prediction error band. This corroborates that there were insignificant evaporative influences on the local precipitation and were further substantiated by the EIV-LMWL slope 8.0 (±0.3), which is characteristic of non-evaporated rains.

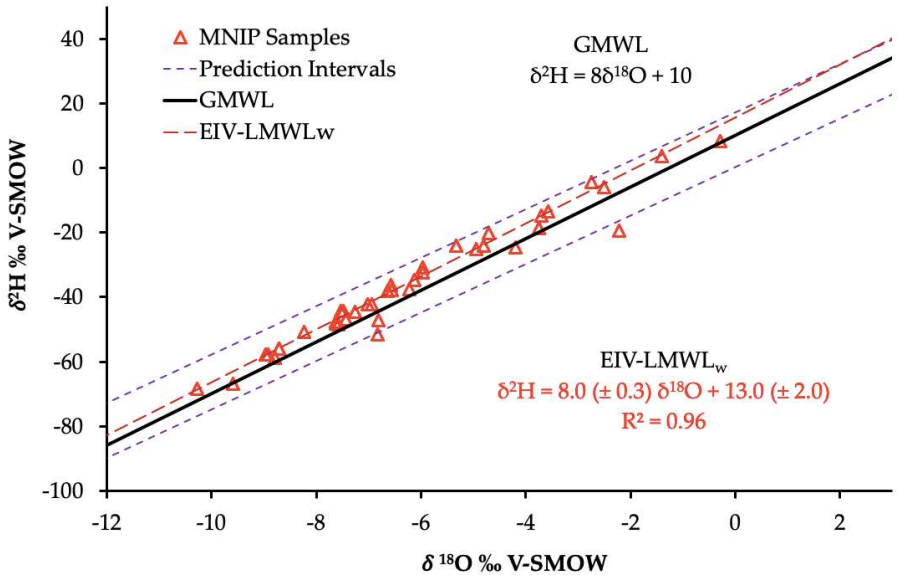

Figure 3. Monthly precipitation stable-isotope data for MNIP stations (n = 37). Error–in–variables local meteoric water line (EIV–LMWLw) represents the weighted local meteoric water line for Ma–lawi (calculated based on error–in–variables regression analysis). MNIP: Malawi network of iso–topes in precipitation; GMWL: Global Meteoric Water Line.

3.2. Isotopic Signature of Local and Regional Precipitation

The current MNIP stations' dataset was judged insufficient to meet our goals, and hence, characterization of the local meteoric conditions was augmented by surrounding GNIP stations' datasets. This permitted a more regionally representative LMWL relative to the origin of air masses that was defined as $\delta^2H = 7.6 \pm (0.1)\ \delta^{18}O + 10.0\ (\pm 0.5)$ (Figure 4). The EIV-LMWL is quite consistent with the regional meteoric water line defined as $\delta^2H = 7.6\ (\pm 0.1)\ \delta^{18}O + 9.9\ (\pm 0.5)$ (Figure 4) derived from the surrounding GNIP stations datasets. The slopes of both meteoric water lines are identical but somewhat less than the GMWL slope of 8. This is ascribed to evaporative influence on the isotopic signatures of

precipitation events as well as possible isotopic non-equilibrium conditions affecting the rain-out process.

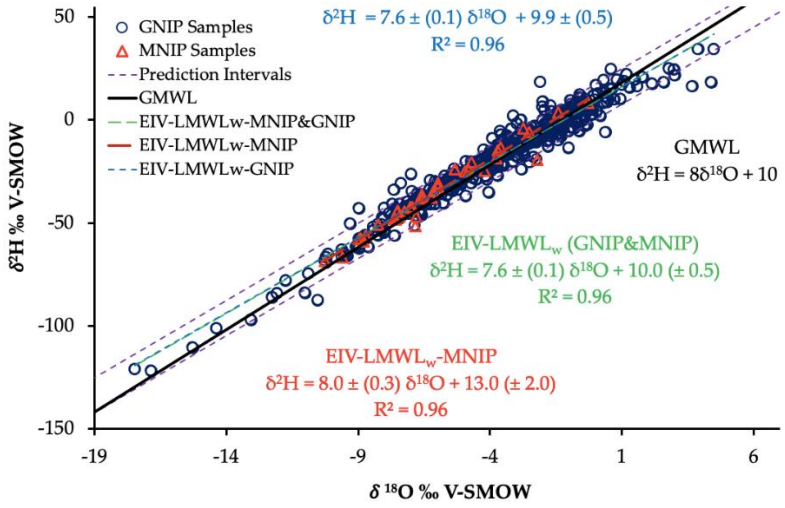

Figure 4. Plot of δ^2H and $\delta^{18}O$ for precipitation stable-isotopic samples from MNIP stations (n = 37) and GNIP stations (n = 409). Error–in–variables local meteoric water line (EIV–LMWLw) represents the weighted local meteoric water line calculated based on error–in–variables regression analysis. MNIP: Malawi network of isotopes in precipitation; GMWL: Global Meteoric Water Line.

The scenario reinforces the need for continuity and long-term collection of water stable-isotopic data from the MNIP stations to significantly improve both the EIV-LMWL local representativeness and its significance in contributing to the regional global water stable-isotopic meteoric characterization.

3.3. Isotopic Signature Variability of Local and Regional Precipitation

The MNIP stations' monthly dataset displayed wide variations spanning a range of 76.8‰ for δ^2H and 10‰ for $\delta^{18}O$ (Table 3). This is attributed to distinct rain-bearing systems and varying geographic factors resulting from the country's extremely diverse physiographic zones. The wide variation evident in the water stable-isotopic signatures is consistent with the expected water stable-isotopic signatures of Indian Ocean monsoon-derived precipitation [57]. The surrounding GNIP stations dataset displayed even wider variation (range: 159‰ for δ^2H; 22‰ for $\delta^{18}O$) relative to the MNIP stations dataset (Table 3). This was attributed to spatial and/or intra-seasonal variability among other factors such as temporal and geographic scales. Plotting of the MNIP dataset within the prediction band supports evaporative effects on local precipitation were insignificant (Figure 5). A GNIP stations sub-dataset, however, did plot outside the prediction band, below the GMWL, signaling an oxygen-18 excess. This feature might indicate secondary evaporation of raindrops during the fall and above the GMWL (representing excess deuterium), from which precipitation originated from recycled air moisture is inferred.

3.4. Intra-Seasonal Isotopic Signature Variability of Local Precipitation

The stable isotopic signatures of local precipitation varied significantly monthly, with the largest isotopic signatures variation depicted between January and April ascribed to weather systems transitioning (SM-Figure S1). The most depleted isotopic signatures of $\delta^{18}O$ and δ^2H were recorded in January, the peak month of the wet season, whereas the most enriched isotopic signatures of $\delta^{18}O$ were recorded in April, the end of the wet season. The enriched isotopic signatures of $\delta^{18}O$ and δ^2H are indicative of drier–warmer conditions during the end of the wet season (SM-Figure S1. Overall, the isotopic compositions of rainfall in Malawi increase as the ITCZ migrates northwards around April. Therefore, there is a need for further investigation at a regional scale coupled with the collection of

high-resolution isotopic data across various catchments in Malawi to better understand the spatial distribution variation with time across the country.

Table 3. Summary of stable isotopic signatures of precipitation from (a) MNIP stations and surrounding GNIP stations.

MNIP Stations							
Variable	**Count**	**Min.**	**Max.**	**Mean**	**Median**	**StDev.**	**Range**
δ^2H	40	−68.4	8.40	−35.9	−38.0	18.7	76.8
$\delta^{18}O$	40	−10.3	−0.29	−6.15	−6.61	2.30	9.98
D–excess	40	−1.64	18.6	13.3	13.9	3.80	20.3
GNIP Stations							
δ^2H	489	−122.1	36.4	−20.6	−17.7	23.9	158.5
$\delta^{18}O$	489	17.5	4.5	−4.0	−3.7	3.2	22
D–excess	489	17.3	34.6	11.2	12	5.48	51.8

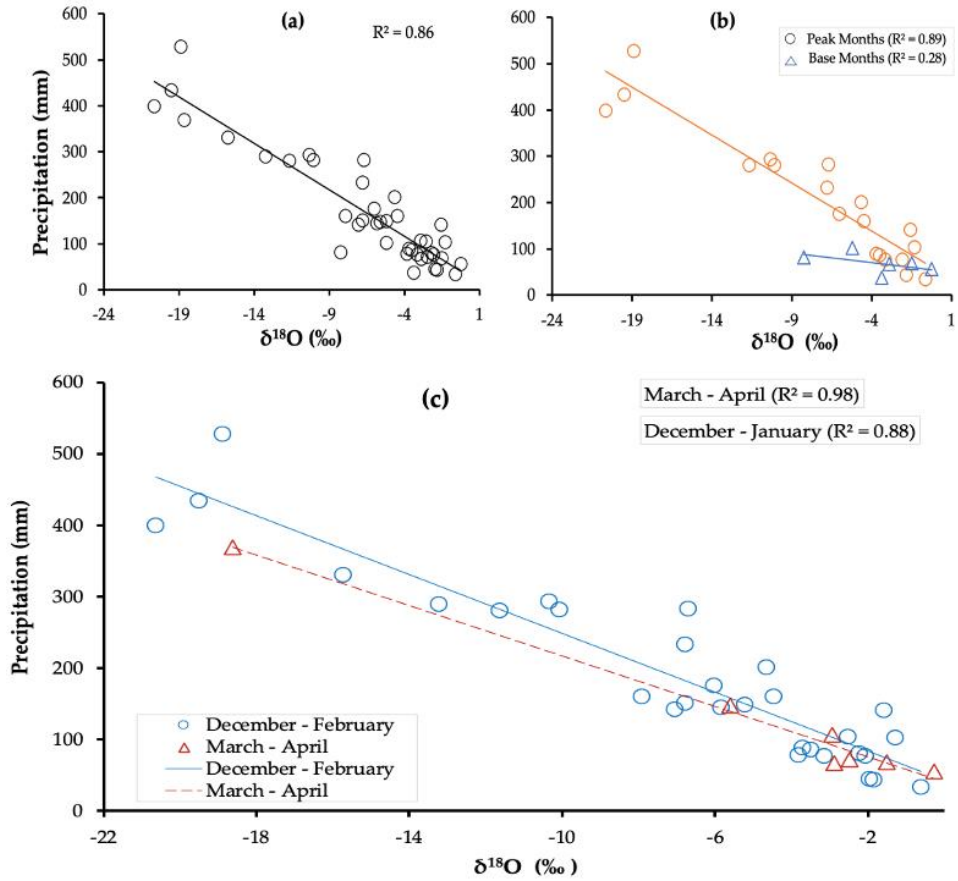

Figure 5. Precipitation amounts plotted versus $\delta^{18}O$ values for (**a**) all monthly data and (**b**) the intra–seasonal relationship for MNIP stations for peak and base months over the period 2014–2019. (**c**) the intra–seasonal relationship for MNIP sta–tions for early (December–February) and late (March–April) phases of the wet season over the period 2014–2019.

3.5. Isotopic Signature and Precipitation Amount Relationship: 'Amount Effect'

A strong correlation (R^2 = 0.86) was observed between precipitation amount and stable isotopic signatures of local precipitation at the monthly scale (Figure 5a). An increasing trend in precipitation amounts corresponded to highly depleted isotopic signatures. The '*amount effect*' is generally influenced by actual precipitation amount with precipitation intensity dominating [52]. Thus, several precipitation events of lesser intensity, with a

cumulative higher amount, can result in less depleted isotopic signatures, and contrasts with a few precipitation events of higher intensity, with a cumulative low amount, that can exhibit highly depleted isotopic signatures [2]. Peak months of the wet season (December–January) study depicted a stronger relationship (R^2 = 0.89), suggestive of precipitation derived considerably more from convective events. This contrasts with the onset and end of wet season months (base months) (November and April, respectively) having a weaker relationship (R^2 = 0.28), ascribed to precipitation episodes under the influence of frontal origins (Figure 5a), as echoed by Darling (2003) [2].

The precipitation '*amount-effect*' was also investigated considering the dual nature of Malawi's wet season, which, after the early phase (December–February), has a slight break or lull in precipitation, followed by the late phase (March–April). Precipitation during these phases is derived from contrasting atmospheric circulation regimes [42]. During these phases, the stable isotopic signatures of local precipitation are strongly influenced by precipitation amounts (Figure 5c). The '*amount effect*' varied considerably at higher precipitation amounts as compared to low precipitation amounts between the early and late phases. Overall, the current dataset has not depicted clear dependencies of the isotopic signatures on altitude or temperature but rather the influence of the ITCZ as it migrates southward and northward in Malawi. Considering the present data records limitation, especially for the late phase, it will be extremely interesting to further investigate the nature of the isotopic relationships that exists in local precipitation using more robust temporal and spatial isotopic data records.

3.6. Isotopic Signature and Altitude/Temperature Relationships

An observed altitude effect is indicative of a temperature effect attributed to cooling air masses with increasing elevation. This has largely been reported to be insignificant in lowlands and significant in uplands/highlands [58,59]. Altitude effects were investigated during the months of December and January for the period 2014–2019 (SM—Figure S2). These are the months with good records for all the five stations. The rest of the months have significant data gaps and do not warrant investigation. Moderately correlated relationships between altitude and $\delta^{18}O$ signatures were observed for December and January precipitation events, but weak correlations for February (SM—Figure S2). In both instances, precipitation tended to be isotopically depleted with increasing altitude. A poor correlation of isotopic signatures ($\delta^{18}O$) with altitude was found and most likely ascribed to the geographical separation of the precipitation stations (Malawi being a long stretch of land from north to south, with contrasting topographic settings) and varying sources of air moisture. The precipitation stations in southern Malawi are predominantly influenced by Indian Ocean air Masses and El Niño, while other stations in northern Malawi are mainly influenced by the ITCZ. Thus, it could be that this lack of climatic relationship between some of the stations may potentially render it impossible to conclude a national altitude effect for Malawi at this stage, but local scale data collection is advised for future study.

A poor correlation between isotopic signatures ($\delta^{18}O$) and temperatures was also observed and attributed to the extreme geographical separation among the precipitation stations as observed for the altitude effect (SM—Figure S3). The other factors attributing to such poor correlation could be the varying air moisture sources influencing rainfall at the stations. Additionally, intense secondary evaporation effects in southern Malawi compared to elsewhere in the country alongside re-evaporation influence may be significant contributing factors to isotopic variation with respect to temperature.

3.7. Deuterium Excess Variability and Frequency Distribution

The monthly variation of deuterium excess in precipitation over the period 2014–2019 shows that the highest deuterium excess values were recorded during the month of January, while the lowest deuterium excess values were recorded during February. The deuterium excess values are greater than 10‰ for GMWL, indicating that there is a considerable con-

tribution of air masses that generate precipitation by recycling of continental air moisture (SM—Figure S4).

The frequency distribution of deuterium excess of the fledgling MNIP network (n = 40) is compared to the surrounding GNIP station record (n = 489). The mean and standard deviation calculated from data of the MNIP stations (13.3‰, standard deviation: 3.80) compare to the ones (11.2‰, standard deviation: 5.48) calculated from the GNIP stations. (Figure 6a). Observation of the MNIP peak at 13–15‰ is important in assessing the provenance of air masses. The frequency distribution of deuterium excess supports that precipitation from the MNIP station is influenced by recycled continental moisture of the atmospheric reservoir. Most deuterium excess values (87.5%) fell within the range of 10–20‰ that are characteristic of wet season rains which are typical of and expected for MNIP stations due to the high wet season precipitation proportion. A few deuterium excess values (12.5%) occur within the range of 2–10 and are characteristic of dry-season rains. The surrounding GNIP record (Figure 6b) exhibits a contrasting isotopic fingerprint characteristic of both wet season and dry season rains, more characteristic of the surrounding country localities (shown by precipitation analysis of the GNIP station locations). This is consistent with the slight difference in the characteristics of the LMWL and the regional meteoric water line derived from surrounding GNIP stations datasets. These differences may also provide insight and investigation opportunities into the varying origin of air masses contributing to the seasonal precipitation events at the surrounding GNIP stations (considered beyond our scope herein). The growing dataset from the MNIP stations in future years will test our initial interpretation that appears consistent with the physical expectations. Additional MNIP stations and long-term isotopic data records are required to achieve both spatial resolution enhancement and temporal records increase. Up-scaling of the MNIP will be informed by a detailed geostatistical evaluation of optimal location for additional MNIP stations [47].

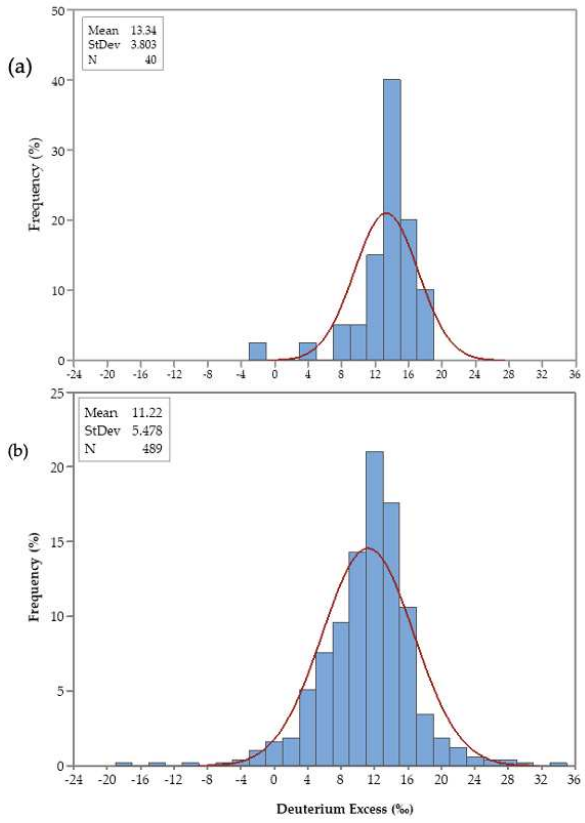

Figure 6. Frequency distribution of deuterium excess signatures for monthly precipitation from (**a**) MNIP stations over 2014–2019 and (**b**) surrounding GNIP stations for the period 1960–2016.

4. Relationship with Precipitation Moisture Sources

Malawi's Local Meteoric Water Line (EIV-LMWL$_W$) generated $\delta^2H = 8.0\ (\pm 0.3)\ \delta^{18}O + 13.0\ (\pm 2.0)$‰; confirmed the country's local precipitation was generally consistent with global precipitation expectations, but with the EIV-LMWL$_W$ displaying a slight shift above the GMWL, suggesting kinetic fractionation during evaporation [60,61]. The LMWL's intercept (13.0 ($\pm$2.0)‰) representing the deuterium excess value, greater than the GMWL intercept of 10‰, is probably due to the influence of the Salima and Central Water Laboratory station samples in Central Malawi and Chinyonga station samples in southern Malawi which recorded higher d-excess values. The LMWL's slope of 8.0 ($\pm$0.3) is comparable with 8.0 for the GMWL, from which it is reasonably inferred that a condensation process leading to local precipitation formation occurred under equilibrium conditions and without significant evaporation phenomena [18,62].

The stable isotopic signatures recorded in local precipitation were clearly distinct and varied widely, suggesting differences in water vapor sources and varying weather systems [61]. This is reasonably ascribed to the country's different precipitation-bearing systems, i.e., the Inter Tropical Convergence Zone (ITCZ), Congo Air Boundary (CAB) and Tropical Cyclones, alongside the influence of geographic controls upon local precipitation variation. This calls for further investigation on how these weather-bearing systems link to the varying water vapor sources. The stable isotopic input signatures of local precipitation were found to be less seasonal than those recorded at the surrounding GNIP stations. This was attributed to the fact that the available dataset largely covered one season (wet season), a period when the country mostly receives rains (wet season rains). As a result, the seasonal variation in the stable isotopic signatures of local precipitation has not been fully investigated at this stage. Going forward, deliberate efforts will be made to fully capture isotopic signatures of dry season rains to provide meaningful resolution of seasonal variability. The altitude effect was investigated, considering significant isotopic variations in local precipitation. However, based on the available isotopic dataset, evidence of the influence of the altitude effect was rather erratic and contrary to conventional trends. Consequently, there is a need for further investigation requiring enhancement of the MNIP temporal and spatial isotopic data records to provide high resolution of the altitude effect. This can be achieved through continuous generation of isotopic data and expansion of the MNIP station from the existing five (5) to at least ten (10) stations. There is also a need for investigation on how daily/weekly precipitation $\delta^{18}O$ signatures relate to air mass characteristics that contribute to the formation of the local precipitation across the country.

The study findings will largely contribute to the operational component of the MNIP, which was established to collect systematic data on isotopic signatures of precipitation on a national scale, and to establish temporal and spatial variations of environmental isotopes in precipitation. The study provides important foundational isotopic data that will underpin the use of environmental isotopes in hydrological investigations within the scope of water resources management and development.

5. Conclusions

The study successfully established a national-scale deuterium and oxygen-18 stable-isotope baseline for precipitation in Malawi. This is a first for this developing country and was achieved through the sampling of the recently commissioned Malawi Network of Isotopes in Precipitation (MNIP) and isotope analysis at its own recently established national laboratory facility, removing previous hindrances of sample export abroad for analysis. The Local Meteoric Water Line (LMWL) developed is proposed as a reference benchmark for future and more focused hydrological and climatic studies. The study demonstrates the stable isotope composition of local precipitation was consistent with global precipitation expectations; its condensation-forming process occurring under equilibrium conditions evidenced by a slope of 8.0 ($\pm$0.3) quite comparable to a slope of 8.0 for the Global Meteoric Water Line (GMWL). The precipitation-forming process was also closely associated with atmospheric vapor recycling across the region, the LMWL and

GMWL slopes being consistent. Variation in stable isotopic signatures of precipitation was attributed to differences in atmospheric vapor sources arising from Malawi experiencing diverse precipitation-bearing systems and distinct geographic–topographic controls within its Rift Valley setting.

The established LMWL will enhance understanding of the hydrological–hydrogeological cycle in Malawi. It is pivotal to providing increased insight into the provenance of meteoric waters, especially of groundwater recharge sources, but also the confirmation of seasonally variant dependency of surface water flows on runoff, baseflow and evaporation losses. The latter process may also impact near-surface groundwater resources, especially in Malawi's semi-arid lowlands. The use of isotopic tools underpinned by the isotopic precipitation characterization herein is already beginning to provide insight into such processes, as demonstrated in our recent basin- [39] and catchment-scale studies [40].

The characterized precipitation isotopic baseline principally contributes to the newly established national stable isotopic database. Looking forward, this is expected to provide a critical underpinning of IWRM implementation in Malawi due to the resolving power of stable-isotope signatures providing forensic insight into the key challenge of understanding the mixing and provenance of the various possible water sources. This is expected to greatly facilitate Malawi's ambition to achieve integrated use and improved protection of its surface water and groundwater resources in its response to mounting climate change, growing population and land-development concerns. Finally, the study valuably contributes to the global network of isotopes in precipitation (GNIP) database by the infilling of the data-record gap previously existed in Malawi. This allows increased certainty in regional and global hydrological and climatic modeling study predictions. The current isotopic data record is regarded as foundational, and spatial network expansion and increased temporal records are both required to reach its full potential and IWRM goals.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/w13141927/s1, Figure S1: Plots of weighted monthly mean values of $\delta^{18}O$ (a) and $\delta^{2}H$ (b) recorded at MNIP stations between 2014 and 2019, indicating monthly variations in isotopic signatures of local precipitation. Figure S2: Altitude effects on the $\delta^{18}O$ signatures of local precipitation in MNIP stations for the months of (a) January (b) February and (c) December over the period 2014–2019. Figure S3: Mean temperatures plotted versus $\delta^{18}O$ values for all monthly data for the MNIP stations over the period 2014–2019. Figure S4: Deuterium excess for each month of the wet season recorded at MNIP stations, indicating monthly variations in precipitation derived from weighted mean monthly values over the period 2014–2019.

Author Contributions: Conceptualization, L.C.B., M.O.R. and R.M.K.; methodology, L.C.B. and M.O.R.; validation, L.C.B. and A.S.K.Z.; formal analysis, L.C.B. and M.O.R.; investigation, L.C.B.; resources, L.C.B. and A.S.K.Z.; data curation, L.C.B. and A.S.K.Z.; writing—original draft preparation, L.C.B. and M.O.R.; writing—review and editing, M.O.R., L.C.B. and R.M.K.; visualization, L.C.B.; supervision, R.M.K. and S.K.; project administration, R.M.K. and S.K.; funding acquisition, S.K., R.M.K. and L.C.B. All authors have read and agreed to the published version of the manuscript.

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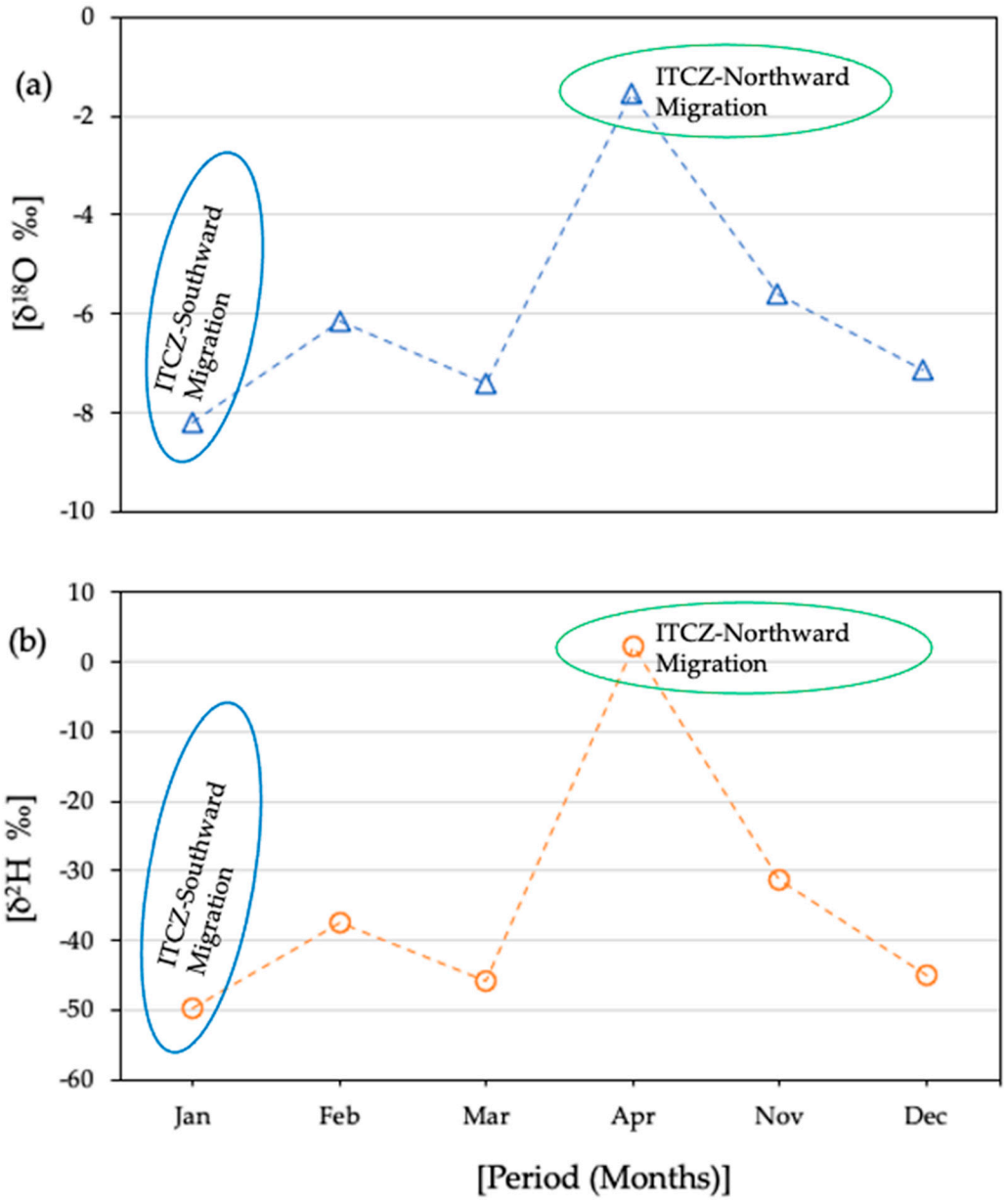
4.3 Research Article 1: Supplementary Materials

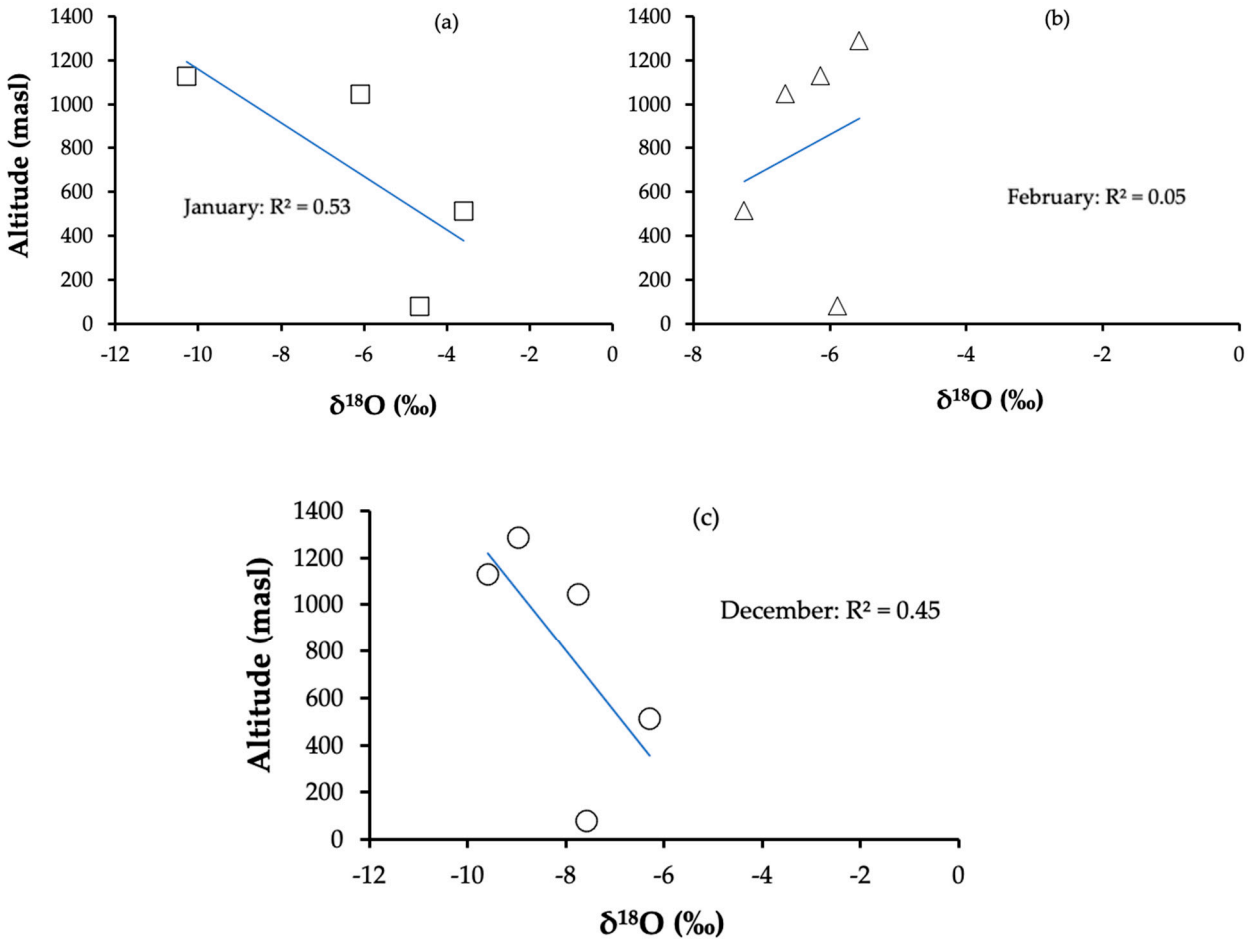
National Stable Isotope Baseline for Precipitation in Malawi to underpin Integrated Water Resources Management

Limbikani C. Banda[1], *, Michael O. Rivett[1], Anold S.K. Zavison[2], Sydney Kamtukule[2], and Robert M. Kalin[1]

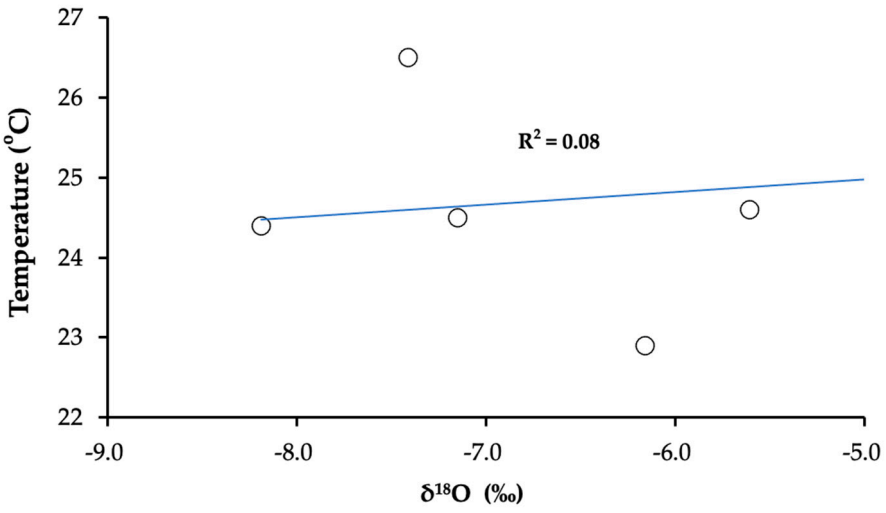
SM Figures



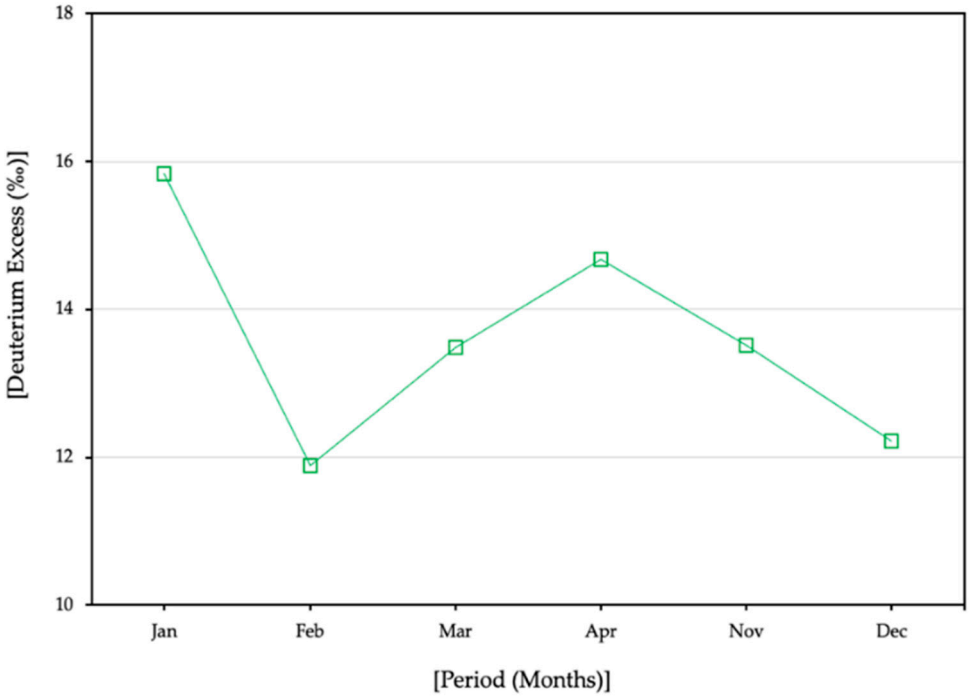
SM-Figure S1. Plots of weighted monthly mean values of $\delta^{18}O$ (a) and $\delta^{2}H$ (b) recorded at MNIP stations between 2014 and 2019, indicating monthly variations in isotopic signatures of local precipitation.



SM-Figure S2. Altitude effects on the $\delta^{18}O$ signatures of local precipitation in MNIP stations for the months of (a) January (b) February and (c) December over the period 2014-2019.



SM-Figure S3. Mean temperatures plotted versus $\delta^{18}O$ values for all monthly data for the MNIP stations over the period 2014-2019.



SM-Figure S4. Deuterium excess for each month of the wet season recorded at MNIP stations, indicating monthly variations in precipitation derived from weighted mean monthly values over the period 2014-2019.

4.4 Postface

The thesis systematically addressed three research questions (RQ) through a novel multi-method approach, integrating stable isotopic and hydrogeochemical tracers. RQ 1 explored local precipitation using water isotope tracing to establish a national-scale isotopic baseline, develop a local meteoric water line, and identify the moisture sources impacting regional precipitation. This foundational work is vital for integrated water resource management within the basin. RQ 2 focused on groundwater, utilizing an isotopic and hydrogeochemical multi-tracer strategy to establish a basin-scale conceptual understanding. This included setting baselines and identifying the sources and geochemical reactions that influence groundwater's chemical properties and its evolutionary path. RQ 3 examined surface water resources through a mixed-proxy approach of isotopic and hydrochemical analysis. This study established a basin-scale baseline and investigated the factors influencing surface water hydrochemistry and the dispersal of isotopic signals in water inputs. The combined exploration of these elements led to an enhanced conceptual understanding of the Lake Malawi basin's water resources, detailed in Chapters 4 through 7. This comprehensive understanding aids in addressing the pressing issues of water quality and availability, particularly in rural areas of Malawi, affected by environmental degradation and climate change. By thoroughly examining the roles and interactions of precipitation, groundwater, and surface water, and by developing a substantial repository of data, this thesis contributes decisively to the body of knowledge required for informed decision-making in water resource management in Malawi and potentially other similar regions. In conclusion, this thesis not only achieved its foundational aims and objectives but also paved the way for future research directions. It offers targeted policy recommendations that are hoped to inspire and inform future strategies and interventions aimed at sustaining the hydrological resources of the Lake Malawi basin. The following Chapter 5

constitutes second phase of this thesis, focusing on the dynamics of groundwater resources within the Lake Malawi aquifer systems. This phase aims to enhance the conceptual understanding of these aquifers through an innovative multi-tracer methodology that employs stable isotopic and hydrogeochemical tracers.

CHAPTER 5: GROUNDWATER RESOURCE CONCEPTUALISATION

5.1 Preface

The preceding chapter, Chapter 4, established a baseline for oxygen ($^{18}O/^{16}O$) and deuterium ($^{2}H/^{1}H$) isotope ratios in precipitation and defined a first-ever Local Meteoric Water Line (LMWL) for Malawi. It identified moisture sources affecting local precipitation using deuterium excess tracer method and characterised fractionation processes influencing "input isotopic signal" of meteoric water. These insights are critical for tracing origin of groundwater and surface water in the Lake Malawi basin.

The current chapter, Chapter 5, advances to the second phase of this thesis, focusing on the dynamics of groundwater resources within the Lake Malawi aquifer systems. This phase aims to enhance the conceptual understanding of these aquifers through an innovative multi-tracer methodology that employs stable isotopic and hydrogeochemical tracers. Central to this investigation is research question R2: How do stable isotopic and hydrogeochemical signatures elucidate groundwater quality, recharge dynamics, and aquifer system conceptualization within the Lake Malawi basin? To address this query, the following specific objectives were established and achieved:

RO 2.1: Identify and analyse the stable isotopic and hydrogeochemical signatures within the basin's aquifer systems, creating a comprehensive baseline for conditions.

RO 2.2: Explore the processes and pathways influencing groundwater recharge, with emphasis on differentiating the sources and mechanisms of recharge.

RO 2.3: Delineate the principal geochemical factors that influence groundwater quality and evolution, thereby enriching the conceptual framework of the aquifer systems through detailed isotopic and hydrochemical analyses.

The outcomes of this second phase were published in a peer-reviewed journal, which forms the core content of this chapter. This chapter explores hydrogeochemical processes, groundwater recharge, and the evolution of groundwater within the basin. It identifies controlling processes such as mineral-rock interactions, and the dynamic interplay of precipitation and evaporation. Additionally, the chapter categorizes the five groundwater types prevalent in the aquifers, predominated by the Ca-Mg-HCO_3 water type, and sheds light on isotopic and hydrochemical variability across the basin. This highlights the complex interactions between meteoric water inputs, evaporative effects, recharge mechanisms, and mixing dynamics. The chapter also reveals the presence of nitrate in groundwater throughout the basin, emphasizing a significant concern due to extensive use of pit latrines and nitrogen-based fertilizers in the predominantly rural and agricultural areas of the Lake Malawi basin. Overall, Chapter 5 not only deepens our scientific understanding but also significantly advances the field of hydrology by elucidating complex interactions that govern groundwater systems in the Lake Malawi basin. This research is essential for the ongoing development of sustainable water resource management strategies in the region.

5.2 Research Article 2: Main Paper

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IMPACT FACTOR 3.0

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Article

Isotope Hydrology and Hydrogeochemical Signatures in the Lake Malawi Basin: A Multi-Tracer Approach for Groundwater Resource Conceptualisation

Limbikani C. Banda, Robert M. Kalin and Vernon Phoenix

MDPI

https://doi.org/10.3390/w16111587

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Article

Isotope Hydrology and Hydrogeochemical Signatures in the Lake Malawi Basin: A Multi-Tracer Approach for Groundwater Resource Conceptualisation

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Abstract: Reliance on groundwater is outpacing natural replenishment, a growing imbalance that requires detailed and multi-faceted water resource understanding. This study integrated water-stable isotopes and hydrogeochemical species to examine hydrogeochemical processes during groundwater recharge and evolution in the Lake Malawi basin aquifer systems. The findings provide insights into groundwater source provenance, with non-evaporated modern precipitation dominating recharge inputs. Grouped hydrochemical facies exhibit five groundwater water types, prominently featuring Ca-Mg-HCO_3. Modelled hydrogeochemical data underscore dominant silicate dissolution reactions with the likely precipitation of calcite and/or high-Mg dolomitic carbonate constrained by ion exchange. Isotope hydrology reinforces water resource system conceptualisation. Coupled isotopic-hydrogeochemical lines of evidence reveal a discernible spatial-seasonal inhomogeneity in groundwater chemical character, revealing a complex interplay of meteoric water input, evaporative effects, recharge processes, and mixing dynamics. Findings show that measurable nitrate across Malawi highlights a widespread human impact on groundwater quality and an urgent need for detailed modelling to predict future trends of nitrate in groundwater with respect to extensive fertiliser use and an ever-increasing number of pit latrines and septic systems arising from rapid population growth. This study not only refined the Lake Malawi basin aquifer systems conceptualisation but also provided isotopic evidence of groundwater and lake water mixing. This study sets a base for groundwater management and policy decisions in support of the Integrated Water Resources Management principles and Sustainable Development Goal 6 objectives for groundwater sustainability in the transboundary Lake Malawi basin.

Keywords: isotope tracers; hydrogeochemistry; sustainable development goal 6 (SDG 6); geochemical modelling; groundwater sustainability

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1. Introduction

Access to safe drinking water and sanitation is a fundamental human right, as stated in the United Nations (UN) resolution 64/292 [1]. The provision of clean water is further enshrined as a critical global priority in Sustainable Development Goal 6, 'Clean water and sanitation'. Despite this, a considerable proportion of the global population lacks access to adequate water services. Recent figures estimate that *ca* 2.4 billion people reside in water-stressed countries, and *ca* 2.2 billion people lack access to safely managed drinking water (2020 and 2022, respectively) [2]. This issue is particularly prevalent in many rural and peri-urban communities in sub-Saharan African (SSA) countries, including Malawi. Groundwater plays a vital role in supplying drinking water and supporting domestic needs, especially in regions with limited water distribution networks. It constitutes approximately 50% of global freshwater resources, serves about 40% of irrigated agriculture, and provides around one-third of the water supply for industry. Its significance extends to

human development and economic growth [3]. However, excessive groundwater extraction and declining groundwater levels present sustainability challenges [4]. Sustainable management approaches are necessary to ensure the long-term availability of groundwater resources. Groundwater has been particularly critical in building resilience to climate change and ensuring water security in the Southern African Development Community (SADC) region [5]. Approximately 65% of Malawi's population heavily relies on groundwater for drinking and domestic use [6,7]. This is even more significant in rural areas where 82% of the population relies on groundwater. Considering the unpredictable nature of precipitation and inconsistent surface water flows in Malawi [8], groundwater is viewed as a reliable alternative for water supply provision, especially during drought periods [9]. The significance of groundwater in surface water dynamics in Malawi, through its significant role in base flow, further emphasises the importance of groundwater within Malawi's water security.

Malawi's aquifer lithology influences groundwater quality [6]. Geogenic and geochemical factors influence groundwater quality in Malawi, in some instances leading to elevated levels of salinity, fluoride, iron, sulphate and chlorides [10–13]. Raised levels of sulphate in weathered basements [14] and high salinity in alluvial aquifers have been reported, with the latter resulting in the abandonment of several boreholes [15]. Malawi also faces challenges regarding groundwater supply impacted by aquifer stress and improper infrastructure development by non-governmental organisations, resulting in a scourge of stranded groundwater assets across the country [16]. Rapid population growth, changing lifestyles, unpredictable precipitation, higher agricultural demands, water resource degradation, and climate change add to a list of drivers confounding Malawi's water problems [17,18]. The agricultural sector, employing over 80% of the population and driving Malawi's economy, uses a substantial amount of the country's renewable freshwater resources, exerting heavy pressure on Malawi's water resources [19]. To address these issues, Integrated Water Resources Management (IWRM) and sustainable water management techniques such as borehole garden permaculture [20,21], alongside advanced technologies like isotope hydrology tracers, can play a crucial role in understanding and managing groundwater resources sustainably [22]. Notably, isotope hydrology tracers provide insights into the conceptualisation of hydrological–hydrogeological systems [23,24], groundwater dynamics, recharge processes, and water-source provenance [25–28], aiding in science-led policy decisions [29]. Yet, despite their benefits, the use of advanced technologies to facilitate sustainable water resource management is limited in low-income countries, and their potential to inform SDGs (e.g., SDG 6) has not been fully explored [30–32]. Establishing shared laboratories for the routine use of isotope hydrology tracers can significantly improve water resource management in low-income countries.

The overarching aim of this work was to establish a conceptualisation of the groundwater in the Lake Malawi basin (LMB) aquifer systems, focusing on isotope hydrology and hydrogeochemical baseline characterisation, spatial-seasonal effects on groundwater mineral signatures, geochemical controls on groundwater quality and evolution, groundwater-resource provenance, and hydrogeological system conceptualisation. Specifically, this study addressed the following research questions: (a) What are the background isotope hydrology and hydrochemical signatures of groundwater in the LMB? (b) How are the LMB aquifer systems recharged, and what are the isotope hydrology and hydrochemical signatures of distinct recharge inputs? (c) What are the geospatial and seasonal effects on groundwater quality and mineralisation? (d) What are the key geochemical controls on groundwater quality and evolution? and (e) How do isotope hydrology, hydrogeochemical and geospatial characteristics help refine the conceptualisation of the LMB aquifer systems? This study is consistent with the IWRM principles and SDG 6 objectives, with the potential to underpin sustainable groundwater resource management in Malawi and the wider region. This study aligns with the International Atomic Energy Agency (IAEA) Technical Cooperation (TC) project objectives (RAF7021 regional project) for sustainable water management and supports transboundary water management initiatives under the

2004 ZAMCOM agreement and was supported by the Scottish Government's Climate Justice Fund Water Futures Programme (CJF).

2. Study Area

The Lake Malawi basin (LMB) is a transboundary region that covers Lake Malawi and its surrounding surface areas in Malawi, Mozambique, and Tanzania (Figure 1a). It lies within a seismically active belt at the southernmost region of the East African Rift System (EARS), with a combined lake and land surface area of ca. 126,500 km^2, 97,740 km^2 of which is land surface [6]. The study area is constrained to the Lake Malawi basin section within Malawi's international boundary (Figure 1b), spanning ca. 64,785 km^2 of land surface, with ca. 32,955 Km^2 of land surface occupied by Mozambique and Tanzania. The study area covers 13 water resource areas (WRAs) of national significance, mainly focusing on the 11 major water resource areas with a substantial contribution to Lake Malawi hydrology (Figure 1b). It leaves out two minor WRAs encompassing Chizumula and Likoma islands in the middle of Lake Malawi with minimal contributions to the Lake Malawi hydrology.

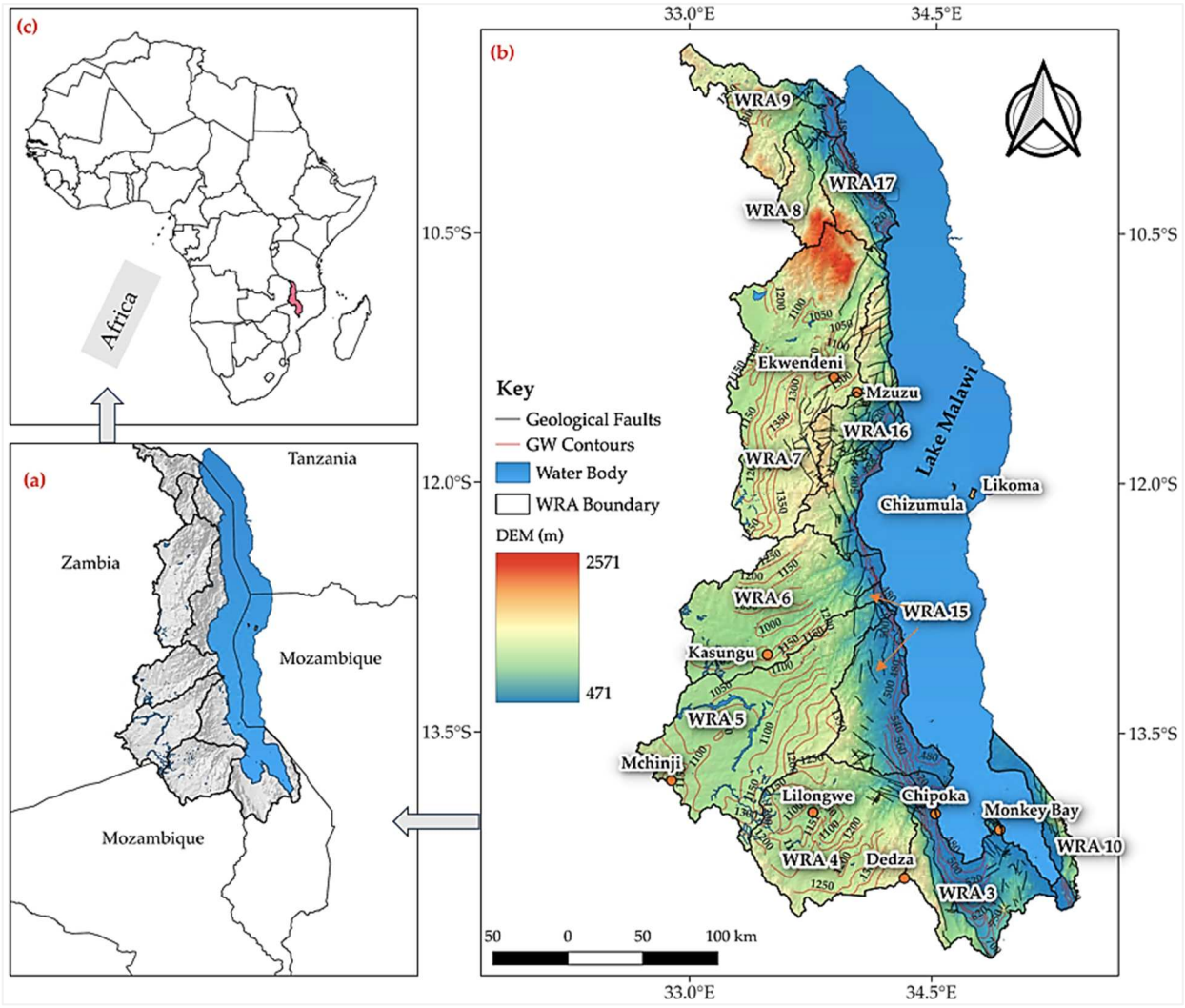

Figure 1. Study area showing (**a**) study area location in Malawi and its transboundary extent (Malawi, Mozambique, Zambia, and Tanzania), and (**b**) study area extent with water resource areas (WRAs) (**c**) Malawi location in Africa.

2.1. Water Resources

Water resources in the study area consist of surface waters such as rivers, lakes, lagoons, and water reservoirs, as well as groundwater reserves found in aquifers [33]. The surface water and groundwater resources are, in part, shared across borders, requiring a multinational approach for equitable and sustainable management such as the 2004 ZAMCOM agreement. With a total of 49,032 groundwater points (community water supply boreholes and protected shallow wells) distributed across the basin, only approximately 85.8% are functional or partially functional [6]. The majority (63.8%) of these groundwater points consist of community water supply boreholes fitted with hand pumps, followed by protected dug wells [6]. Annual averaged surface runoff contributions to Lake Malawi are around 391 m^3/s (for Malawi), 486 m^3/s (for Tanzania), and 41 m^3/s (for Mozambique), with a mean outflow of 395 m^3/s [6]. Lake Malawi's stand fluctuates between 471.5 and 477 masl, with a range of 474 to 475.3 masl recorded in 2022, contributing to an annual recharge input of 35.9 km^3 [6]. The highlands and catchment areas contribute to surface water runoff, which eventually replenishes rivers and streams flowing into Lake Malawi, with 63% of Malawi's surface runoff water discharging into Lake Malawi [33]. Key surface water storage reservoirs include Kamuzu Dam I and Kamuzu Dam II on Lilongwe River, with a combined supply capacity of 125,000 m^3/day. The Lunyangwa Dam on the Lunyangwa River has a supply capacity of 25,900 m^3/day [34], and the Bwanje Valley Dam on the Naminkokwe River has a supply capacity of 5.6 million m^3 [30]. The Kamuzu Dams primarily supply water to Malawi's capital, Lilongwe, while the Lunyangwa Dam serves Mzuzu City, Ekwedeni township, and other surrounding areas. The Bwanje Valley Dam supports the Bwanje Valley irrigation scheme, providing a water supply source, hydropower generation potential, and environmental flows. Other water storage reservoirs include the Chitete Dam in the Kasungu township and the Lusa Dam in Mchinji, which are mainly used for water supply, irrigation, and supporting small-scale fish farming for rural livelihoods.

2.2. Topography

The Lake Malawi basin has a diverse topography, ranging in altitude from 471 to 2521 m, with a mean of 1102 masl (Figure 2a). It consists of highlands, plateaus, rift valley escarpments, rift valley plains, and rift valley floors (Figure 2b). Notable highland features include Dedza mountain, the Dzalanyama range, the Mchinji highlands, the Viphya mountains, and the Nyika highlands, which vary from 667 to 2521 m, with a mean elevation of 1618 m asl. The plateaus primarily feature gentle slopes, including wetland ecosystems locally known as '*dambos*' that easily flood with no well-defined channels. The *dambos* play a significant role in groundwater storage and subsequent draining within the plateaus. The Kasungu–Lilongwe plain is the most extensive plateau, covering *ca* 6000 km^2 and ranging in altitude from 1000 to 1800 m asl [30]. This area is predominantly agricultural, with few remaining areas of indigenous savannah scrub woodlands and forests. The underlying strata of the plateaus consist mainly of colluvium overlying in situ layers of saprolite (weathered bedrock) [15]. The rift valley escarpment spans from north to south, containing rivers that erode the rift valley scarp as they flow into the rift valley plain, exposing the bedrock [13]. The escarpment varies in altitude from 480 to 2035 m, with a mean of 924 m asl. The western Lake Malawi shoreline is dominated by the rift valley plain, featuring steep sloping land between the Lake and plateaus. The rift valley plain ranges in altitude from 471 to 1550 m, with a mean of 574 m asl. The rift valley floor encompasses the Lake Malawi basin and its surrounding walls, including rocky slopes and escarpments. It also includes a series of terraces that slope from the rift valley walls towards the Lake Malawi shoreline [35]. The topography significantly impacts climate, hydrology, groundwater occurrence, and population distribution and influences water supply demands.

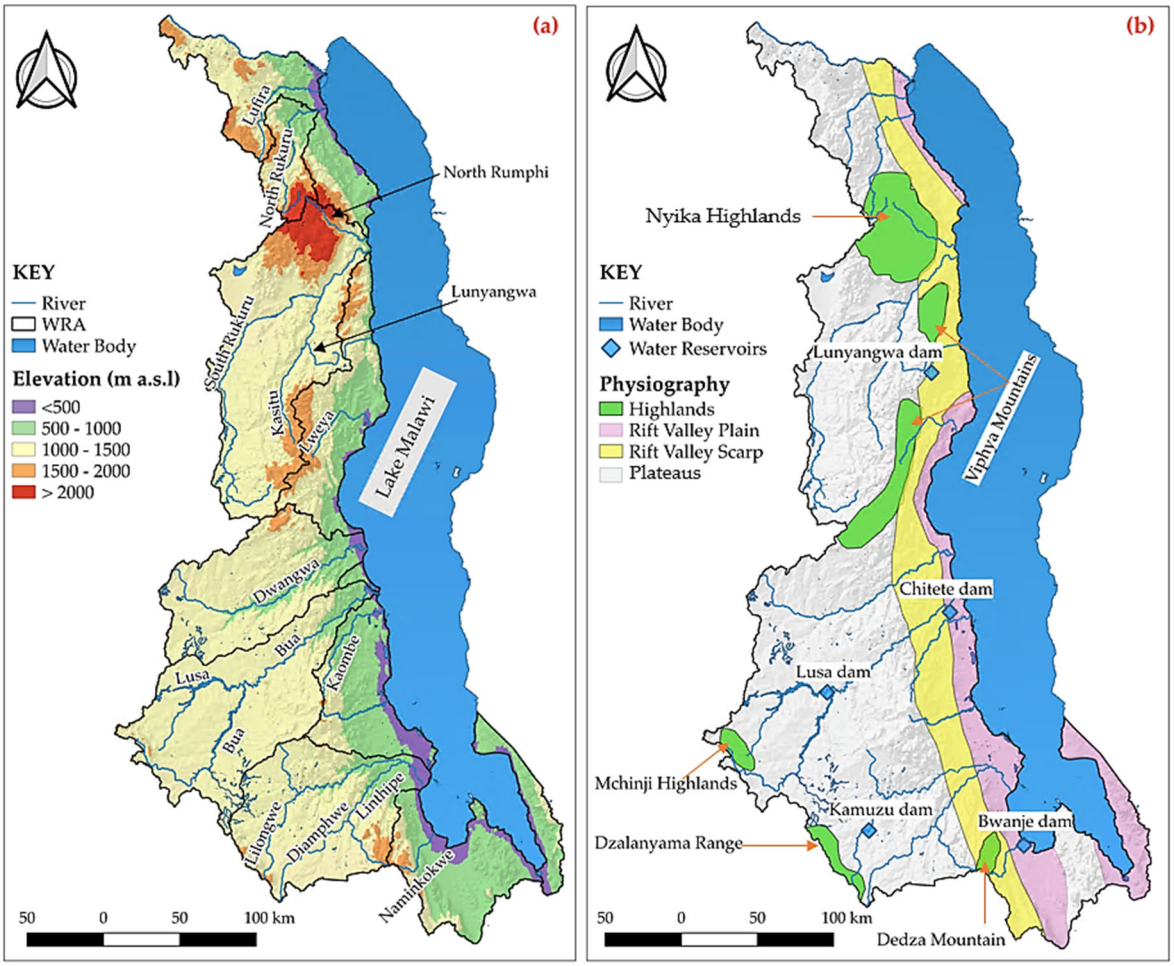

Figure 2. Study area showing (**a**) topography (SRTM elevation data: USGS) and main drainage systems and (**b**) physiographic zones and water reservoirs.

2.3. Geological Setting

The Lake Malawi basin is a rift valley basin mostly made up of basement complex rocks, constituting metamorphic and igneous rocks from the late Precambrian to lower Paleozoic periods [36]. The geological successions across the basin include Quaternary Alluvium and Colluvium, Cretaceous to Pleistocene formations, Jurassic Age Chilwa Alkaline Province formations, Jurassic Age Karoo Stromberg Volcanic formations, the Karoo Sedimentary Series from the Permo-Triassic period, and the Basement Complex formations from the Late Precambrian and Lower Paleozoic periods [36]. The basin is characterised by various geological processes such as escarpment formation, faulting, fracturing, erosion, rift valley floor development, and sedimentation [37]. There are major faults occurring from north to south and north-northwest to south-southwest, with notable fault lines along Lake Malawi [38]. The geological features of the basin exhibit a dynamic environment where geological and geomorphological processes are continuously occurring with a potential influence on its hydrogeology [33]. The presence of basement-complex rocks, consisting of late Precambrian to lower Paleozoic metamorphic and igneous rocks, forms the basin foundation, resulting in low-yielding aquifers. However, the weathered zones of these aquifers, about 15–30 m thick in plateau areas, serve as important sources of domestic water supplies [33]. Uplift and erosion resulting from the rift valley's development have reduced aquifer thickness, especially along escarpment crests and near bedrock outcrops, impacting groundwater availability. Alluvial deposits beneath lakeshore plains, formed by sedimentation from rivers and the lake, create high-yielding aquifers with varied characteristics both vertically and laterally. The fracture zones of the rift valley escarpment,

formed by faulting and fracturing processes which increase permeability and water flow, create medium-yielding aquifers [38]. Ongoing geological processes, such as faulting, fracturing, erosion, and sedimentation, continuously impact aquifer permeability, storage capacity, and water resource availability [37]. Thus, an understanding of the geological characteristics and processes is crucial for effectively managing and sustaining the water resources of the basin.

2.4. Hydrogeological Setting

The hydrostratigraphic units within the aquifer system of the Lake Malawi basin encompass a weathered and fractured basement, as well as consolidated and unconsolidated sedimentary units (Figure 3). These units constitute three primary aquifer groups: consolidated sedimentary rock, unconsolidated sedimentary units overlying weathered basement, and weathered basement overlying fractured basement [6]. The unconsolidated sedimentary units overlying weathered basement aquifer constitutes intergranular pore spaces that facilitate groundwater transmission. The weathered basement units overlying fractured basement aquifer comprises intergranular pore spaces, fissures, fractures, and joints that enable groundwater flow. The consolidated sedimentary rock largely constitutes sandstone and shale, while the unconsolidated sedimentary units overlying weathered basement aquifer is mostly made up of colluvium and alluvium. The weathered basement overlying fractured basement aquifer mostly constitutes charnockitic gneiss and hornblende-biotite-gneiss. The basement complex is a primary source of groundwater in Malawi, and its mineral content largely influences the groundwater quality in the basin. Key rock minerals include plagioclase, pyroxenes, feldspars, amphiboles, and biotite [39]. These are largely natural sources of chemical species like calcium, magnesium, sodium, and potassium. Plagioclase minerals are sources of calcium and sodium during weathering, and the type of plagioclase in Malawi is more calcium-rich than sodium-rich. Therefore, there is more calcium in groundwater as it dissolves [13]. The dissolution of mafic minerals releases magnesium ions (as well as iron and other ions) in groundwater, some of which bear fluoride ions [12]. The consolidated sedimentary aquifers are found in the northern part, where they occur sparsely, while the unconsolidated sedimentary units overlying the weathered basement group largely occur on the western side. The weathered basement units overlying the fractured basement aquifer group are mostly found on the eastern side, particularly along the rift scarp zones. Isolated outcrops of basement lithologies occur in the basin, with some folded exposures, especially along the Malawi–Zambia border [6]. The Lake Malawi shoreline areas within the rift valley plain are characterised by unconsolidated fluvium, colluvium, and alluvium sedimentary units where they overlay weathered basement units. The potential yield of the unconsolidated sedimentary units overlying the weathered basement aquifer is estimated to be around 20 L/s, while water supply boreholes within the weathered basement overlying the fractured basement aquifer have a lower yield of up to 2 L/s [13].

2.5. Climate

The Lake Malawi basin climate is classified as tropical-continental, influenced by various factors such as altitude, relief, and presence of Lake Malawi [6]. The Köppen–Geiger system categorises the climate as Aw or Savannah, described as "Not (Af) and Pdry < 100 − MAP/25", where Af is rainforest, MAP is mean annual precipitation, and Pdry is the precipitation of the driest month [40]. The basin has a dual-season system, with a wet season from November to April and a dry season from May to October. The dry season, driven by south-easterly winds, is mostly cool-dry from May to August and hot-dry from September to October. The wet season is influenced by north-easterly winds; the Intertropical Convergence Zone (ITCZ), the Congo Air Boundary (CAB), and Tropical Cyclones and accounts for ca 90% of annual precipitation [41,42]. The majority of rain falls between December and March, with January receiving the highest amounts in most areas

of the basin. However, there is a contrasting pattern near the western shoreline of Lake Malawi, where peak precipitation is usually observed in March [43].

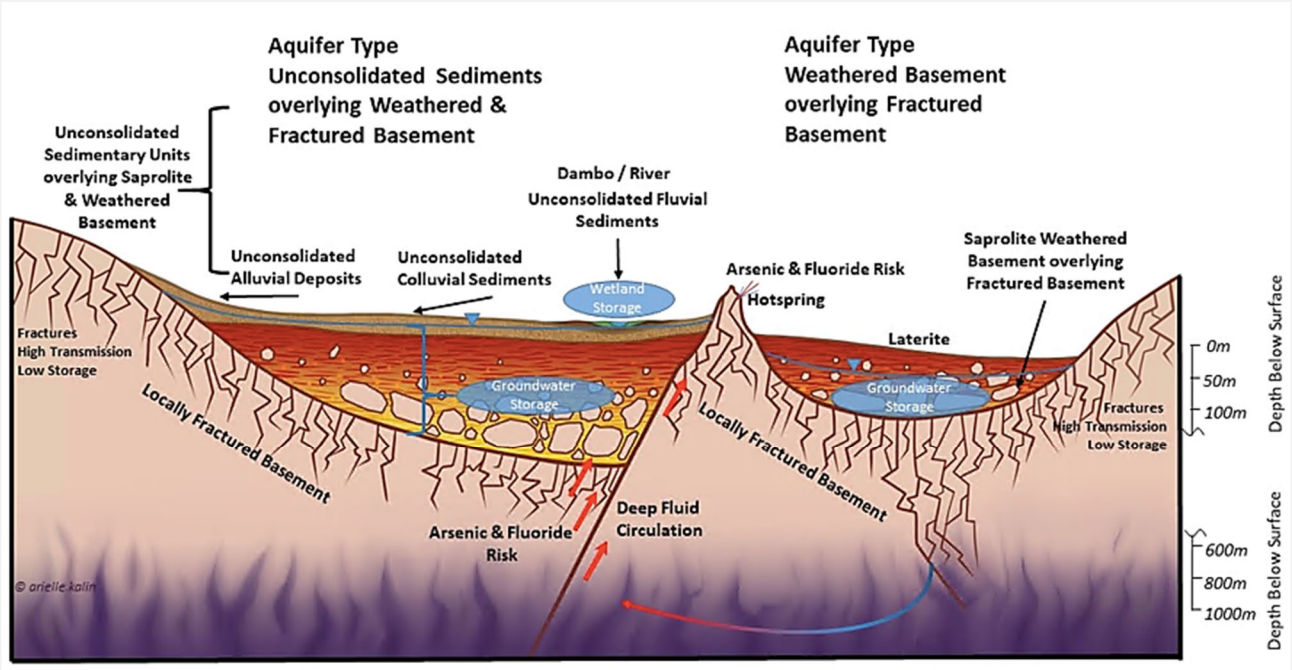

Figure 3. Idealised cross-section hydrostratographic units (aquifers) in the Lake Malawi basin (after [6]).

Annually, precipitation ranges from 623 to 1654 mm, averaging 927 mm. The rift valley plain, bordering Lake Malawi, receives the most rain, with a mean of 1036 mm, which is linked to lake effects [44]. In contrast, the western plateaus exhibit more aridity, which is linked to topographic isolation. The basin's diverse relief and proximity to Lake Malawi have a significant impact on the spatial distribution of precipitation [44,45]. The mean annual temperature ranges from 12.9 to 24.7 °C, averaging 20.5 °C. The Nyika highlands experience cooler temperatures, averaging 17.6 °C, whereas the rift valley lakeshore plain, with the lowest topographic extremes, experiences hotter temperatures, averaging 23.4 °C. The coldest months in the LMB are June and July, while the hottest months are October and November. The presence of Lake Malawi moderates the surrounding areas, resulting in a mean daytime temperature of 30.3 °C and a night-time temperature of 10.3 °C [46].

3. Materials and Methods

3.1. Sampling and Analytical Techniques

Three groundwater sampling surveys were conducted between 2021 and 2022. The sampling design provided a representative geographical spread and balanced hydrogeological coverage. The sampling timelines captured seasonal and topographic effects on groundwater dynamics. Sampling coverage was constrained by ease of access, more so in the wet season when travel to remote or low-lying flood-prone areas was risky. Water samples were collected from boreholes, dug wells fitted with handpumps, and hot springs that were in constant use for water supply during sampling and purged when not in use to ensure the samples were representative.

Isotope hydrology samples (n = 327 subdivided into 160 wet season samples and 167 dry season samples) were collected in 50 mL high-density polyethylene (HDPE) bottles with inner caps, sealed with waterproof tape, preserved at 4 °C, and kept away from direct sunlight during transportation and at the laboratory. A set of samples was analysed using a laser spectroscopy-based technique using the Picarro isotopic water analyser (Model: L2140-*i*, Picarro Inc., Santa Clara, CA, USA) at the IAEA laboratory in Vienna, Austria. Another

set of isotope hydrology samples was analysed using a Picarro isotopic water analyser (Model: L2110-*i*, Picarro Inc., Santa Clara, CA, USA) at the Central Water Laboratory in Lilongwe, Malawi. The isotope hydrology samples were analysed in non-consecutive duplicates in high-precision mode with dry synthetic air carrier gas. Each such analysis consisted of six injections. Lake Kyoga and Standard-09 (Greenland Ice) working reference materials (RMs) were enriched and depleted, respectively. The controls were Standard 11 (Monaco Lagoon) and Standard 06 (Heidelberg tap water) for quality assurance and quality control purposes. Data reduction was performed in the Laboratory Information Management System (LIMS) for lasers [47] using residual memory correction after ignoring the first three injections. Two reference points were used to normalise the Vienna Standard Mean Ocean Water (VSMOW)-Standard Light Antarctic Precipitation (SLAP) scale. The long-term deviation of control samples demonstrated that the measurements were accurate to within 0.1‰ or better for $\delta^{18}O$ and 0.5‰ or better for $\delta^{2}H$, and the isotope analysis results were reported as ratios compared to V-SMOW standards (Equation (1)).

$$\delta_{s/std} = \left(\frac{R_s - R_{std}}{R_{std}}\right) \times 1000 \quad (1)$$

In Equation (1), Rs is the isotopic ratio of the sample, Rstd is the isotopic ratio of the standard, and δ is the delta notation, where δs/std is reported in per mil (‰). The d-parameter (d) was calculated from Dansgaard's equation [48] relating to the $\delta^{18}O$ and $\delta^{2}H$ of water, defined as $d = \delta^{2}H - 8\delta^{18}O‰$. The process of handling water samples, including onsite measurements, sample collection, transportation, holding, preparation, and analysis, followed the International Standard Procedures (ISP) [49]. This adherence ensured the consistency and reliability of the isotopic data generated.

On-site measurements (electrical conductivity (EC), total dissolved solids (TDS), and pH) were conducted using a portable multi-meter (Model: HI-98194, Hannah Instruments, Woonsocket, RI, USA). A pair of water samples were collected from each site, one acidified and the other non-acidified, using 1L polyethylene bottles rinsed with distilled water. The water quality samples (n = 727) were labelled, preserved at 4 °C during transportation and storage, and filtered through 0.45 µm Whatman filters prior to analysis at the laboratory. Anions (F, Cl, NO_3, and SO_4) were measured using Metrohm ion chromatography (Model: 850 Professional IC, Metrohm, Switzerland), while cations (Na, K, Mg, Ca, Fe and Mn) were measured using an inductively coupled plasma spectrometer (Model: iCAP 6200, Series Thermo-Fisher Scientific, Waltham, MA, USA) at the Environmental Analytical Laboratory of the University of Strathclyde in Glasgow, Scotland. Carbonate and bicarbonate were measured using a titrimetric method, while alkalinity was measured using a photometric analyser (Model: KONE Aquakem V.7.2.AQ2, Skalar, Breda, The Netherlands). All field sampling measurements and laboratory analyses were conducted in line with the ISP [50], and the accuracy of the hydrochemical analysis was validated using the ionic balance method, adhering to an allowable ionic balance error (IBE) of ±5% (Equation (2)) [50].

$$IBE\% = \frac{\sum(Cations - Anions)}{\sum(Cations + Anions)} x100 \quad (2)$$

3.2. Computation of Gibbs Diagram, Chloro-Alkaline Indices, and Saturation Index (SI)

Gibbs diagram plots used the anionic weight ratio $Cl^-/(Cl^- + HCO_3{}^-)$ and cationic weight ratio $Na^+/(Na^+ + Ca^{2+})$ as functions of log-transformed TDS) [51] and was used to identify geochemical reactions controlling groundwater chemical evolution in Lake Malawi basin. Schoeller chloro-alkaline indices, defined in Equations (3) and (4), were employed to refine evidence of cation exchange reactions and ascertain the nature and extent of their occurrence in groundwater within the Lake Malawi basin.

$$CAI(I) = \frac{Cl^- - (Na^+ + K^+)}{(Cl^-)} \quad (3)$$

$$\mathrm{CAI(II)} = \frac{\mathrm{Cl^- - (Na^+ + K^+)}}{\left(\mathrm{HCO_3^- + CO_3^{2-} + SO_4^{2-} + NO_3^-}\right)} \quad (4)$$

In Equations (3) and (4), if the CAI-I and CAI-II are less than zero, the cation exchange is a forward reaction. If the CAI-I and CAI-II are greater than zero, the cation exchange is a reverse reaction [52]. The saturation index (SI) was used to evaluate the equilibrium state with respect to groundwater and solid mineral phases [53–55]. The SI, defined in Equation (5), was calculated using PHREEQC software (version 3.7.3), which calculates the logarithm of the ratio between ion activity product (IAP) and solubility product (Ksp) [56].

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{\mathrm{K_{sp}}}\right) \quad (5)$$

In Equation (5), IAP = ion activity product, K_{sp} = solubility product, where an SI equal to zero indicates an equilibrium state. If the SI is less than zero, the groundwater is undersaturated with respect to the mineral phase, and there is potential for mineral dissolution. When the SI is greater than zero, the groundwater is oversaturated.

4. Results

4.1. Hydrogeochemical Characteristics

The groundwater pH ranged from acidic to alkaline (pH: 4.5–9.4), with a mean of 6.9 and a median of 6.4. The Total dissolved solids (TDS) varied widely from 23 to 2662 mg/L, with a mean of 305 mg/L and a median of 210 mg/L (Figure 4, Supplementary Material (SM)-Table S1). The dominant cations were calcium, sodium, and magnesium, with considerable variation. The majority of groundwater samples (88%) had TDS below 600 mg/L, which falls within the World Health Organisation (WHO) recommended guidelines for good taste. The remaining 12% had elevated TDS concentrations exceeding 1000 mg/L [57]. While most groundwater samples were aligned with the WHO's recommended guidelines, there were cases where the groundwater may not fully meet the taste and palatability expectations. Bicarbonate, chloride, and sulphate were the dominant anions, with nitrate and fluoride present at generally low to moderate concentrations.

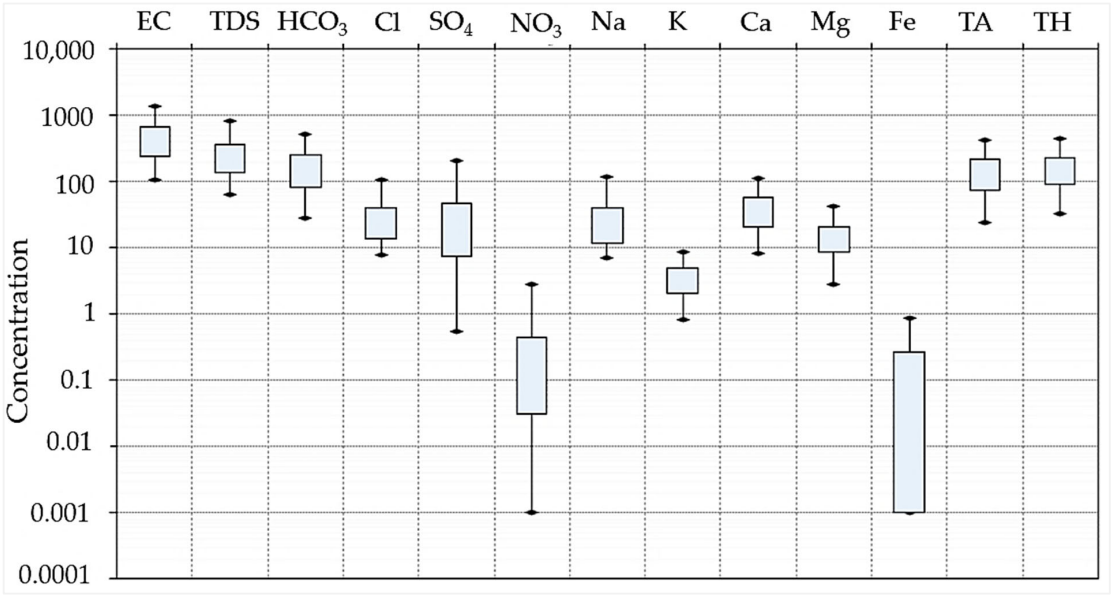

Figure 4. Observed hydrochemical interquartile plot for groundwater in Lake Malawi basin: It shows the distribution of electrical conductivity (EC) (µS/cm), total dissolved solids (TDS) (mg/L), total alkalinity (TA) as $CaCO_3$ (mg/L), total hardness (TH) as $CaCO_3$ (mg/L), and major ions (mg/L) in groundwater.

Previous studies reported arsenic occurrence [11] and widespread risks of fluoride [12] in groundwater. This study found that nitrate was ubiquitous in groundwater, detected in most of the groundwater points (93.1%) and varied widely from <0.001 to 235 mg/L, with isolated outliers recorded in the northern part of the basin (Figure 5a). The nitrate concentrations were generally consistent with the recommended WHO guidelines for drinking water (Figure 5b). Given there is no natural source of nitrate in Malawi's groundwater, the ubiquitous nature of this contaminant points towards human-induced pollution. This highlights a critical need to model nitrate-related contamination sources across the country, considering a surge in likely sources, including pit latrines, septic systems, and extensive fertiliser use due to SDG 6 drivers and the current population boom.

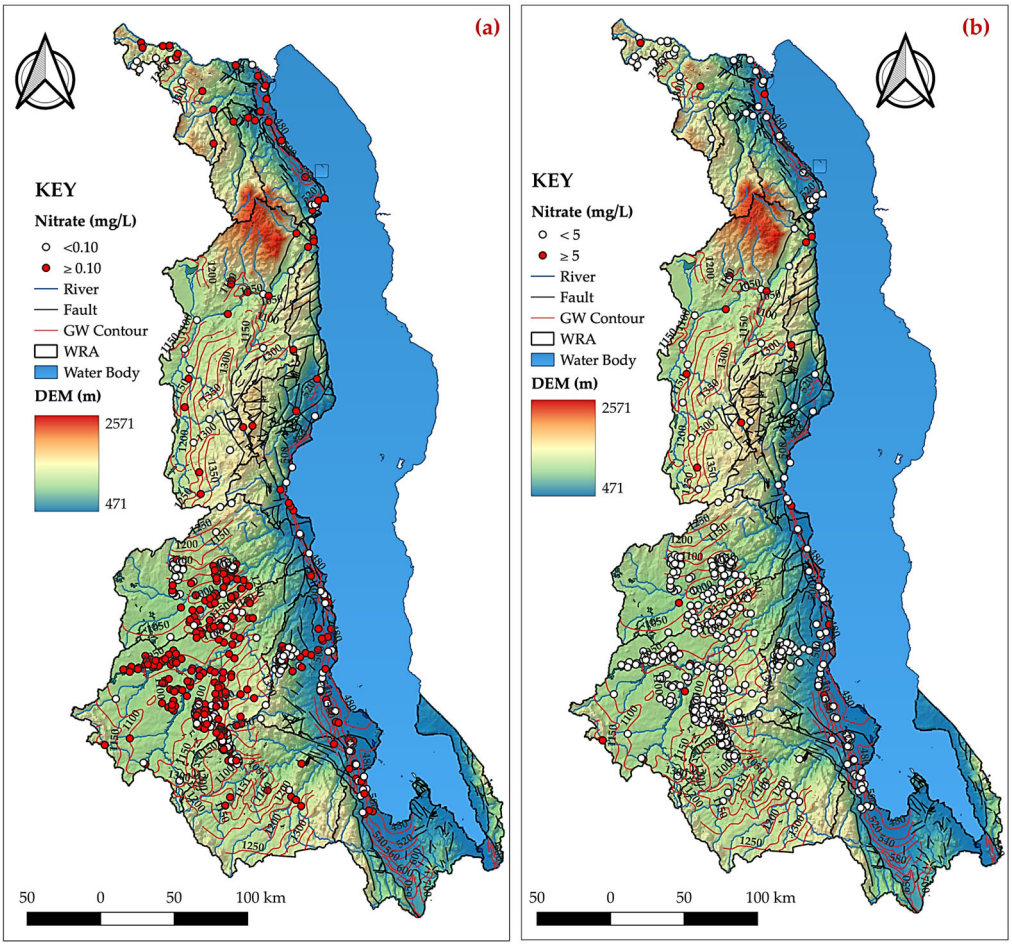

Figure 5. Spatial distribution of nitrate concentrations in groundwater across the LMB. (**a**) shows general distribution of measurable nitrate and (**b**) shows measurable nitrate concentration projecting potential impact.

4.2. Hydrogeochemical Facies

A Piper plot was used to examine groundwater hydrogeochemistry, delineating distinct hydrogeochemical facies based on dominant cationic and anionic species [58]. This approach refined the understanding of the hydrogeochemical signatures of Lake Malawi basin groundwater and how minerals in the host rock matrix impact the groundwater along its flow path. The classification of hydrogeochemical facies identified five groundwater types (Figure 6): (1) Ca-Mg-HCO_3, (2) Ca-Mg-SO_4, (3) Na-Cl, (4) Ca-Mg-SO_4-Cl, and Na-HCO_3-Cl (5). The most prevalent groundwater type was Ca-Mg-HCO_3, comprising 73.9% of the groundwater samples. This dominance suggests groundwater evolves from recharge through geochemical reactions with primary silicates and secondary carbonates and/or high-Mg dolomitic carbonate rock matrices. The close proximity of distinct hydrochemical

facies suggests groundwater mixing from multiple sources, supported by the presence of mixed water types (Ca-Mg-SO_4 and Na-HCO_3-Cl). A mixing trend observed in a cation ternary diagram (Figure 6) suggests cation exchange reactions, increasing the dissolved sodium concentration by exchanging with calcium in clays.

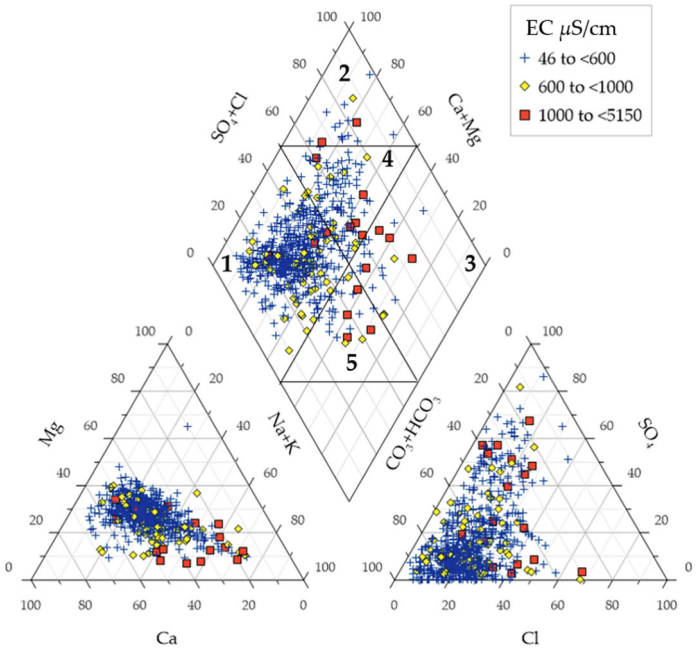

Figure 6. Piper plot for groundwater samples: Various colours show hydrochemical facies based on electrical conductivity (EC), a proxy indicator of total dissolved salts (TDS).

The spatial distribution of the water types aligned with the TDS, exhibiting greater uniformity in highland plateau areas and more inhomogeneity in low-lying areas, especially in the lakeshore and flood plains (Figure 7a,b). This inhomogeneity suggests the influence of various factors, such as the seepage of surface water into groundwater, the presence of older groundwater with higher calcium or sodium concentrations due to prolonged travel time, and the dissolution of minerals resulting in calcium, sodium, and magnesium in solution.

4.3. Mechanisms Controlling Mineral Enrichment

Groundwater mineral enrichment is influenced by geochemical reactions (e.g., eva–oration, precipitation, and mineral weathering) along a flow path [29]. The Gibbs diagram (Figure 8) identifies water–rock mineral reactions as the dominant geochemical mechanism controlling groundwater mineral enrichment. It also depicts an increasing cationic weight ratio $Na^+/(Na^+ + Ca^{2+})$ with a corresponding minimal change in the TDS, suggesting cation exchange as another controlling geochemical reaction. Table 1 and Table S5 display various rock minerals and their respective interactions with water, resulting in the release of ionic species into groundwater that influence its chemical composition.

The calcium vs. bicarbonate (Ca^{2+}/HCO_3^-) weight ratio was used to examine carbonate mineral-related geochemical reactions (e.g., the dissolution of calcite and apparent high-Mg dolomitic carbonate controlled by the dissolution of Mg-silicates and plagioclase) controlling Lake Malawi basin groundwater mineral enrichment. The results identified high-Mg dolomitic carbonate dissolution as a controlling geochemical reaction, revealed by the clustering of groundwater data within 1:1 and 1:2 HCO_3^-/Ca^{2+} weight ratios (Figure 9a).

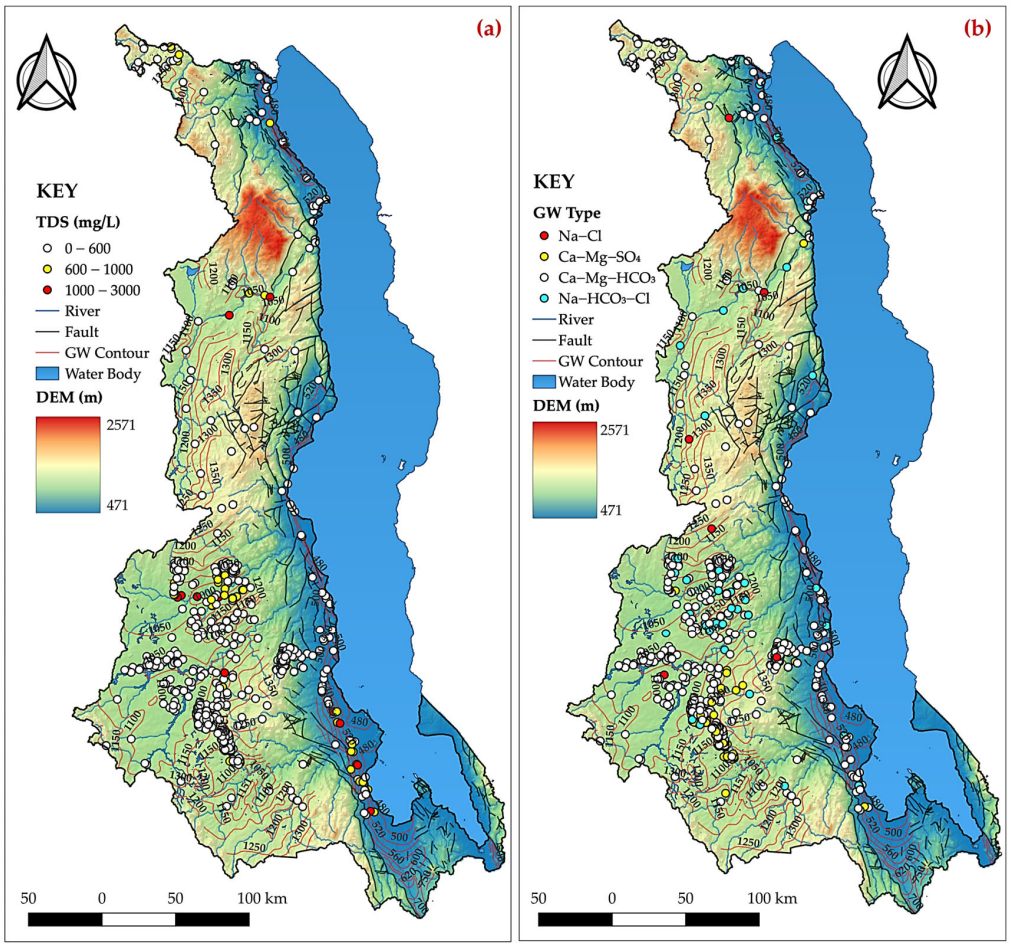

Figure 7. Spatial distribution of (**a**) TDS and (**b**) water types in groundwater across LMB.

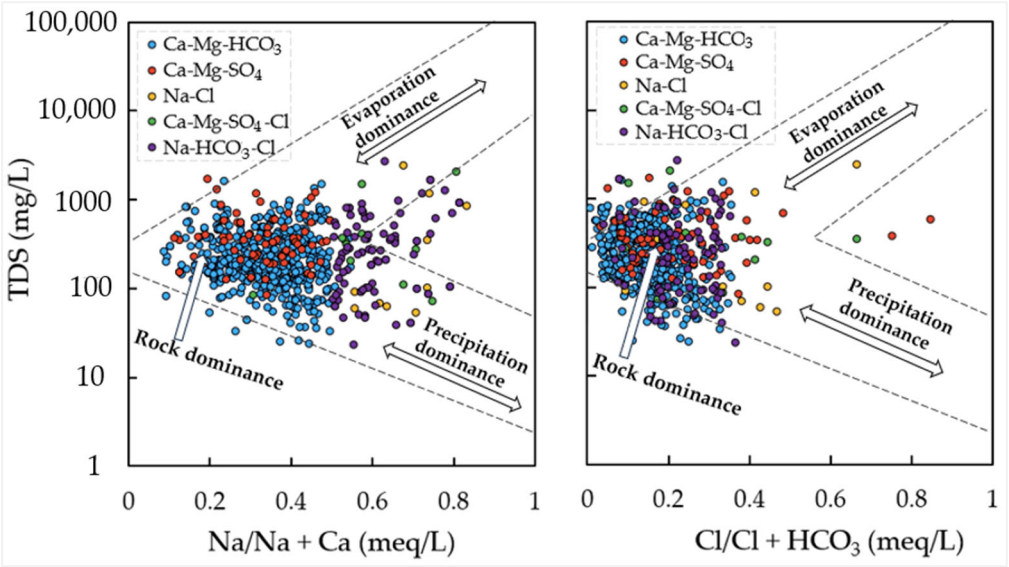

Figure 8. Gibbs diagram showing key mechanisms controlling groundwater chemistry.

Table 1. Natural sources of ionic species in groundwater present in Lake Malawi basin aquifers.

Mineral/Ion Species Source	Chemical Formulas	Ionic Species	Reaction Type
Carbon Dioxide (CO_2)	CO_2 ($+H_2O$)	H^+, HCO_3^-	Congruent
Plagioclase	$(Na,Ca)(Al,Si)_4O_8$	Ca^{2+}, Na^+	Incongruent
Anorthite	$CaAl_2Si_2O_8$	Ca^{2+}, HCO_3^-	Incongruent
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$	K^+, Mg^{2+}, F^-	Incongruent
Calcite	$CaCO_3$	Ca^{2+}, CO_3^-, HCO_3^-	Congruent
Albite	$NaAlSi_3O_8$	Na^+	Incongruent
Muscovite	$KAl_2(AlSi_3O_{10})(F,OH)_2$	K^+, F^-	Incongruent
Olivine	Mg_2SiO_4	Mg^{2+}	Incongruent
Amphiboles	$Ca_2(MgFeAl)_5(AlSi)_8O_{22}$	Mg^{2+}, Ca^{2+}	Incongruent
Fluorapatite	$Ca_5(PO_4)_3F$	Ca^{2+}, F^-, PO_4	Incongruent
Fluorite	CaF_2	Ca^{2+}, F^-	Congruent
Pyrite	FeS_2	SO_4^{2-}	Incongruent

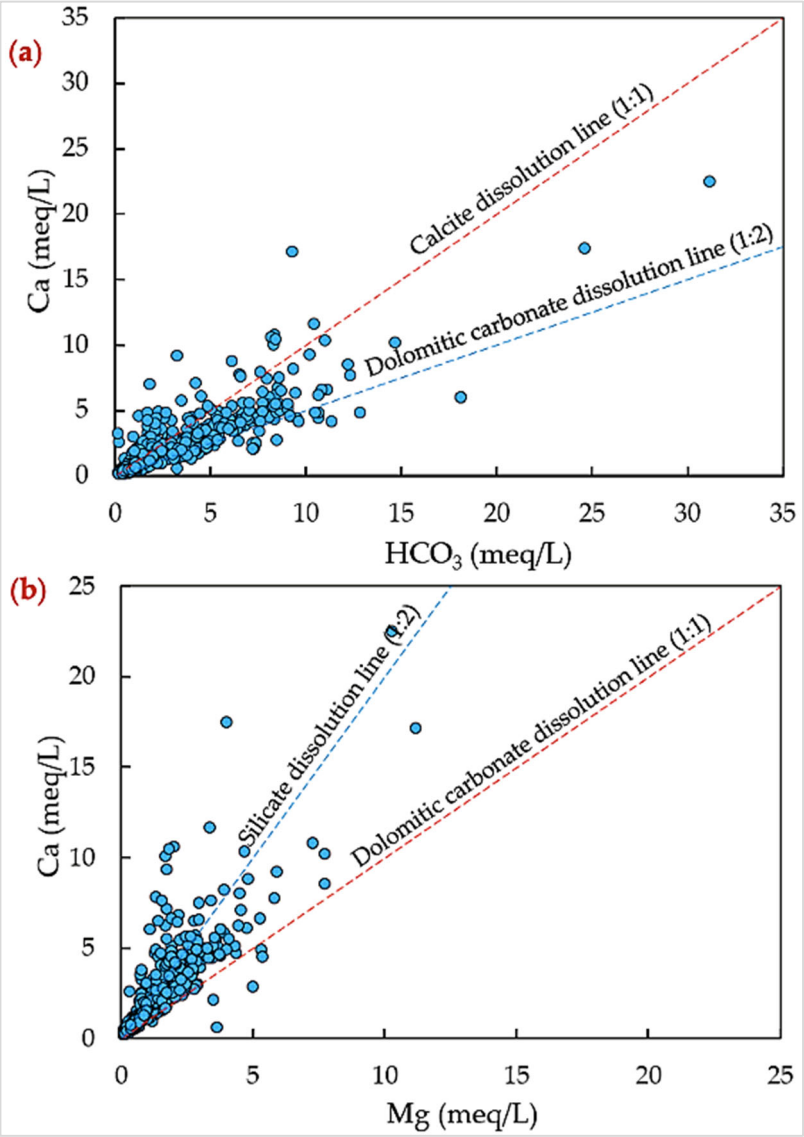

Figure 9. Relationship between major ion concentrations of groundwater samples, (**a**) Ca^{2+} vs. HCO_3^-, and (**b**) Ca^{2+} vs. Mg^{2+}.

The calcium vs. magnesium (Ca^{2+}/Mg^{2+}) weight ratio was used to further examine the carbonate and silicate mineral-related geochemical reactions controlling the Lake

Malawi basin groundwater mineral enrichment. The results identified dolomitic carbonate dissolution and calcium or magnesium silicate dissolution as the controlling geochemical mechanisms of groundwater mineral enrichment (Figure 9b), revealed by a dominant Ca^{2+}/Mg^{2+} weight ratio greater than 1:1, clustering within 1:2 equiline. A groundwater data subset plotted above the 1:1 equiline for the Ca^{2+}/Mg^{2+} weight ratio suggests excess Ca^{2+} derived from other geochemical reactions.

Cation exchange reactions were examined using the linear relationship of adjusted calcium and magnesium concentrations ($Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-}$) vs. sodium and potassium adjusted concentrations ($Na^+ + K^+ - Cl^-$) to refine the cation exchange reaction controlling insights. The aforementioned adjustments were made to eliminate any potential influence deriving from silicate weathering, gypsum (unlikely), and halite (unlikely) dissolution reactions. The resulting slope for the linear relationship agrees with the expected ideal slope of −1, suggesting silicate mineral reactions with forward cation exchange reactions (Figure S1a) [59]. The Schoeller chloro-alkaline indices (CAI-I; CAI-II) calculated based on Equations (3) and (4) suggest the dominant occurrence of cation exchange forward reaction influencing groundwater mineralisation (Figure S1b).

4.4. Geochemical Modelling

Geochemical modelling identified probable reactions controlling chemical evolution and chemical changes resulting from such reactions [29]. The saturation index (SI) calculated based on Equation (5) provided insights into an equilibrium state with respect to groundwater and solid mineral phases [53–55]. The results showed that groundwater from 58% of the samples was undersaturated ($SI_{calcite}$: −2.8 to 0) with respect to mineral phase calcite ($CaCO_3$), while the remaining 42% was at equilibrium or oversaturated ($SI_{calcite}$: 0 to 1.9) with respect to mineral phase calcite ($CaCO_3$) (Figure 10a). The negative $SI_{calcite}$ suggests a thermodynamic potential for calcite to dissolve in the groundwater. The positive $SI_{calcite}$ suggests conditions likely to reverse the reaction, resulting in the precipitation of calcite from the solution phase. The $SI_{calcite}$ near zero or remaining as a constant down gradient along the groundwater flow path suggests apparent equilibrium conditions in the groundwater system (where the mass transfer precipitation/dissolution of carbonate minerals continues as silicate weathering occurs). The negative $SI_{calcite}$ is associated with groundwater recharge in highlands, which is characterised by low pH. The positive $SI_{calcite}$ is associated with high groundwater pH, likely influenced by the weathering of silicate minerals, raising carbonate ions (CO_3^{2-}) while reducing hydrogen ions (H^+). It should be noted that the saturation index for carbonate species is co-dependent on an accurate field measurement of alkalinity, pH, temperature (in situ), and pCO_2; thus, with uncertainty, the slightly positive values may, in fact, be in equilibrium. Given calcite is generally not kinetically hindered, the results shown in Figure 10a likely, therefore, converge to equilibrium (through the precipitation of carbonate phases or, where highly undersaturated, dissolution).

Groundwater from 61% of the samples exhibited undersaturation conditions ($SI_{dolomitic\ carbonate}$: −5.6 to 0) with respect to mineral phase dolomite ($CaMg(CO_3)_2$), which here is considered the end-member of a high Mg dolomitic carbonate (the source of Mg most likely from the incongruent dissolution of ferromagnesian silicate minerals). The remaining 39% exhibited oversaturation ($SI_{dolomitic\ carbonate}$: 0 to 3.6) with respect to mineral phase dolomite (Figure 10b). The negative $SI_{dolomitic\ carbonate}$ suggests a thermodynamic potential for a high Mg dolomitic carbonate to dissolve in groundwater. The positive $SI_{dolomitic\ carbonate}$ suggests conditions are likely to reverse the reaction, resulting in high Mg carbonate precipitation from the solution phase. The precipitation of dolomite is kinetically hindered, and, therefore, high SI values may be due to slow rates of high Mg carbonate precipitation. These geochemical reactions suggest the presence of carbonate minerals undergoing continuous dissolution and precipitation in groundwater. The SI ranges for Gypsum ($CaSO_4.2H_2O$) (SI_{gypsum}: −6.9 to −0.4) indicate this evaporite mineral is not actively involved in geochemical reactions but is able to dissolve in the Lake Malawi basin groundwater should it locally exist (Figure S2). Given there is no current geologic

evidence for the occurrence of these minerals, a detailed mineralogic analysis of aquifer materials is needed, and thermodynamic interpretation should be avoided.

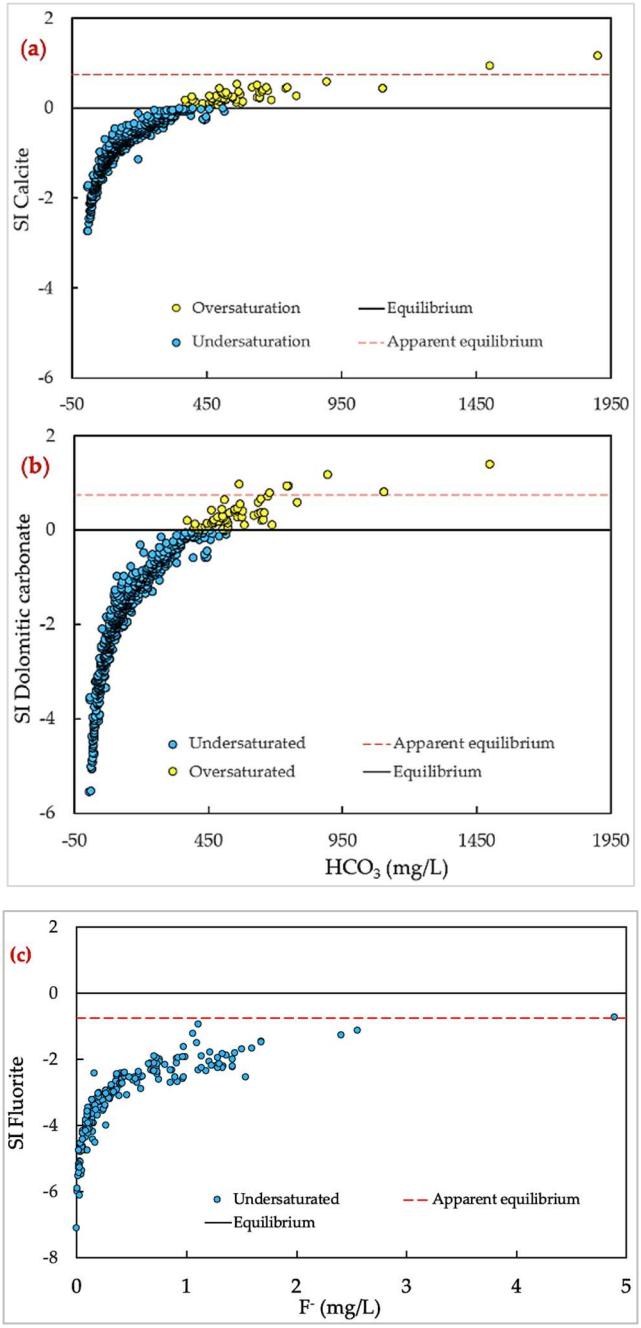

Figure 10. Saturation indices (SI) for (**a**) calcite, (**b**) dolomitic carbonate, and (**c**) fluorite from groundwater samples in the Lake Malawi basin.

It is possible that deep fluid flow (hidden hot springs) is also a source of sulphate and fluoride and requires further investigation [60]. The SI of Fluorite (CaF_2) spanned from −8.8 to −0.8, approaching apparent equilibrium. This trend may be a common ion effect with calcite (Figure 10a,c), but given the increasing concentrations of fluoride, there is a need for further substantiating evidence of deep fluid circulation from geothermally active areas, herein the source of fluoride ions in groundwater [60].

4.5. Isotope Hydrology Characteristics

4.5.1. Precipitation Stable Isotope Signatures

The isotope hydrology of precipitation in the Lake Malawi basin was measured on samples collected at four observatory stations as part of the Malawi Network of Isotopes in Precipitation (MNIP) (Table S2). The precipitation δ^2H signatures (n = 91) ranged from −111.2‰ to +12.4‰, with a mean of −35.6‰, and $\delta^{18}O$ signatures ranged from −14.3‰ to +1.0‰, with a mean of −6.1‰ (Figure 11a,b; Table S3). The precipitation d-parameter was distributed between −2.2‰ and +19.3‰, with a mean of +13.3‰. The mean d-parameter of +13.3‰ showed that the recycling of atmospheric moisture by large-scale evaporation process off Lake Malawi was highly likely, a proxy indicator of an isotopic offset of the local air mass from the global air mass (Figure 11a). This isotopic offset ascribed to the d-parameter in precipitation is consistent with the African Great Lakes region isotopic effect.

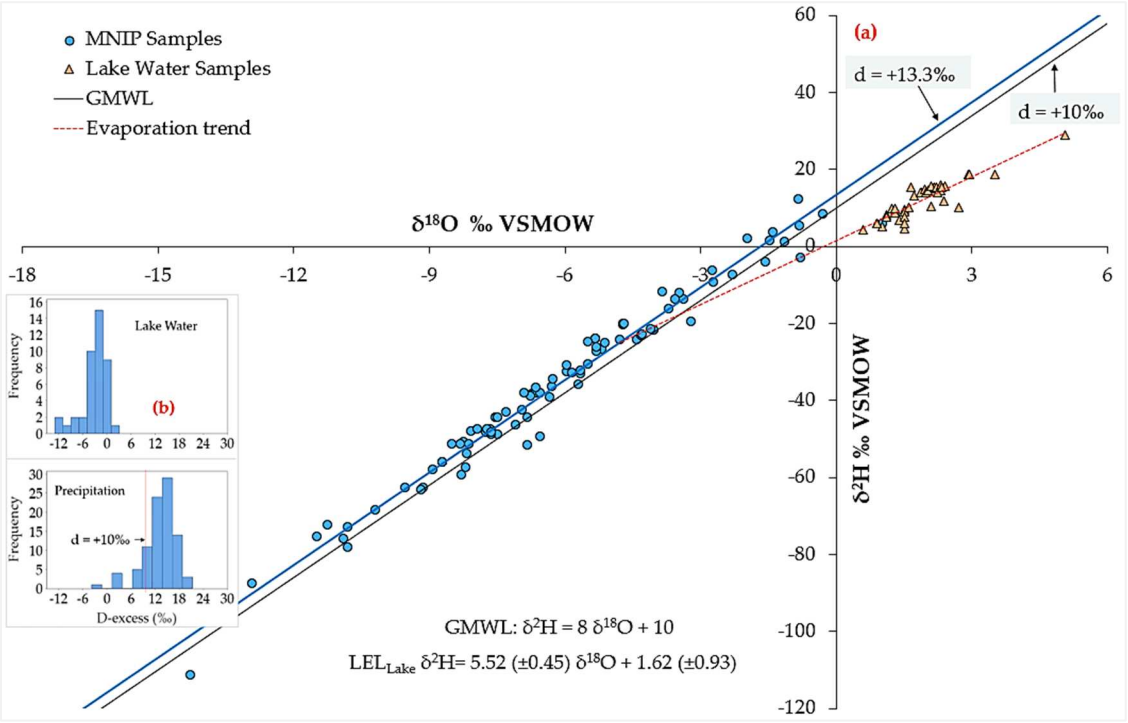

Figure 11. (**a**) Plot of δ^2H–$\delta^{18}O$ signatures for precipitation samples from MNIP stations and lake sites in the Lake Malawi basin. A blue line (slope of 8; d-parameter of +13.3‰) represents the distribution of the d-parameter for local precipitation, a proxy for an isotopic offset of local air mass from the global air mass represented by the Global Meteoric Water Line (GMWL). The red line represents the lake evaporation line (LEL). (**b**) Histogram providing the distribution of d-parameter for precipitation and lake water samples.

The wide range of measured isotopes (range: +123‰ for δ^2H, +15.3‰ for $\delta^{18}O$) is attributed to controlling factors such as evaporation, different moisture sources, and the influence of Lake Malawi producing spatial and seasonal variations [30,42,44,45].

4.5.2. Groundwater Stable Isotope Signatures

Groundwater δ^2H range from −47.4 ‰ to −15.8 ‰, with a mean of −34.6‰, and $\delta^{18}O$ ranged from -8.9‰ and −2.5‰, with a mean of −5.6‰ (Figure 12a; Table S4). The d-parameter ranged from −10.5 to +28.6‰, with a mean of +10.0‰ (Figure 12b). Most groundwater samples, categorised as Group G1, were depleted in heavier isotopes and aligned with the Global Meteoric Water Line (GMWL), suggesting groundwater recharge from modern non-evaporated local meteoric waters (Figure 12a). This is defined by the mean groundwater signatures corresponding to the mean precipitation signatures. A

subset of samples, Group G2, deviated below the GMWL, exhibiting isotopic enrichment, prominent during the 'dry season' in low-lying and near-lake sites, ascribed to secondary evaporative fractionation. The secondary evaporative fractionation prior to groundwater recharge occurs either during the initial runoff preceding infiltration, within the groundwater body itself, or from infiltrating isotopically enriched surface water (e.g., from irrigation return). The Group G2 could also be influenced by deep-seated hydrothermal waters (Figure 12c). The Group G3 samples plot above the meteoric water line. Precipitation, which comes from moisture in a closed evaporative basin and/or is initially snow, may have significantly enhanced the d-parameter for this group [61,62]. Recent studies of $\delta^{17}O$ further elucidate these effects, and future studies of $\delta^{17}O$ in precipitation in the African Great Lakes region are highly warranted [63].

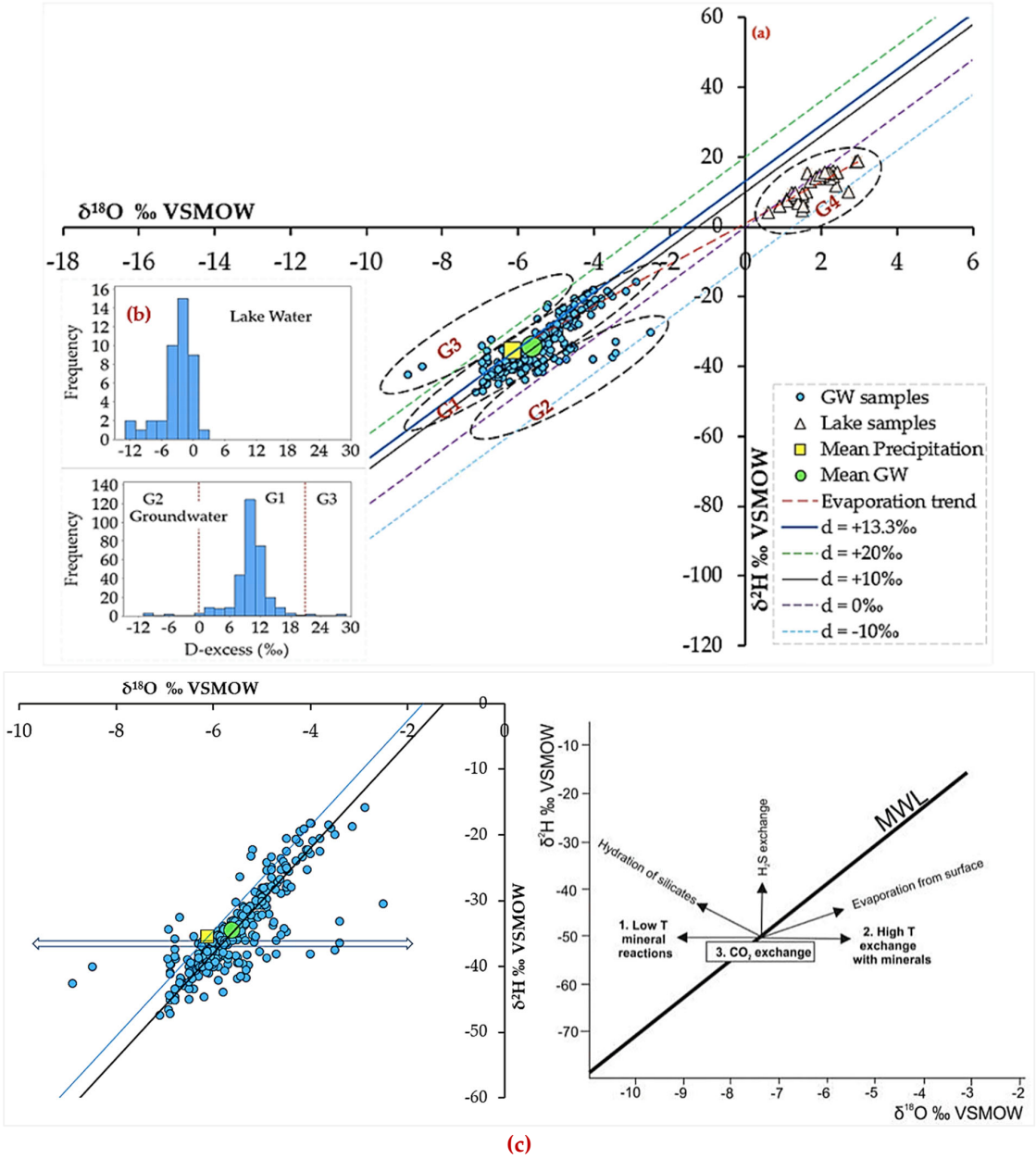

Figure 12. (**a**) Plot of δ^2H–$\delta^{18}O$ signatures for groundwater and lake samples in Lake Malawi basin. (**b**) Histogram showing the distribution of the d-parameter for groundwater and lake water samples. (**c**) Plot of δ^2H–$\delta^{18}O$ signatures for groundwater samples and associated controlling process influencing isotopic signatures in Lake Malawi basin.

Overall, the mean $\delta^{18}O$–$\delta^{2}H$ signatures of groundwater were consistent with the mean $\delta^{18}O$–$\delta^{2}H$ signatures of modern local precipitation. The evaporation trend in Figure 12a is a proxy indicator of lake water and groundwater mixing, suggesting lake water infiltration to the aquifer and groundwater discharge to the lake water system.

4.5.3. Dynamics: Spatial Distribution and Seasonal Effects

The spatial distribution of $\delta^{2}H$–$\delta^{18}O$ signatures aligns with geographic expectations, with enriched $\delta^{2}H$–$\delta^{18}O$ signatures predominant in low-lying and near-lake sites and depleted $\delta^{2}H$–$\delta^{18}O$ signatures dominant in highland plateau sites (Figure 13). Nonetheless, there was no statistically significant evidence of a distinct elevation effect on isotopic signatures of groundwater (Figure S3). There was a discernible seasonally variant disparity in the spatial distribution of $\delta^{2}H$–$\delta^{18}O$ signatures, wherein certain upland and lowland sites exhibited enriched and depleted $\delta^{2}H$–$\delta^{18}O$ signatures, respectively (Figure S4). The order of magnitude of the hydraulic head is consistent with progressive groundwater isotopic fractionation, whereby shallow groundwater (susceptible to phreatic evaporation) exhibits less negative $\delta^{2}H$–$\delta^{18}O$ signatures than deep groundwater. Near-geologic fault groundwater sites exhibit complex isotopic signatures' inhomogeneity ascribed to multi-influential process controls linked to groundwater sample flow path chronicle and/or evaporative effects (Figure 13).

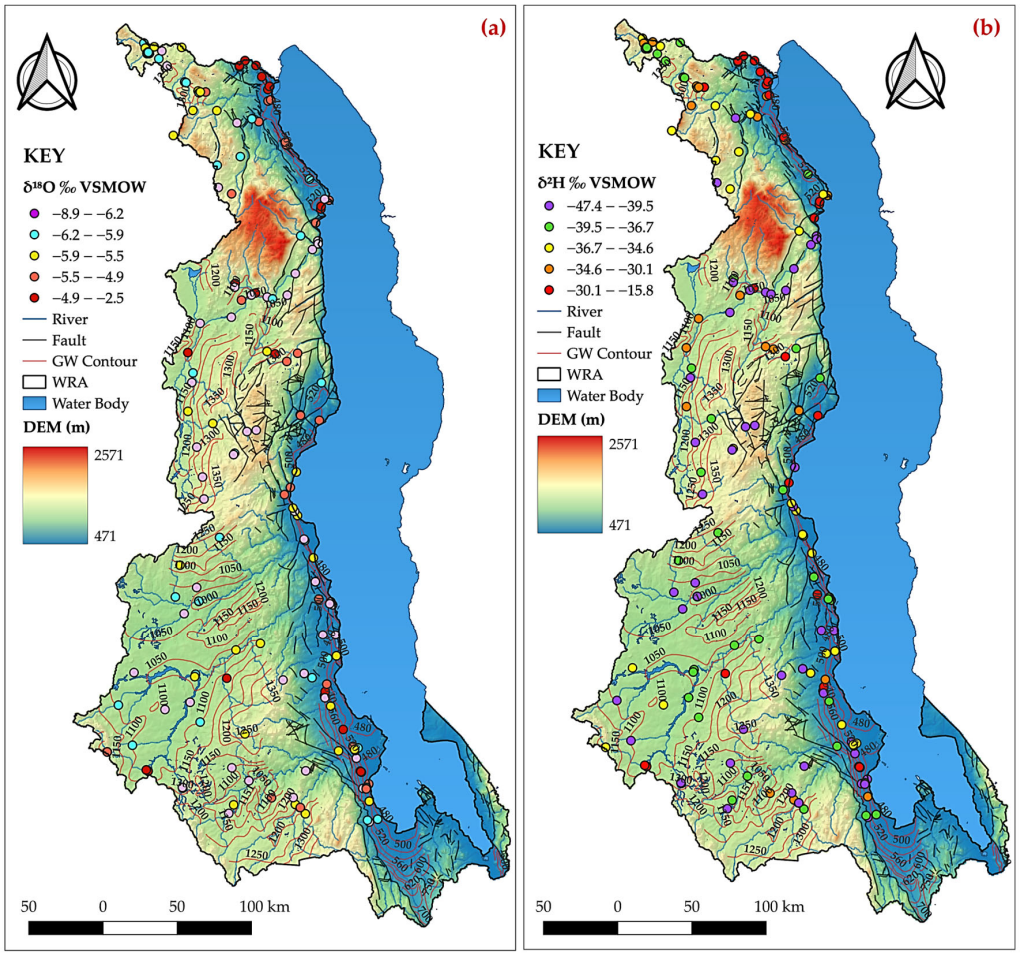

Figure 13. Spatial distribution of groundwater (**a**) $\delta^{18}O$ and (**b**) $\delta^{2}H$ signatures in the Lake Malawi Basin.

Groundwater $\delta^{2}H$–$\delta^{18}O$ signatures for wet and dry seasons reveal distinct patterns (Figure 14). Dry season $\delta^{2}H$–$\delta^{18}O$ signatures exhibited evaporative influences on groundwater either pre- or post-recharge and the potential infiltration of enriched lake water.

They were enriched in heavier isotopes than wet season δ^2H–$\delta^{18}O$ signatures, with a wider intra-seasonal inhomogeneity. However, some anomalies defy seasonal expectations, with enriched δ^2H–$\delta^{18}O$ signatures in the wet season and depleted δ^2H–$\delta^{18}O$ signatures in the dry season. These anomalies may be attributed to a combination of factors, including local recharge mechanisms, mixing of water sources, and anthropogenic influences. This basin's hydrogeological system complexities highlight the intricate interplay of meteoric water input, evaporation effects, recharge processes, deep fluid circulation, and mixing sources within the Lake Malawi basin.

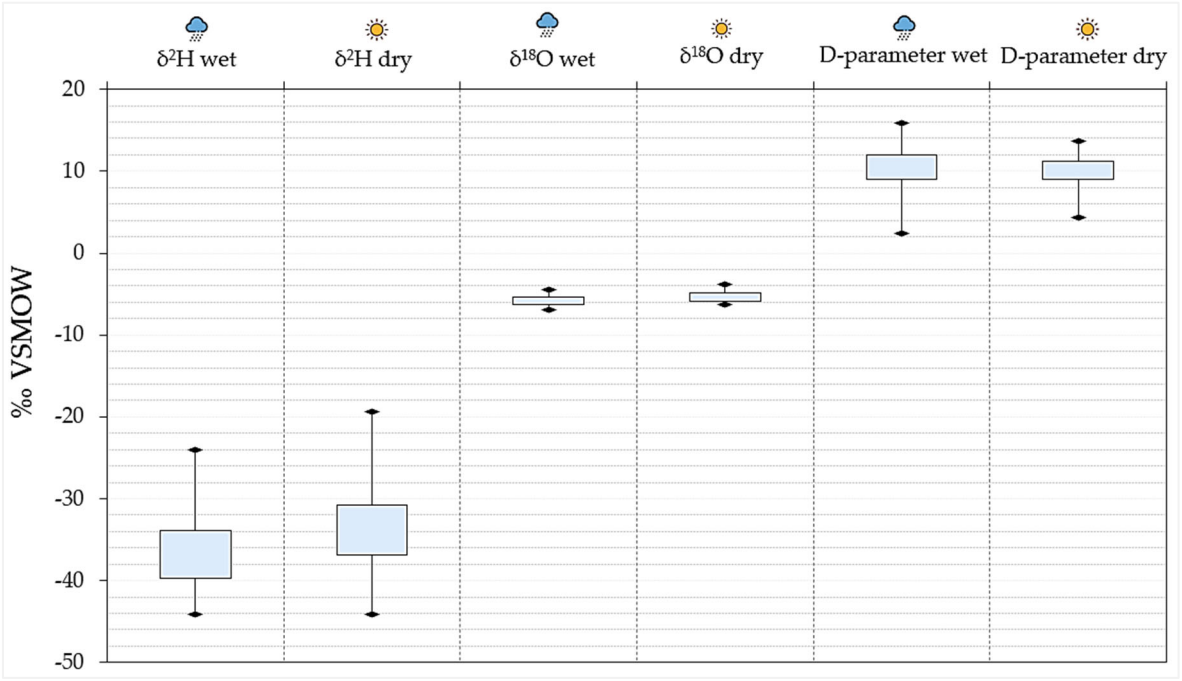

Figure 14. Box plot of groundwater δ^2H–$\delta^{18}O$ signatures and d-parameter for wet and dry seasons in the Lake Malawi Basin.

4.6. Integrated Isotopic-Hydrogeochemical and Geospatial Insights

Examining δ^2H–$\delta^{18}O$ signatures in conjunction with hydrogeochemical data provides a refined understanding of the groundwater recharge process and evolution. The prevalent Ca-Mg-HCO_3 groundwater type, characterised by low mineralisation and alignment with the GMWL, indicates a recent recharge from local precipitation that has not undergone significant evaporation (Figure 15). Another common type, Ca-Mg-SO_4 groundwater with a slightly higher electrical conductivity that plots just below the meteoric water line, suggests evaporative effects either pre- or post-recharge. The mixed groundwater types, Na-HCO_3-Cl and Ca-Mg-SO_4-Cl, plot along the GMWL but with outliers, suggesting the mixing of groundwater from multiple sources. Diverse processes, such as mineral–water reactions and evaporative effects, contribute to these mixed groundwater types. The Na-Cl groundwater type plots along and slightly below the GMWL, suggesting the mixing of older groundwater with newer meteoric water, with the latter dominating isotopically. Given the limited constraints on this observation, additional investigation is necessary to elucidate the findings. The combined isotope hydrology and hydrogeochemistry results point towards a mix of processes impacting groundwater evolution. The complexity of hydrochemical types and isotopic signatures, particularly near the lakeshore area at Lake Malawi, suggest intricate groundwater flow patterns and historical influences converging in this region.

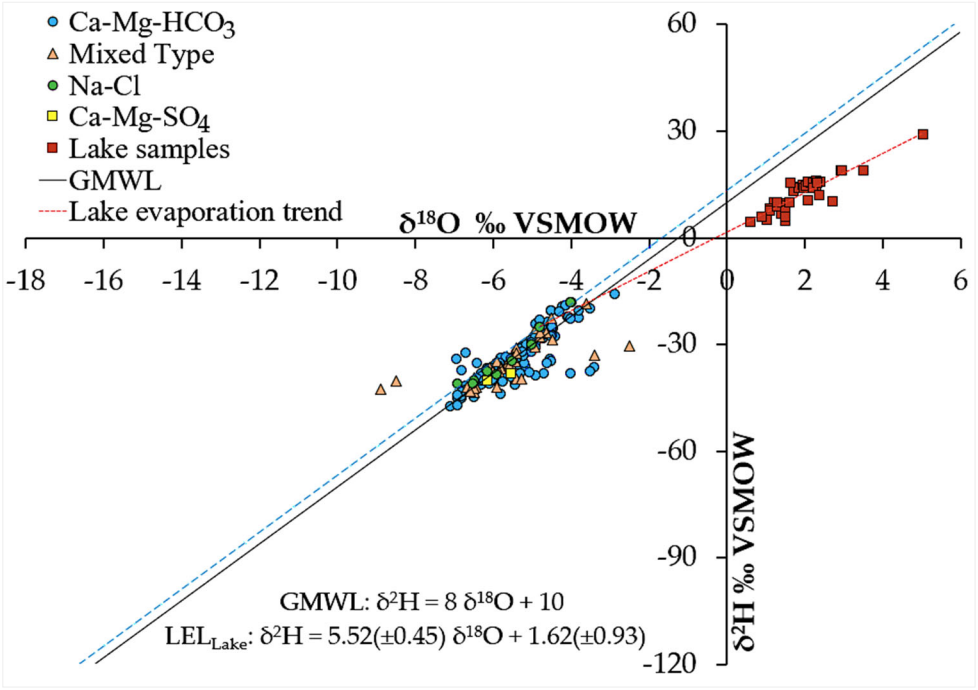

Figure 15. Plot of δ^2H and $\delta^{18}O$ signatures for groundwater samples based on groundwater types and electrical conductivity in Lake Malawi Basin. The mixed water type group comprises Ca-Mg-SO_4-Cl and Na-HCO_3-Cl.

5. Discussion

5.1. Origin of Ionic Species in Groundwater

Groundwater hydrochemistry exhibits a wide array of cationic and anionic species, dominated by Ca^{2+}, Na^+, HCO_3^-, and Cl^-. These ionic species are attributed to a range of natural and anthropogenic processes. Sodium (Na^+) is mainly obtained through the weathering of silicate rocks like albite ($NaAlSi_3O_8$), a sodium-rich plagioclase feldspar. Other sources of Na^+ include cation exchange reactions that exchange calcium (Ca^{2+}) from sodium-rich groundwater in clay. Highly localised evaporation and precipitation of trona ($Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$) in thermal spring sites constrained in the northern part of the basin yields sodium bicarbonate ($NaHCO_3$) deposits, which dissolve to release Na^+ in groundwater. Calcium (Ca^{2+}) is primarily derived from anorthite ($CaAl_2Si_2O_8$), a calcium-rich plagioclase, along with other rock minerals like hornblende ($Ca_2(MgFeAl)_5(AlSi)_8O_{22}$) and calcite. Magnesium (Mg^{2+}) sources include the weathering of magnesium-bearing silicate minerals like biotite ($K(Mg,Fe)_3(AlSi_3)_{10}(OH,F)$), olivine ($Mg_2SiO_4$), and amphibole (hornblende ($Ca_2(MgFeAl)_5(AlSi)_8O_{22}$)). Potassium ($K^+$) is likely derived from muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$ and biotite, typically found in sediments. Carbonate species (CO_3^{2-} and HCO_3^-) in groundwater are derived from carbonate mineral reactions, primarily calcite dissolution. The presence of SO_4^{2-} in groundwater suggests the occurrence of oxidation reactions of pyrite rock mineral (FeS_2) or deep fluid migration. The detection of NO_3^- in Malawi's groundwater, where no geogenic source exists, suggests human influence. Identifying and addressing human-driven nitrate contamination sources is crucial for achieving Sustainable Development Goal 6 objectives. Fluoride (F^-) occurrence in groundwater can be attributed to various minerals, including micas, fluorapatite ($Ca_5(PO_4)_3F$), fluorite (CaF_2), and concealed thermal springs [60].

5.2. Groundwater Evolution

Groundwater recharge in the Lake Malawi basin primarily occurs as a result of the infiltration of precipitation, a fundamental process that introduces fresh meteoric water into the subsurface. This influx of water initiates a complex series of geochemical reactions

with rock minerals driven by soil carbon dioxide as an acid source. Plagioclase feldspars, essential components of the rock matrix, undergo incongruent reactions upon interaction with meteoric water, leading to the release of calcium and sodium ions along with insoluble secondary clay minerals from complex smectites to simple kaolite (Table S5). The dissolution of carbonate species contributes to the overall chemical composition of groundwater in the basin. As groundwater flows through the rock matrix, incongruent reactions with silicates continue until saturation with carbonate minerals, predominantly calcite, is reached, after which mass transfer reactions continue at equilibrium, exerting significant control over groundwater chemistry. The weathering of plagioclase feldspar thus maintains an equilibrium with calcite. The presence of substantial carbonate in groundwater leads to the accumulation of calcite over time, especially in fractures and cavities within aquifer rocks. These fractures and cavities serve as crucial sites for the initiation of carbonate crystal formation, further influencing the groundwater system's chemical and isotopic composition. Noteworthy changes in the aquifer's composition and characteristics occur gradually due to the progressive buildup of calcite, and it is strongly advised that future studies include carbon isotope ($\delta^{13}C$) dynamics. Moreover, the formation of secondary calcite following the initial precipitation adds diversity to the range of minerals present in the groundwater system. Secondary calcite is widely distributed in fractures, veins, and cavities within granite and aquifer rocks, underscoring its importance across various geological formations. Where geothermal water mixes with meteoric water, fluorite is likely controlling levels of fluoride in groundwater, and further investigation is needed. In essence, the intricate interplay between precipitation, geochemical reactions, mineral dissolution, and carbonate mineral precipitation shapes the groundwater mineralisation processes in the Lake Malawi basin, highlighting the dynamic nature of hydrogeological systems in this region.

5.3. Implications for Water Resource Management

This study establishes a current baseline for understanding the isotope hydrology and hydrogeochemistry of groundwater in the Lake Malawi basin. This baseline is critical for monitoring future changes in the region's water resources. This study's findings are particularly relevant in water resource areas like WRA 4, WRA 5, WRA 6, WRA 8, and WRA 9 (Figure 1), where the Malawi Government aims to restore catchments and improve water security, agricultural productivity, and rural livelihoods. Insights gained from this research on groundwater recharge, evolution, and hydrogeochemical characteristics are valuable in shaping future policies in this domain as follows:

- Understanding the origins and influences impacting groundwater recharge can guide the development and implementation of sustainable water resource management policies. These policies can focus on safeguarding and maintaining groundwater quality, especially in areas at risk of pollution or contamination, thereby underpinning efforts towards SDG 6 targets related to water and sanitation;
- Utilising knowledge about different groundwater types and their unique characteristics can shape decisions related to land-use planning. Areas with sensitive groundwater recharge zones may necessitate stricter regulations to preserve water quality and promote responsible usage;
- Policy initiatives should emphasise the importance of the ongoing monitoring of groundwater quality and quantity. Regulations could be implemented to govern land practices near recharge zones and protected groundwater areas based on identified hydrochemical features and isotopic markers;
- Recognising the potential impact of evaporation on groundwater quality can spur the development of strategies to mitigate these effects. Policies targeting the reduction of evaporation-related factors, such as managing surface–water interactions or regulating land use activities, may be essential;
- Given the intricate nature of groundwater recharge processes highlighted in this study, policies promoting collaboration among various stakeholders, including governmen-

tal bodies, researchers, and local communities, can be instrumental. This collaborative approach can facilitate a comprehensive strategy for groundwater management and conservation;

- The nitrate concentration in the groundwater aligns with the recommended guidelines by the World Health Organisation for safe drinking water, as illustrated in Figure 5. Despite this compliance, there is a pressing necessity to develop a detailed model that specifically addresses groundwater contamination associated with nitrates, particularly in light of the upsurge in fertiliser use, pit latrines, and septic systems arising from the rapid population growth. By creating a more comprehensive and focused analysis of nitrate-related pollution, we can better understand and mitigate the potential risks posed by these sanitation systems to ensure the continued safety of our drinking water sources;
- Future isotope hydrology studies should include $\delta^{15}N-\delta^{18}O$ (NO_3), $\delta^{13}C$ (dissolved and mineral phases), and $\delta^{34}S-\delta^{18}O$ (SO_4) along with methods to study groundwater ages;
- In essence, this study's outcomes provide valuable insights to guide policymakers in crafting regulations and actions that support sustainable groundwater management, ensure water availability, and safeguard water resources for future generations.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w16111587/s1, Table S1: Descriptive statistical summary of hydrochemical analysis results of groundwater samples from Lake Malawi Basin, Table S2: List of Malawi-Network of Isotopes in Precipitation (MNIP) stations in Lake Malawi Basin, Table S3: Descriptive statistical summary of stable isotopic signatures of precipitation from MNIP stations in Lake Malawi Basin, Table S4: Descriptive statistical summary of stable isotopic signatures of groundwater from Lake Malawi Basin. Table S5: Natural sources of ionic species in groundwater and corresponding geochemical reactions. Figure S1: Cross plot of ion weight ratios on cation exchange in groundwater, Figure S2: Plot of saturation indices for gypsum and halite minerals in groundwater, Figure S3: Relationship between stable isotopes signatures and elevation, Figure S4: Relationship between $\delta^{18}O$ signatures and Elevation in Lake Malawi Basin.

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Data Availability Statement: The research data provided in this study can be obtained upon reasonable request from the corresponding author.

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Conflicts of Interest: The authors declare no conflicts of interest.

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5.3 Research Article 2: Supplementary Materials

5.4 Postface

Chapter 5 presented findings of an investigation conducted in the Lake Malawi basin, the second phase of the PhD research study. It addressed the research question (RQ 2): "How do water stable isotopic and hydrogeochemical signatures enhance our understanding of groundwater quality, recharge dynamics, and the conceptualisation of the Lake Malawi basin aquifer systems?" This question is supported by three main research objectives. The first objective (RO 2.1) analysed the stable isotopic and hydrochemical signatures of groundwater within the Lake Malawi basin aquifer systems and established baseline conditions. This objective was achieved by compiling groundwater data from production boreholes, protected dug wells, and spring discharges across the basin for detailed isotopic and hydrochemical characterization. The second objective (RO 2.2) investigated the processes and pathways of groundwater provenance and identified distinct groundwater recharge inputs in the Lake Malawi basin aquifer systems. This was accomplished through a critical analysis of isotopic and hydrochemical data, which provided insights into key groundwater recharge inputs and the evolution of groundwater along its flow paths. The third objective (RO 2.3) identified key geochemical control processes that affect groundwater quality and evolution, thereby improving the conceptualization of the Lake Malawi basin aquifer systems. This objective was met using a mixed-methods approach, including the use of Gibbs diagrams, geochemical modelling, and evaluation of ionic weight ratios for major ions.

Key insights from the second phase of the PhD study include the significant influence of modern precipitation on groundwater recharge and the presence of diverse hydrochemical facies within the aquifer systems. The study identified five distinct groundwater types, notably the prevalent Ca-Mg-HCO_3 type. It also pinpointed water-rock reactions, such as silicate dissolution and precipitation reactions associated with calcite and high-Mg dolomitic carbonates, as critical

geochemical processes influencing groundwater evolution. An important finding of this investigation is the spatial and seasonal variations in groundwater chemistry, which arise from the interplay of various hydrological processes including meteoric input, interaction with surface water, and evaporation. These variations underline the complexity of the groundwater system in the Lake Malawi basin and the need for continuous monitoring and assessment, especially as human pressures intensify. Notably, detectable levels of nitrate across the region underscore the human impact on groundwater quality and highlight the urgent need for proactive measures to prevent contamination and protect the integrity of water resources.

The implications of this study extend beyond academic research; they emphasize the urgent need for integrated management strategies that align with Sustainable Development Goal 6. The findings provide a valuable resource for policymakers and stakeholders committed to achieving groundwater sustainability in the transboundary Lake Malawi basin. By promoting a multisectoral approach to water management, we can better tackle the intertwined challenges of water scarcity, declining quality, and increasing demand, issues that are exacerbated by population growth and agricultural intensification. The next chapter (Chapter 6) will present research aimed at refining the conceptual understanding of the Lake Malawi basin's hydrology. It marks the third stage of the PhD study, building on the enhanced conceptual understanding of the local hydrological cycle and groundwater system presented in Chapters 4 and 5, respectively.

CHAPTER 6: SURFACE WATER RESOURCE CONCEPTUALISATION

6.1 Preface

Chapter 5 of the thesis detailed findings from the second phase of the PhD research conducted in the Lake Malawi basin, addressing the following research question (RQ 2): "How do water stable isotopic and hydrogeochemical signatures enhance understanding of groundwater quality, recharge dynamics, and conceptualisation of the Lake Malawi basin aquifer systems?" This chapter primary aimed to deepen the conceptual understanding of the groundwater resource system in the Lake Malawi basin.

Chapter 6, presents findings from the third phase of the study, also conducted in the Lake Malawi basin. This phase of the research primarily utilises isotopic input signals from both precipitation and groundwater systems to enhance the conceptual understanding of the basin's hydrology. The chapter specially addresses the third research question (RQ 3): "How do stable isotopic and hydrochemical signatures of surface water in the Lake Malawi basin inform our understanding of hydrological processes, climatic influences, and water provenance, and how can these findings help predict the hydrological responses of the Lake Malawi basin to changing climatic conditions?" The research objectives (RO) guiding this phase are outlined as follows**: RO 3.1** conduct a comprehensive analysis of the stable isotopic and hydrochemical signatures of surface water in the Lake Malawi basin to identify distinct patterns and variations; **RO 3.2** examine surface water isotopic responses to climatic factors such as solar radiation and precipitation; **RO 3.3** develop a conceptual model of the Lake Malawi basin's hydrology that integrates stable isotopic and

hydrochemical data with climatic factors to inform the prediction of future hydrological responses under varying climate scenarios.

The findings of this phase have been documented in a published peer-reviewed article that constitutes the principal content of this chapter. Noteworthy discoveries include significant influence of heavy cyclonic storms on the origins of surface water during the wet season, and the impact of groundwater baseflow and localized spring discharges on the basin's hydrology during the dry season. Moreover, evaporation effects, which are significant in lakes and reservoirs, are characterized by distinct isotopic signatures. The study reveals isotopic co-variability along surface water flow paths and unique system interactions at the confluence of highland-plateau rivers and rift margin headwaters in the rift valley escarpments. The research highlights seasonal variability that further illustrates the dynamic nature of surface water isotopic responses. Thus, this chapter not only contributes to the foundational knowledge necessary for future hydrological studies but also provides practical insights that are crucial for integrated water resources management in the Lake Malawi basin and the broader region. The implications of this work extend beyond academic discourse, possessing the potential to inform policies and strategies aimed at ensuring the long-term sustainability of water resources in the face of climate change and increasing anthropogenic pressures.

6.2 Research Article 3: Main Paper

Isotopic and Hydrochemical Tracers Reveal Surface Water Dynamics in the Lake Malawi Basin: A Mixed-proxy Approach for Water Resource Conceptualization

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Abstract: This study integrated isotopic and hydrochemical tracers that improved conceptualization of Lake Malawi basin hydrology. Findings show surface water provenance is primarily influenced by wet season heavy precipitation with insignificant evaporative effects, followed by increased dry season groundwater baseflow and localized spring discharges. Lakes exhibit high evaporation with stable isotope enrichment (δ^2H = +12.1 ‰; $\delta^{18}O$ = +1.9 ‰; *d*-excess = +3.1 ‰), while river and reservoir stable isotopic responses are more seasonally and/or spatially driven. Stable isotopic co-variability along surface water courses is marked by distinct isotopic changes, predominant when highland-plateau rivers converge with rift margin headwaters in rift valley escarpments. This convergence results in isotopically depleted-excess highland-plateau rivers, becoming enriched in rift valley lakeshore plains. Stable isotopic composition of river water varies between seasons; predominantly enriched in the dry season and depleted in the wet season.

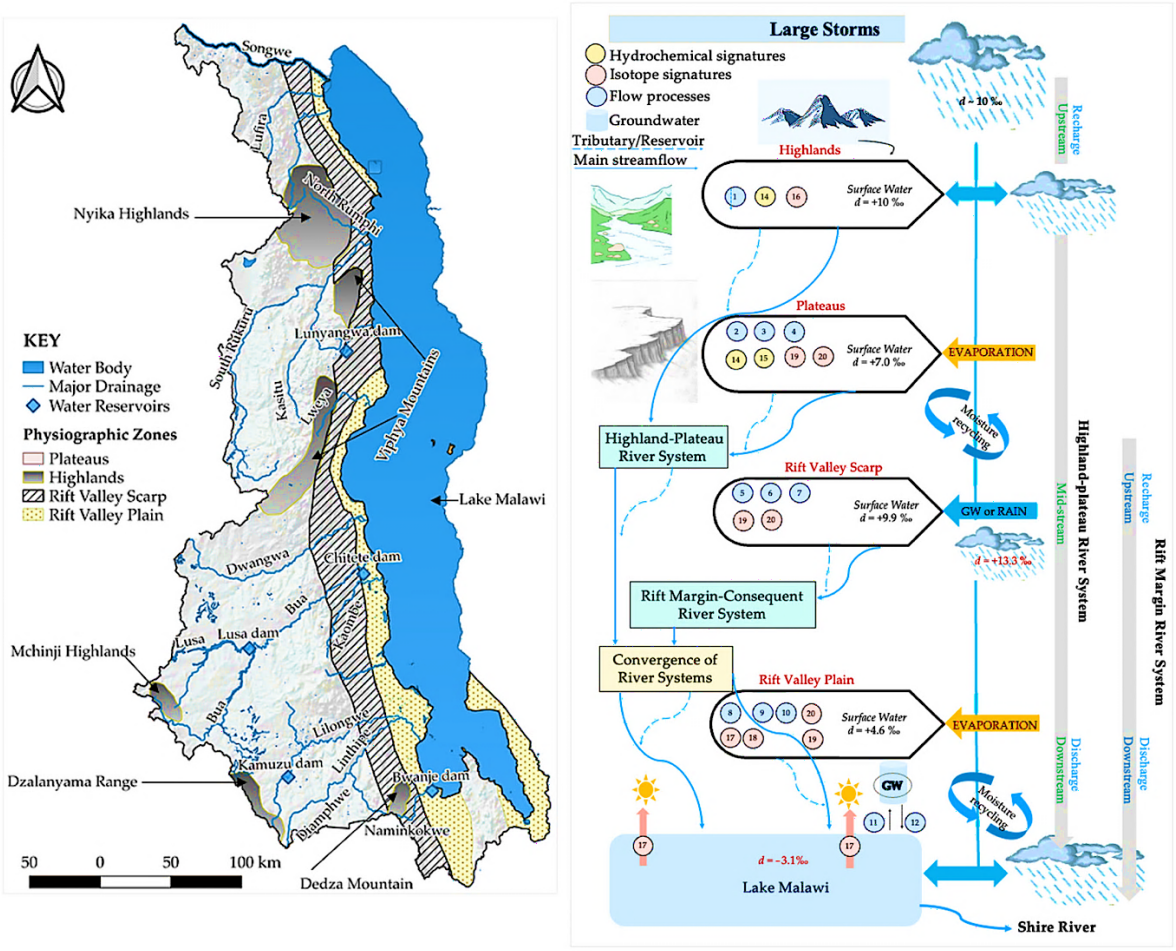
Lake waters exhibit minimum stable isotopic co-variability, retaining an enriched excess between low and high lake stands. The study underscores the effect of evaporation on surface water, most pronounced for lake waters. Where high total dissolved salts are found in surface water, they appear to be associated with localized isotopic enriched-excess, suggesting groundwater base-flow (water-rock reactions) mixing with runoff (precipitation). This foundational knowledge will inform current and future studies, especially on surface water and groundwater interactions at sub-basin scale and the wider region, critical for integrated water resources management.

Key words: transboundary water resource, *d*-excess, stable isotope tracing, integrated water resource management, evaporation effect, conceptual model

Highlights

- Recycling of continental air moisture and migration of oceanic air moisture are distinct controls of meteoric water input isotopic signal.
- Stable isotope signatures reveal streamflow is largely influenced by air moisture from cyclonic storms and/or trade winds from Indian ocean and moisture from Central Africa.
- *d*-excess revealed significant influence of evaporative enrichment in lake water.
- Riverine flow paths are marked by distinct stable isotopic and hydrochemical co-variability influenced by multiple inflow sources and evaporative fractionation.
- Isotopic homogeneity of surface water exhibit hydrologic system complexity.

Graphical Abstract



1. Introduction

Water stress and scarcity are escalating challenges worldwide, driven by unsustainable demand and environmental degradation, with poorer communities bearing the brunt of these impacts. Climate change is likely to compound these challenges by inducing water deficits and increasing unpredictability in water availability, which could disrupt societal dynamics (Haddeland., et al., 2024; UNEP., 2021). While approximately 60% of monitored global water bodies reportedly maintain good ambient water quality, significant gaps in data at national and basin levels hinder accurate global water quality assessments (UN-Water., 2021). Over three billion

individuals lack access to reliable information regarding water quality, heightening their susceptibility to waterborne illnesses (UN-Water, 2021). This is particularly concerning in low-income countries like Malawi, where limited budgets, insufficient human capacity investments, and lack of advanced monitoring systems present ongoing water resource management challenges (Kelly et al., 2019; Singh et al., 2019, Kalin et al, 2019). Even in regions with increasing regulations and investments aimed at mitigating point source pollution, persistent challenges of under-regulated diffuse pollution still remain (WWAP., 2017; Giri and Qiu., 2016). This scenario underscores the reality that mere economic development is inadequate for resolving water and environmental challenges, emphasizing the necessity for a nuanced understanding of our water and environmental systems.

Climate change shocks characterized by changing precipitation patterns and rising temperatures, further complicate water resource management (IPCC., 2014; Hipsey., 2013). Lake Malawi is highly vulnerable to seasonal weather fluctuations endemic to subtropical regions, manifesting a pronounced hydrological "short memory" and experiencing evaporation losses ranging between 60% and 90% (Beadle, 1974; Cochrane, 1958). Prolonged droughts threaten to lower Lake Malawi water levels, which could adversely affect Shire River flow rates, leading to significant energy insecurity and economic repercussions for downstream users in Malawi and Mozambique (Shela., 2000; Lyons et al., 2011). The Lake Malawi basin's vulnerability to climatic shocks exacerbates food insecurity through failed growing seasons, impacting local food supplies and cash crops. Failures in cash crop production could diminish the purchasing power of rural communities, where agriculture constitutes *ca*. 27% of the economy that heavily depend on exports (Pauw et al., 2011; World Bank., 2003; World Bank., 2015). This intricate chain reaction accentuates Malawi's vulnerability to extreme climatic episodes. The transboundary nature of the Lake Malawi basin, characterized by the Songwe River traversing Malawi-Tanzania border,

alongside Lake Malawi and shared aquifer systems among Malawi, Zambia, Mozambique, and Tanzania, necessitates informed international water cooperation. Such collaboration is crucial for balancing interests of upstream and downstream users especially during periods of water deficit, thus promoting equitable water allocation and mitigating potential conflicts (Liu et al., 2024; Fraser et al., 2021; Yuan et al., 2019; UNEP., 2016).

Lake Malawi plays a pivotal role in poverty reduction and local economic stability, offering jobs and sustenance to numerous communities. Lake Malawi's only outlet is the Shire River at the Kamuzu Barrage, which is essential for maintaining steady streamflow rates for hydroelectric power generation, especially during dry spells when tributary inflows significantly decline (Kumambala et al., 2010; Kelly et al., 2019). The lake contributes approximately 80-82% of total Shire River flows year-round, with the wet season accounting for 78% (Kumambala et al., 2024). The lake is not only a vital economic resource but also a cornerstone of nutritional security, covering *ca*. one-fifth of Malawi's land area and supporting *ca*. 2 million people (NSO, Malawi, 2021). The lake provides nearly 70% of animal protein and 40% of total protein supply consumed in Malawi, playing a vital role in food security and economic growth (GoM., 2018; Hara and Njaya., 2015). Fisheries value chain contributes *ca*. 7.2% to Malawi's GDP (Torrell et al., 2020), with the travel and tourism accounting for *ca*. 6.7% and *ca*. 516, 200 jobs (WWTC., 2021). This critical role necessitates an integrated management approach that ensures environmental sustainability while maximizing economic benefits and safeguarding livelihoods.

The Lake Malawi basin, like many global river and lake basins, faces pressing challenges such as water scarcity and declining water quality in a changing climate, impacting local livelihoods and economic growth (Kumambala et al., 2010). This situation underscores a critical need for sustainable water resource management rooted in reliable knowledge and data. Innovative approaches, like application of stable isotope tracers, provide valuable and unique insights vital for

effective water resources assessment and management. Integrating data collection, modelling, and tracer methodologies, underpins development of reliable frameworks for informing decision-making in water resource management (Banda et al., 2024; Zhou et al., 2024; Horton et al., 2016; Nimmo et al., 2005; Scanlon et al., 2002). Water isotope tracing provides detailed insights into workings of water resource systems, making these techniques particularly advantageous for studying critical aspects like groundwater recharge, residence times, and hydrologic response to climate change, especially where traditional field monitoring data are scarce (Kalin., 2000, Cartwright et al., 2017). Recent local applications of isotope tracers explored various critical issues, including groundwater salinization (Monjerezi et al., 2011), groundwater recharge and flow patterns (Kambuku et al., 2018a; Kambuku et al., 2018b), river and lake systems conceptualization (Banda et al., 2019; Banda et al., 2020; Banda et al., 2024). Other studies examined localized groundwater salinity sources, evaporation effects in inland drainage basin lake system (Rivett et al., 2020; Missi et al., 2020), meteoric characteristics of local rainfall (Banda et al., 2021), and geothermal reservoir composition and enthalpy potential (Dávalos-Elizondo et al., 2021; Kalebe., 2017). This highlights applicability of isotopic tracers in a Malawian context, justifying its application here. This study integrated isotopic and hydrochemical tracers to improve conceptualization of Lake Malawi basin hydrologic system.

The overarching aim of this study was to develop a refined conceptual understanding of Lake Malawi basin hydrologic system, with the following specific objectives; (i) to establish a baseline for isotopic and hydrochemical signatures of surface water, critical for future hydrologic and climatic studies, (ii) to identify surface water provenance and hydrochemical evolution control processes, (iii) to develop a water resource conceptual model of Lake Malawi basin, and (iv) to examine surface water isotopic responses to solar radiation and meteoric water input isotopic signal precipitation).

2. Methods and Materials

2.1 Study area description

Lake Malawi Basin is a transboundary water resource shared by Malawi, Tanzania, and Mozambique, spanning a total area of 126,500 km² (Bootsma and Hecky, 1999) (Figure 1a). This study focused on the Malawian portion of the Lake Malawi Basin, which covers approximately 64,785 km². This area includes 13 of Malawi's 15 water resource areas (WRAs), all of which contribute to the drainage of the Malawian side of the lake basin.

2.1.1 Major drainage system and topography

The study area features an extensive network of major river systems, including the Songwe River, Lufira River, North Rukuru River, North Rumphi River, South Rukuru River, Kasitu River, Lweya River, Dwangwa River, Kaombe River, Bua River, Lusa River, Linthipe River, Diamphwe River, Lilongwe River, and Namikokwe River, along with numerous tributaries and wetlands (Figure 1b). These rivers are classified into two main systems: (i) highland-plateau and (ii) rift margin-consequent river systems (Pike and Rimmington, 1965). Converging in the rift valley escarpments, these systems are characterized by distinct drainage patterns influenced by topography. The highland-plateau rivers predominantly flow northeast, navigating fault-controlled, grassy, swampy valleys known as dambos. As these rivers descend through the rift valley escarpments, they transition from a mature to a more youthful state, marked by steeper gradients, deeper valleys, and narrower drainage areas. In contrast, rift margin-consequent rivers flow through deeply incised channels within the rift valley escarpments, with drainage patterns shaped by varied relief ranging from 471 to 2521 meters above sea level (m a.s.l) (Banda *et al*., 2024). The basin's topography significantly impacts its hydrology, creating a complex drainage network that extends from highlands through plateaus, escarpments, and down to the rift valley floor. Highlands, with an

average altitude of 1618 m, receive substantial rainfall and serve as the source for many rivers. The plateaus, situated between 1000 and 1800 m a.s.l in altitude, feature catchment areas for surface water runoff that contribute to wetland ecosystems typical of grassy-covered swampy valleys "*dambo"*. These "*dambos*" act as natural groundwater reserves, storing and gradually releasing water to maintain streamflow, especially during dry periods (Banda et al., 2019; GoM., 2010). The rift valley escarpments, with a mean elevation of 924 m, play a crucial role in shaping basin hydrology. Rivers from the highland-plateau system carve through these escarpments, transporting

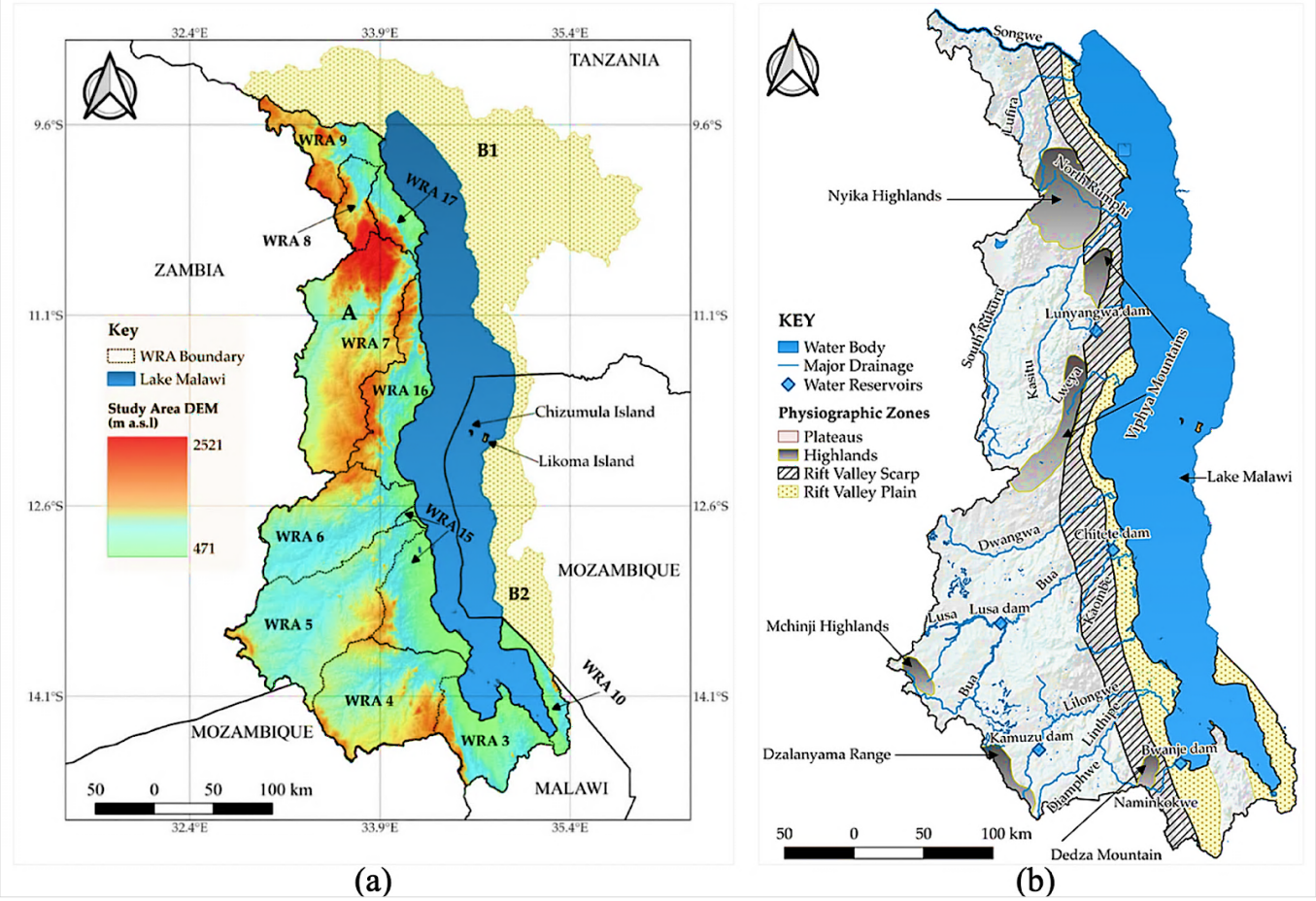


Figure 1: (**a**) Lake Malawi basin (LMB) transboundary extent. (**A**) Malawi part of LMB depicting its topographic spread (SRTM elevation data: USGS) and Water Resource Areas (WRAs). (**B1**) Tanzania part of the LMB. (**B2**) Mozambique part of the LMB; (**b**) Physiographic zones, major drainage network and water reservoirs.

water and sediments toward the low-lying rift valley plains and ultimately into Lake Malawi (Smith-Carrington and Chilton, 1983). The rift valley plains, bordering the lake's western shoreline, facilitate water flow from the plateaus to the lake, contributing to Lake Malawi's overall water budget.

2.1.3 Climate

Lake Malawi basin has a tropical-continental climate, characterised by varying temperature, rainfall and relative humidity, and is influenced by factors such as altitude, relief and the Lake Malawi. Climatologically, the Lake Malawi basin, is categorized as Aw or Savannah climate based on the Köppen-Geiger system, with a distinct pattern of rainfall and dry periods (Peel et al.,2007). The basin has a dual-season system, spanning from November to April (wet season) and from May to October (dry season). The dry season is mostly influenced by south-easterly winds, while the wet season is influenced by north-easterly winds, Intertropical Convergence Zone (ITCZ), Congo Air Boundary (CAB), and Tropical Cyclones, which are primary rain-bearing systems in the basin (Ngongondo et al., 2011; Vincent et al., 2014). Rainfall is concentrated between December and March, with January marking peak of the rainy period in most parts of the basin. The eastern side of the basin bordering Lake Malawi shoreline receives most rainfall in March (Nicholson et al., 2013). The basin rainfall averages 927 mm annually, with maximum rainfall received in rift valley plain (annual mean of 1036 mm). The basin diverse relief and Lake Malawi influence spatial distribution of rainfall (Vincent et al., 2014; Sene et al., 2016; DCCM, accessed January 20, 2023). Lake Malawi basin temperature patterns correspond to topography, cool in highlands and hot in lowlands. Mean temperature ranges between 12.9 and 24.7 °C, averaging 20.5 °C annually. Nyika highlands mark lowest temperatures, ranging between 12.9 and 22.7 °C, with a mean of 17.6 °C. Plateaus are generally cooler, with temperatures ranging between 16 and 26 °C, and with exception

of higher temperatures of greater than 30 °C in October and November. Rift valley escarpment experiences temperatures ranging from 15.6 to 24.7 °C, with a mean of 21.3 °C. The Rift valley lake shore plain, with lowest topographic extreme, experience hotter temperatures ranging between 20 and 29 °C, with a mean of 23.4 °C. The Lake Malawi has a distinct influence on temperature of the lakeshore areas of the basin. Generally, mean daytime temperature of 30.3 °C and nighttime temperature of 10.3 °C are experienced, with June and July marking the coldest temperature extremes and October and November marking the hottest extremes (DCCM, accessed January 20, 2023).

2.2 Water resource availability and management constraints

The study area, characterized by transboundary surface water and groundwater resources, presents unique opportunities and challenges for water resource management (Fraser et al., 2021; Bootsma and Hecky, 1999). Key transboundary surface water bodies include Lake Malawi and the Songwe River, which traverses the border between Malawi and Tanzania (Kalin et al., 2022). Transboundary aquifers facilitate groundwater exchange between Malawi and its neighbouring countries. This dynamic emphasizes the necessity for international collaboration to achieve Sustainable Development Goal (SDG) target 6.5.2 (Fraser et al, 2020) . These water resources are mainly replenished by meteoric water, predominantly during the wet season, while experiencing a decline during the dry season. Numerous reservoirs along major rivers provide water for domestic, industrial, and agricultural purposes, with potential for hydropower production (Banda et al., 2024; W.S. Atkins, 2011a; British Geological Survey, 1996; Kalin et al 2022). Significantly, the Kamuzu and Lunyangwa Reservoirs serve the cities of Lilongwe and Mzuzu (Banda et al., 2024). Groundwater remains a crucial drinking water resource, especially for rural communities, with approximately 49,032 groundwater abstraction points (Kalin et al., 2022). Notably, some water

systems (springs discharges) have potential for geothermal energy production and sustain streamflow (Dávalos-Elizondo et al., 2021; Kalebe., 2017), impacting surface water quality. Despite availability of abundant water resources, the study area confronts several management challenges. One major issue is lack of high-resolution water research critical for evidence-based improvement of water quality and quantity management (Banda et al., 2024; Kalin et al., 2022). Challenges include geogenic and anthropogenic water quality problems, climate change impacts such as prolonged dry spells lowering the water table, and lack of hydraulic resilience and groundwater vulnerability (Mapoma et al., 2017; Addison et al., 2019; Smith-Carrington et al., 1983; Chavula., 2021). Extreme flooding damages infrastructure and worsens water quality, while insufficient installation and maintenance of water supply assets exacerbate these issues. Large-scale illegal waste disposal and unauthorized effluent discharges further degrade water quality, compounded by inadequate municipal sewage systems discharging untreated waste (Owen et al., 2005). Deforestation-related siltation and sedimentation impair water bodies critical for supply, resulting in higher treatment costs. Increased small-scale irrigation, rampant sand mining, and excessive growth of aquatic weeds due to siltation and agricultural runoff complicate management efforts, negatively affecting water quality, hydropower generation, and biodiversity (GoM., 2010). This complex array of challenges underscores the critical need for transformative hydrological studies to guide evidence-based decision-making.

2.3 Sampling and sample handling

Precipitation isotope samples were collected from three Malawi Network for Isotopes in Precipitation (MNIP) stations and an additional temporary station in the study area (Banda et al., 2021). Sampling campaigns, which took place between 2014 and 2022, were conducted on daily, weekly, and monthly schedules, depending on the capacity of each station. For consistency, the

daily and weekly samples were combined into monthly samples (IAEA/GNIP, 2014). The initial phase of sampling, conducted from 2014 to 2019, resulted in collection of 28 monthly samples (Banda et al., 2021). The subsequent phase, conducted from 2020 to 2022, produced 29 monthly samples (Banda et al., 2024) (**Supplementary Material - Table S1**). At the MNIP stations, samples were collected using dip-in-water collectors, which are specifically designed to prevent evaporation and the resulting isotope fractionation, eliminating the need for paraffin preservation. In contrast, samples from the temporary stations were collected using standard rain gauges and therefore required paraffin preservation (IAEA/GNIP, 2014).

Surface water samples were collected from rivers, reservoirs, lagoons, and lakes between 2021 and 2022. The first sampling campaign, conducted during the wet season (November – April 2021/22 hydrologic year), collected 124 isotopic and 131 hydrochemical samples. The second sampling campaign, conducted during the dry season (May – October 2023), collected 156 isotopic and 170 hydrochemical samples. These campaigns targeted the peak of both the dry and wet seasons to examine the influence of dual-seasonal shifts, which have been shown to affect the hydrology of the Lake Malawi basin (Banda et al., 2024; Banda et al., 2020; Kelly et al., 2020). Lake water samples were collected 1 km from the shoreline and away from estuaries using a bespoke depth sampler. Isotopic samples were collected in 50-mL high-density polyethylene (HDPE) bottles with inner caps and sealed with waterproof tape to prevent leakage, atmospheric air exchange, and associated isotope fractionation. These samples were stored at 4°C, away from sunlight, to prevent evaporative fractionation. River samples were collected from the upper, middle, and lower reaches of basin along riverine flow paths. To guarantee uniformly mixed samples, sampling focused on primary flow channels of the rivers. In smaller rivers characterized by narrow channels, standard grab samples were utilized, deemed representative due to the natural mixing effect intrinsic to riverine environments. For major rivers, samples were collected at predetermined intervals across

the river's width to address inconsistent mixing using a scoop sampler (Model: ENVITECH, United Kingdom). Lake water samples were collected 1 km offshore from estuaries using boats and an immersion sampler (Model: ENVITECH, United Kingdom), while reservoir samples were collected from inflow and outflow sites (Banda et al., 2019). Hydrochemical samples were collected during both the dry (n = 170) and wet seasons (n = 131). At each surface water sampling site, two 1-liter HDPE bottles were used: one acidified with 2 ml of concentrated HCl per liter (labelled "+ acid" or "acidified") to reduce pH to < 2, suppress microbial activity, and retain cationic species, and another left unacidified. Non-acidified bottles were acid-washed and rinsed thrice with sample water to prevent cross-contamination. Samples were uniquely identified and stored at 4°C from the field to the laboratory. Due to logistical constraints, samples were filtered using 0.45 μm Whatman filters at the laboratory instead of in the field. Field sampling constraints also included restricted accessibility in some remote or flood-prone areas during rainy periods. Quality control of sampling involved thorough validation of procedures to ensure proper management of samples during collection, handling, storage, and preservation to identify and reduce any potential interferences with target analytes. Blanks were used to detect possible contamination, and reference samples with known analyte concentrations were used to assess any losses or changes (APHA, 2017). For each batch of sample containers sent to the field site, blanks were consistently included. These blanks underwent the same handling procedures such as, opening, closing, and preservation, as the actual samples, ensuring accurate quality control (Nollet et al., 2000).

2.4 Analytical techniques and data processing

Water samples were analysed for $\delta^{18}O$ and $\delta^{2}H$ at the IAEA Isotope Hydrology Laboratory (IHL) in Vienna, Austria. This involved measuring isotopologues signatures using the cavity ringdown spectroscopy (CRDS) technique on Picarro laser spectrometer. This method is widely

and internationally used (Natali et al., 2024; Banda et al., 2024; Hyeroba et al., 2024; Rooyen et al., 2021). Samples were analysed in non-consecutive duplicates using two different Picarro 2140i CRDS laser spectrometers (Model: L2140-i, Picarro Inc., Santa Clara, CA, USA). The Picarro L2140-i laser spectrometers were run on high-precision analysis mode, with dry synthetic air as carrier gas, and sample injection volume of ca 1.2 μL into the vaporizer unit, which transfers sample vapor into the spectroscopic analyzer's cavity (Gupta et al., 2009). To reduce memory effects, sample injections were set at 6 and used the following reference materials (RMs) for in-house quality control: enriched RM from Lake Kyoga and depleted RM STD09 (Green). For quality assurance and control, the standards used were STD11 (Monaco Lagoon) and STD6 (Heidelberg tap water) (Banda et al., 2024). Data-processing was done using LIMS for Lasers (Coplen et al., 2014) which included data reduction, and memory correction was done by discarding the first three sample injections results and calculating the mean value of the last three injections results. The dataset was then normalized to the VSMOW/SLAP scale using two reference points (Nelson, 200). Mean analytical uncertainty of replicate samples, reported as long-term standard deviation of international standards, was ±0.1% and ±0.5% or better for $\delta^{18}O$ and $\delta^{2}H$, respectively. Isotope analysis data are reported as standard delta (δ) values in per mil (‰), representing relative difference of $^{2}H/^{1}H$ and $^{18}O/^{16}O$ between the sample and the standard (Coplen, 2011) (Equation (1)). The sampling and analytical chain of custody (sample collection, storage, treatment, analysis), complied to International Standard Procedures (ISP) (IAEA, 2009).

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) \text{x } 1000 \text{ ‰} \quad (1)$$

In Equation (1), R represents a unitless isotopic ratio, where R_{sample} and $R_{standard}$ are isotopic ratios ($R = {}^{2}H/{}^{1}H$ and $R = {}^{18}O/{}^{16}O$) of sample and standard, respectively. The delta notation (δ) is a metric

for sample deviation from standard, which are relatively small hence, expressed in parts per thousand (per mil (‰)) to account for small isotopic variations (Rozanski *et al*., 1993; Coplen, T.B., 2011; IAEA., 1981). The δ value is positive when relatively enriched in heavy isotope than the VSMOW standard, and negative when relatively depleted in heavy isotope than the VSMOW, where VSMOW values for δ^2H and $\delta^{18}O$ equals zero (0).

Deuterium excess (*d*-excess or *d*)) defined in Equation (2) (Dansgaard., 1964) is a proxy of meteorological conditions in source region where precipitation-bearing initial evaporated moisture originate from (Rozanski *et al*., 1993; Merlivat and Jouzel., 1979; Gat *et al*., 1970). The *d*-excess is primarily influenced by atmospheric relative humidity over the ocean surface expanse (Clark and Fritz., 1997). Where average global humidity is *ca.* 85%, the resulting average global precipitation *d* value is ~ 10 ‰ (Merlivat and Jouzel., 1979; Gonfiantini., 1986). Thus, *d* ~ 10‰ infer precipitation derived from air moisture that originated from the ocean, whereas *d* > 10‰ is attributable to influence of air moisture recycling by large-scale evaporation that corresponds to low atmospheric humidity at source region (IAEA., 2005). The *d*-excess is also influenced by secondary processes like raindrops evaporation underneath clouds and water bodies evaporation on land (Rozanski., 1993; Froehlich *et al*., 2002). This allows *d*-excess to be used as a proxy for differing sources of moisture, with former and latter secondary processes that decrease and increase *d* values, respectively.

$$d = \delta^2H - 8\delta^{18}O \text{ ‰ VSMOW} \quad (2)$$

Field measurement of unstable parameters, such as electrical conductivity (EC), total dissolved solids (TDS), temperature and pH, was conducted onsite, and where possible, in situ using a portable multi-meter (Model: HI-98194, Hanna Instruments, Woonsocket, RI, USA) before and during sampling. The portable multi-meter was calibrated according to manufacturer's instructions

and allowed to stabilize for 2-5 minutes prior to recording any measurements. This was done to ensure field analysis reliability enhanced by duplicate sample analysis conducted at selected sites during each sampling survey. When taking measurements, the meter probe was submerged 100 mm into a flowing water channel, while avoiding stagnant pools. Hydrochemical analysis was conducted at the Environmental Analytical Laboratory of the University of Strathclyde in Glasgow, Scotland. Anions (fluoride, chloride, nitrate, and sulphate) were analysed using an ion chromatography (Model: 850 Professional IC, Metrohm, Switzerland), while cations (sodium, potassium, magnesium, calcium, iron, and manganese) were analysed using an inductively coupled plasma spectrometer (Model: iCAP 6200 Series, Thermo-Fisher Scientific, Waltham, MA, USA). Carbonate species (carbonate and bicarbonate) were analyzed titrimetrically, while alkalinity was analysed using a photometric analyzer (Model: KONE Aquakem V.7.2.AQ2, Skalar, Netherlands). Quality control measures implemented involved robust error analysis and uncertainty quantification. These included conducting repeated measurements during sampling to quantify heterogeneities between sub-samples and duplicate analysis using ICP-MS and IC. Seven-point calibration was conducted for every batch of 10 samples to ensure reliability and quality of measurements. Accuracy of cation and anion analyses was primarily validated using ionic balance error (IBE), with a maximum allowable IBE set at ±5% (Equation 3) (Banda et al., 2024). Overall, sampling, and analytical chain of custody (sample collection, storage, treatment, analysis), complied to ISP for the examination of water and wastewater (APHA, 2017).

$$\text{IBE } \% = \frac{\sum(\text{Cations}-\text{Anions})}{\sum(\text{Cations}+\text{Anions})} \text{ x } 100 \quad (3)$$

Hydrochemical facies characterization was conducted using Piper diagram (1944), generated with Grapher software (Version 24.1.213, Golden Software, LLC, USA). Hydrochemical

evolution processes of surface water was evaluated through Gibbs diagram (1970). The Gibbs diagram employs anionic weight ratio $Cl^-/(Cl^- + HCO_3^-)$ and cationic weight ratio $Na^+/(Na^+ + Ca^{2+})$ as functions of log-transformed total dissolved solids (TDS) (Equations 4 and 5) (Gibbs, 1970). By plotting these ratios against the log-transformed TDS, Gibbs diagrams illustrate dominant control processes, such as rock-water interactions, evaporation, and precipitation, which influence surface water hydrochemistry.

$$\text{Gibbs anionic ratio} = \frac{Cl^-}{(Cl^- + HCO_3^-)} \quad (4)$$

$$\text{Gibbs cationic ratio} = \frac{Na^+}{(K^+ + Na^+ + Ca^{2+})} \quad (5)$$

3. Results and Discussion

3.1 *Hydrochemical characteristics*

Surface water pH ranged from acidic to alkaline (6.2 to 8.9), with 89.7% of the values falling within the alkaline range (7.0 - 8.9). Water hardness ranged from 9 to 378 mg/L, with a mean of 71 mg/L, suggesting that the surface water is mostly soft. Electrical conductivity (EC), a proxy for total dissolved salts ranged from 26 to 1494 μS/cm, with a mean of 215 μS/cm (Figure 2, Table S2)**.** About 44.7% of the surface water samples registered EC between 26 - 200 μS/cm, while the majority (50.6%) fell within a range of 201- 500 μS/cm. High EC values above 500 μS/cm accounted for 4.7% of the surface water samples including Lake Chiwondo, Dwangwa, Mtiti, Luweya, Linthipe, Chikwidzi, Songwe, and Limpimbi Rivers, with Lake Chiwondo registering the highest EC value (1494 μS/cm) (Table S3). Very low EC values below 50 μS/cm were observed in the Chikangawa reservoir, Lunyangwa reservoir, North Rumphi, Kaziwiziwi, and Kambwiya Rivers. One prominent feature of these river sites is their substantial input from highland headwaters. Lowland sites exhibited hydrochemical heterogeneity especially in the flood plain probably relating to complex multi-process control than to homogeneity or uniformity of process

in recent recharge-dominated uplands. In the rift valley/lakeshore plain, enriched hydrochemical signatures hint that older groundwater with longer flow paths and high mineral content discharges to streamflow. That could also be due to lowland evaporation effects, streamflow mixing with isotopically enriched Lake water due to seasonal reversal, or anthropogenic influences (e.g., agricultural runoff, domestic and industrial waste discharges).

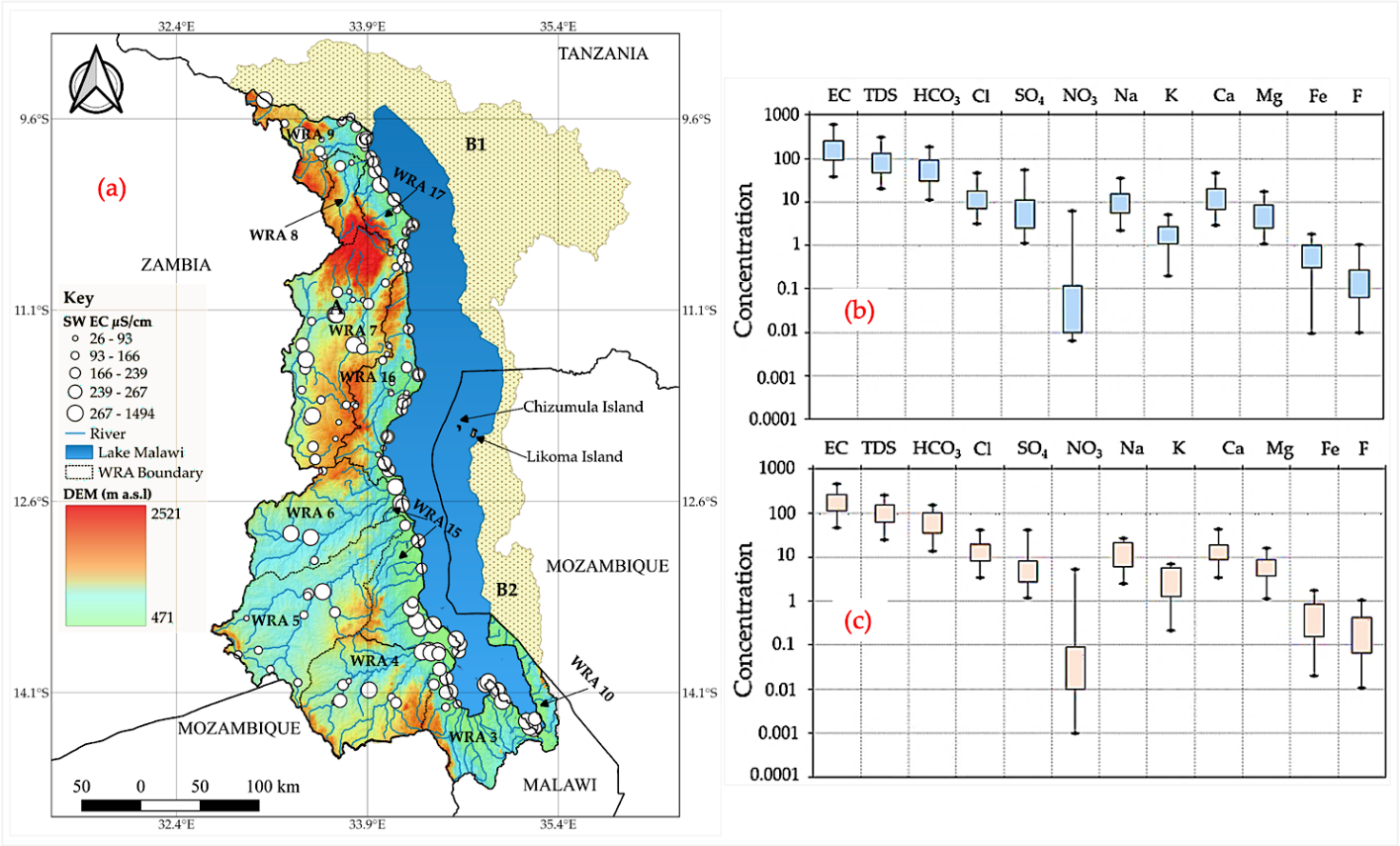


Figure 2. (a) Spatial distribution of electrical conductivity (EC) (μS/cm) across Lake Malawi basin, and Interquartile plots for surface water hydrochemistry for (**a**) wet season (n = 131) and (**b**) dry season (n = 170). The seasonally variant surface total dissolved solids (TDS) are in mg/L and all major ions in mg/L.

3.2 Hydrochemical facies and hydrochemical evolution

Piper plot categorized surface water sources into three water types (Figure 3a): (1) Ca-Mg-HCO_3, (2) Ca-Mg-SO_4-Cl and (3) Na-Cl. Most of the surface water samples are of Ca-Mg-HCO_3

water type, within corresponding EC values below 500 μS/cm (Figure 3b). This hints that the most likely source of surface water in the Lake Malawi basin is modern rainfall, with limited rock mineral interaction (Banda *et al*., 2019; Banda *et al*., 2024). Presence of Na-Cl water type and Ca-Mg-SO_4-Cl mixed water type suggest streamflow contribution from multiple sources such as baseflow where surface water and groundwater systems are hydraulically connected (Banda *et al*., 2019; Kelly *et al*., 2019; Banda *et al*., 2024). Occurrence of Na-Cl water type hints at human-induced influences (e.g., agricultural runoff, industrial/domestic effluent discharges) and mineralized spring discharges into streamflow impacting surface water quality.

The Gibbs diagram (Figure 3c) highlights natural processes that influence the evolution of surface water chemistry (Gibbs, 1970) herein dominated by rock-water reactions. The concentrations of Ca and HCO_3 in streamflow, water reservoirs and lakes are generally higher than those of Na and Cl, respectively. Most of the surface water samples, dominated by streamflow, exhibit low to correspond to water-rock reactions. A subset of surface water samples plotting closer to the upper right (B**)**, mostly lake water, may be influenced by evaporation, while those positioned towards the lower right (C**)**, dominated by water reservoirs, may be affected by a high proportion of recent precipitation influx that has not interacted sufficiently with rock minerals to warrant significant geochemical changes.

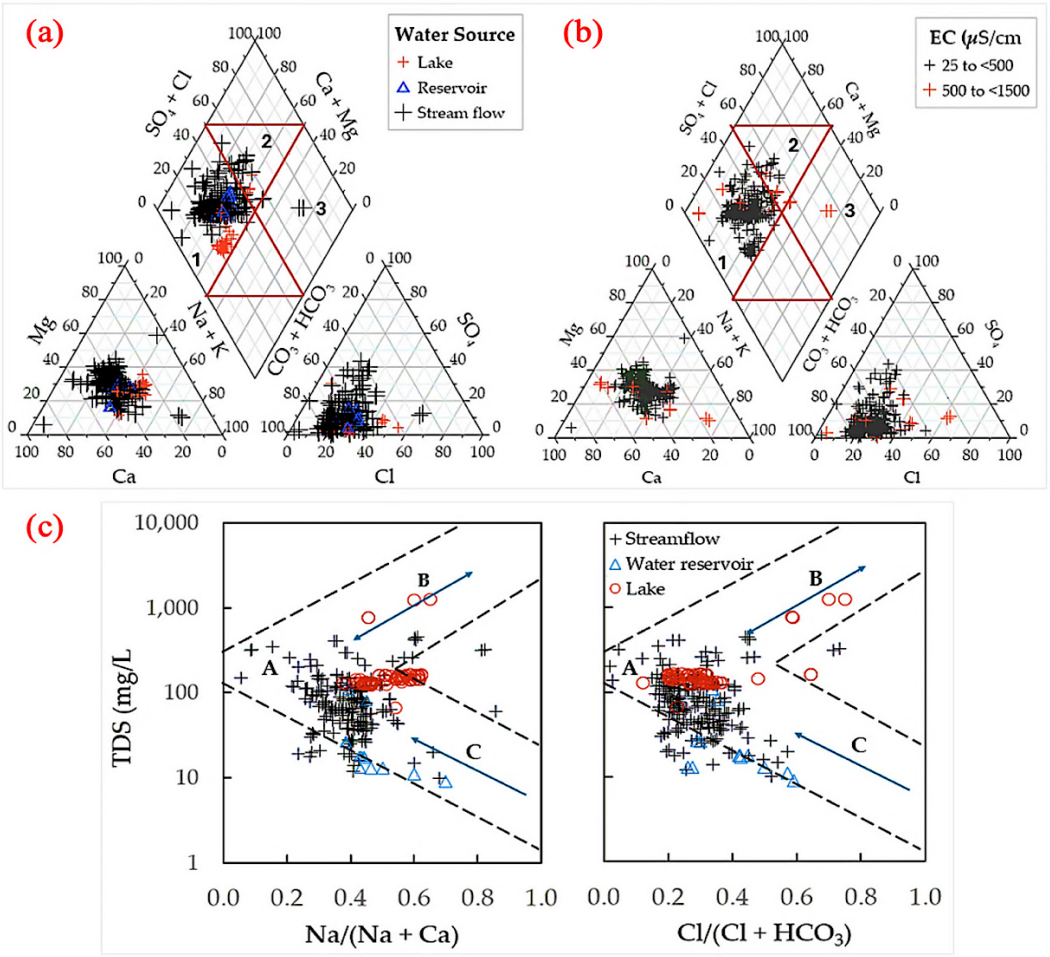


Figure 3. (**a**) Hydrochemical facies of surface water based on water source type; (**b**) Electrical conductivity (EC), a proxy indicator for total dissolved salts (TDS); Group 1 is Ca-Mg-HCO_3, Group 2 is Ca-Mg-SO_4-Cl and Group 3 is Na-Cl water type. (**c**) Gibbs (1970) diagram depicting hydrochemical evolution of surface water; (**A**) Rock dominance, (**B**) evaporation dominance and (**C**) precipitation dominance.

3.3 Precipitation and surface water isotope characteristics

Precipitation in Lake Malawi basin (LMB) exhibits varied stable isotopic signatures ($\delta^{18}O_{range}$ = +15.3‰; $\delta^{2}H_{range}$ = +123‰) influenced primarily by distinct moisture sources (Banda et al., 2024). The precipitation $\delta^{18}O$-$\delta^{2}H$ signatures align with meteoric characteristics of non-

evaporated modern precipitation (Banda et al., 2019; Banda et al., 2021; Banda et al., 2024). The mean d-excess of +13.3‰ for the LMB precipitation is greater than +10‰ for global precipitation, suggesting additional air moisture (derived from repeated continental air moisture recycling) to that from the ocean (Rozanski., 1993; Froehlich *et al*., 2002). This distinct modification of d-excess could be driven by intense evaporation off Lake Malawi, mimicking the African Great Lakes isotopic effect (Banda et al., 2024).

The surface water δ^2H signatures (n = 280) range from −46.7‰ to +28.9‰, with a mean of −21.6‰, and $\delta^{18}O$ signatures range from −7.3‰ to +5.1 ‰, with a mean of −3.5 ‰ (Figure 4a/b; Table S4). For rivers, δ^2H signatures(n = 220) range from −46.7‰ to +15.7‰, with a mean of −27.9 ‰, and $\delta^{18}O$ signatures range from −7.3‰ to +2.5‰, with a mean of −4.4‰. Water reservoir δ^2H signatures (n = 18) range from −45.0‰ to +2.9‰, with a mean of −24.3‰, and $\delta^{18}O$ signatures averages −4.5‰, ranging from −7.3‰ to +0.2‰. The $\delta^{18}O$-δ^2H signatures for lakes (n = 42) are significantly higher than for rivers and water reservoirs, with δ^2H signatures ranging from +4.3‰ to +28.9‰, with a mean of +12.1 ‰, and $\delta^{18}O$ signatures ranging from +0.6‰ to +5.1‰, with a mean of +1.9‰. Most surface water $\delta^{18}O$-δ^2H signatures align with the Global Meteoric Water Line (GMWL) for global precipitation modelled as $\delta^2H = 8\delta^{18}O + 10$ (Craig., 1961), the Local Meteoric Water Line (LMWL) for Malawi precipitation modelled as $\delta^2H = 8.0 (\pm 0.3)\ \delta^{18}O + 13.0 (\pm 2.0)$ (Banda *et al*., 2021) and meteoric characteristics for the Lake Malawi basin (Banda *et al*., 2024) (Figure 4c). This pattern indicates notable influx of recent local precipitation to the surface water system. This precipitation influx could be through direct precipitation influx, runoff or interflow, characterised by minimal or no isotopic fractionation. A subset of surface water $\delta^{18}O$-δ^2H signatures deviate from typical meteoric characteristics, following a trendline modelled as $\delta^2H = 6.11 (\pm 0.07)\ \delta^{18}O - 0.20 (\pm 0.30)$ (R^2 = 0.97, n = 280) (Figure 4c). This indicates that surface water, replenished by local precipitation undergoes a certain degree of isotopic fractionation due to

evaporation and/or influential multiple-source inflow mixing. The lake $\delta^{18}O$-$\delta^{2}H$ signatures forms a highly enriched endmember cluster, highlighting notable influence of large evaporation signal attributable to long residence time (Figure 4c). Some near-lake and upland near-dambo sites also exhibit high isotopic enrichment consistent with the highly enriched endmember cluster. This reinforces the theorized seasonal and spatial mixing dynamics through delayed gradual discharge of baseflow from dambo storage zones and lake water input to streamflow with gaining conditions (Banda *et al*., 2019). The modelled isotopic data for surface water show that lake water isotopic signatures cluster along an isotopic trendline intersecting with a cluster for river isotopic signatures (Figure 4c). This could mean the lake water is mostly progressively evaporated riverine inflows which significantly contribute to the lake water budget.

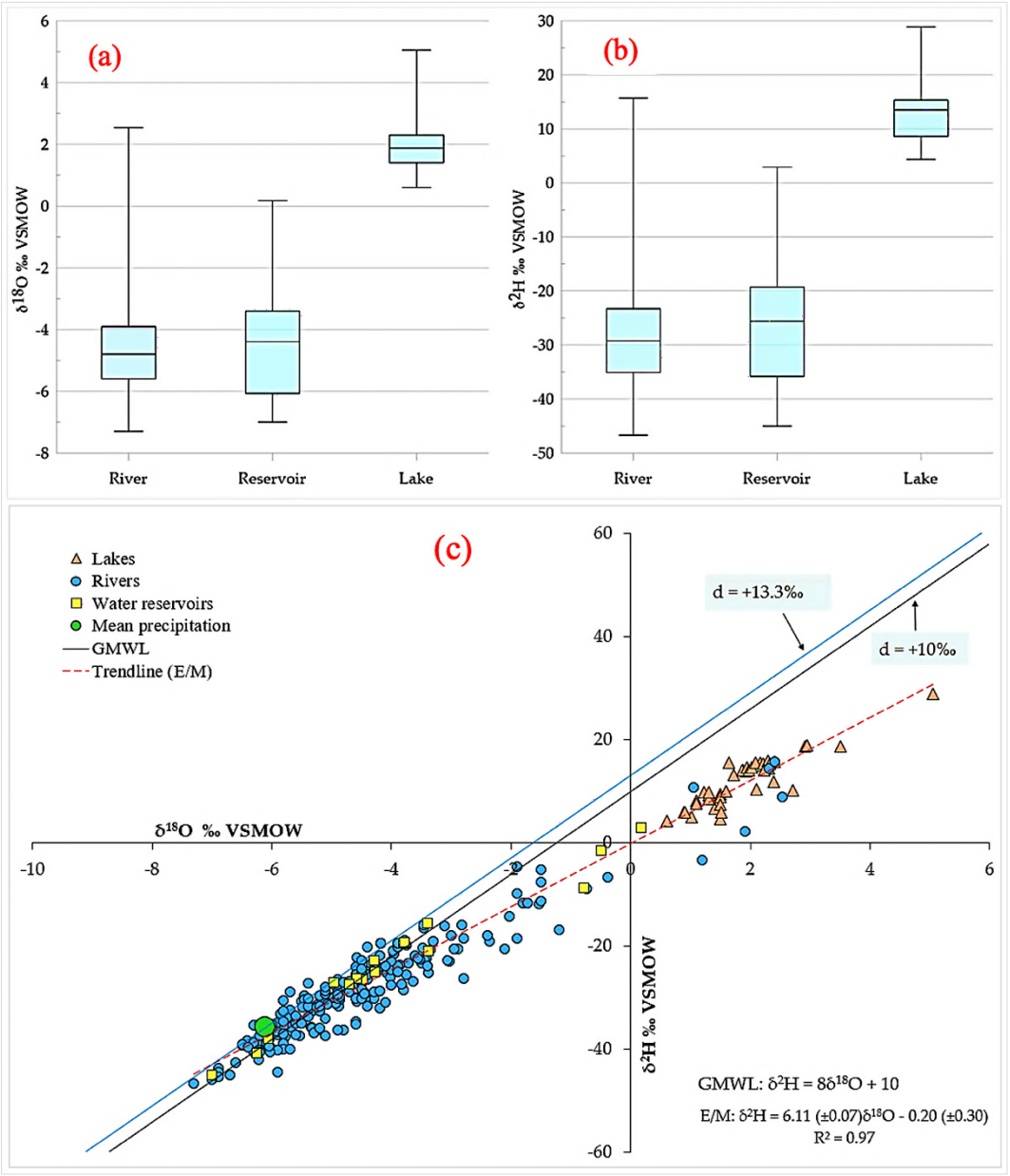


Figure 4. (**a/b**) Box plots of $\delta^{18}O$-$\delta^{2}H$ signatures for rivers, water reservoirs and lakes in LMB. (**c**) scatter plot of $\delta^{18}O$-$\delta^{2}H$ signatures for rivers, water reservoirs and lakes. A blue line (slope of 8; *d*-excess of +13.3‰) represents distribution of d-excess for local precipitation. The red trendline (E/M) represents evaporation and mixing processes.

3.3.1 Surface water isotopic co-variability

Surface water isotopic signatures co-vary widely (range: $\delta^{2}H$ +75.6‰; $\delta^{18}O$ +12.4‰) (Table 1). This could be ascribed to influence of controlling factors such as evaporation, local

precipitation and mixing with groundwater baseflow and lake water (Banda *et al*., 2019; Banda *et al*., 2024). Rivers show a large co-variability response relative to water reservoirs and lakes, as rivers are largely influenced by the aforementioned controlling factors (Kelly *et al*., 2019; Banda *et al*., 2019). Water reservoirs exhibit a moderate co-variability response, with lakes exhibiting a relatively low co-variability response, as lakes are less influenced by the aforementioned controlling factors. Isotopic co-variability of water reservoirs and their corresponding inflow and outflow rivers is largely consistent, indicating that reservoir isotopic signatures are more influenced by their river inflows (Table 2). For Lusa, the isotopic signatures of the river and reservoirs co-vary consistently, but deviate from the local meteoric characteristics, suggesting influence of evaporation ascribed to long residence time. All the water reservoirs, except Lusa reservoir, primarily function as large-scale water supply sources for major cities and townships and are constantly pumped. This minimizes evaporation due to reduced water residence times.

Table 1. Isotopic Co-variability in Rivers, Water Reservoirs and Lakes across LMB

Parameter	Surface Water	Rivers	Water Reservoirs	Lakes
δ^2H_{range}	75.6	62.4	47.9	24.6
$\delta^{18}O_{range}$	12.4	9.8	7.2	4.5

Table 2. Isotopic co-variability in water reservoirs and their corresponding rivers across LMB

Parameter	Kamuzu Reservoir	Lilongwe River	Lunyangwa Reservoir	Lunyangwa River	Lusa Reservoir	Lusa River	Chikangawa Reservoir	Chikangawa River	*Chitete Reservoir
δ^2H ‰	−25.5	−24.1	−22.2	−24.7	−12.1	−8.2	−41.5	−42.9	−31.7
$\delta^{18}O$ ‰	−4.4	−4.2	−4.2	−4.1	−2.1	−1.1	−6.5	−6.9	−4.7
d-excess ‰	9.6	9.2	11	7.7	4.7	1.0	10.8	12.4	5.5

*****No inflow/outflow sampled*

Deuterium excess of surface water ranges from −13.1‰ to +16.7 ‰, with a mean of +6.4‰ and a median of +8.4‰ (Table S4), reflecting a dampened isotopic signature relative to mean global precipitation (d = 10‰) (Craig., 196) and mean Lake Malawi basin precipitation (d = +13.3 ‰) (Banda *et al*., 2024). This dampened d-excess accounts for the $\delta^{18}O$-δ^2H enrichment signatures of

lake, reservoir and river waters ascribed to evaporation effects, predominant in dry season (Figure 4). Lake water exhibits a minimal *d*-excess response to evaporation signal and local precipitation influx between low and high lake stands (Figure 5a). This confirms high retention of isotopic enrichment signature of Lake Malawi (Banda et al., 2020; Banda *et al*., 2024). The *d*-excess of rivers averages +6.3‰ in dry season, considerably lower than wet season mean *d*-excess of +9.7‰ (Figure 5b). This disparity suggests predominant influence of evaporation in dry season, while the wet season is largely influenced by local precipitation influx. The mean *d*-excess of water reservoirs exhibits a relatively least deviation from the *d*-excess of local precipitation, with a dry season mean *d*-excess of +8.0‰ and a wet season mean *d*-excess of +9.9‰ (Figure 5c). The mean *d*-excess of Lusa and Chitete reservoirs shift distinctively from the global and local meteoric expectations, with mean *d*-excess of +1.0 and +5.5‰, respectively (Table 2). This indicates significant influence of isotopic fractionation ascribed to secondary evaporation. The *d*-excess of highland headwaters (d = +10‰) is consistent with *d*-excess of mean global precipitation (d = +10‰), but slightly lower than that of basin precipitation (d = +13.3‰) (Figure 4c). This suggests that local precipitation influx to highland headwaters is less influenced by sub cloud evaporation due to high elevation induced low temperatures and short distances of falling raindrops to the ground (Bershaw *et al*., 2012). The *d*-excess of +9.9‰ and relatively depleted $\delta^{18}O$-$\delta^{2}H$ signatures of surface water in rift valley scarp are consistent with the highland headwaters signatures but varied widely with a d_{range} of +20.1‰. This could be due to an integrated effect derived from mixing of isotopically depleted rift margin-consequent headwaters (originating from rift valley scarp) with highland-plateau rivers that converge within the rift valley escarpment. The *d*-excess of +4.6‰ and enriched $\delta^{18}O$ signatures of surface water in rift valley plain provide evidence of isotopic enrichment ascribed to influential evaporation effect, highly reflected in large water bodies like Lake Malawi, Lake Chiwondo and Chia lagoon.

Table 3. Mean *d*-excess (‰) for physiographic zones in Lake Malawi basin

d-excess	Highland	Rift Valley Scarp	Plateau	Rift Valley Plain
Mean	10	9.9	7.0	4.6
Range	7.7	20.1	28.1	27.7

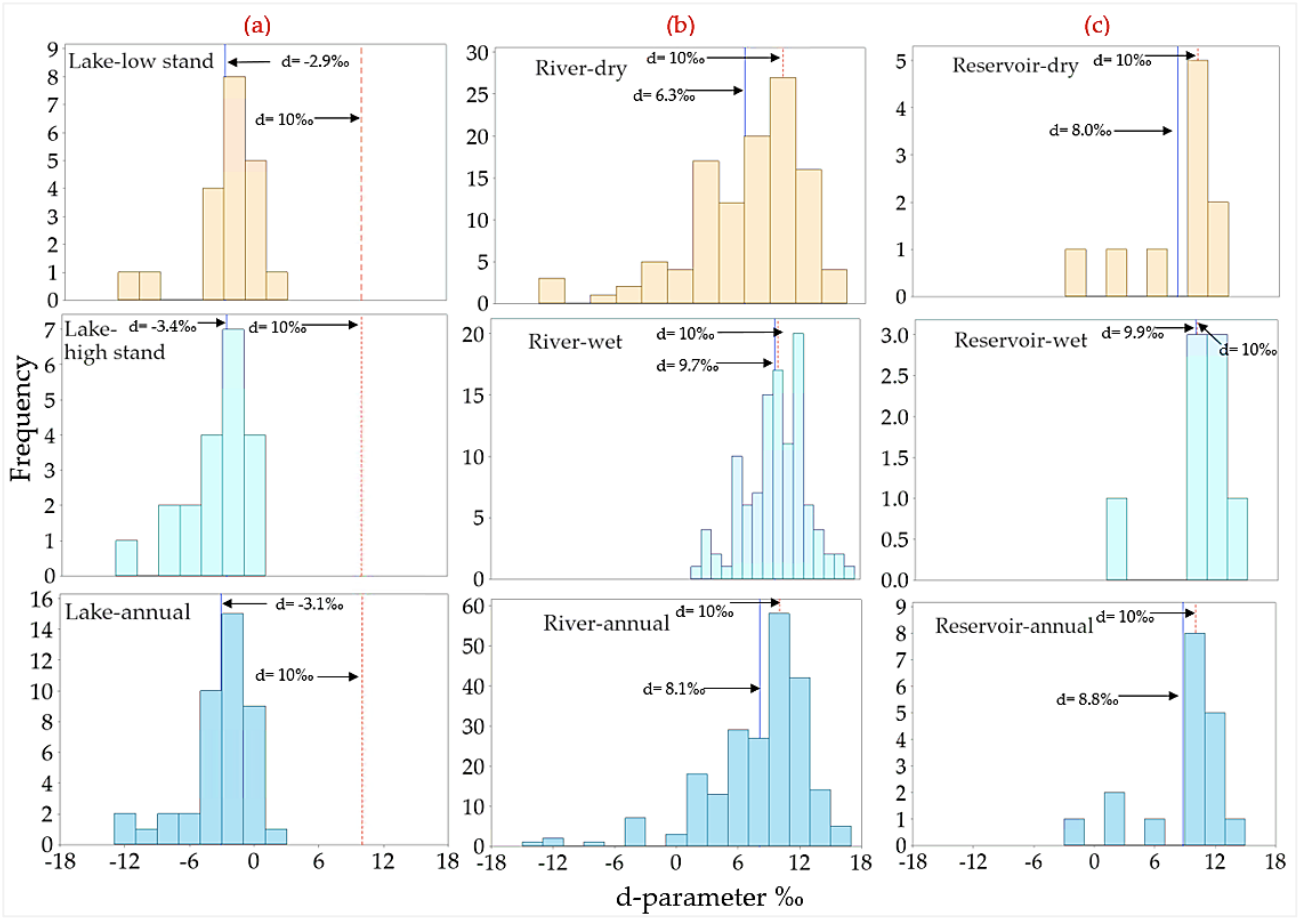


Figure 5. Distribution of *d*-excess for (a) lake water (b) river water (c) reservoir water. The red line represents *d* (*d*-excess) of +10‰ for the global precipitation (GMWL); the blue line represents surface water *d*-excess.

3.3.2 Seasonal and spatial isotopic trends

Surface water is isotopically enriched mostly in dry season than in wet season (Figure 6a; Figure S1). The wet season isotopic signature is largely depleted, suggesting notable inflow contribution from non-evaporated local precipitation influx to surface water, with dry season

isotopic enrichment largely ascribed to intense evaporation and multiple inflow mixing effects. Lake and reservoir isotope signatures exhibit distinct progressive enrichment, predominantly in Lake Chiwondo, Lake Kazuni and Lake Malawi. The lake water enrichment signature exhibits a high signal between low and high lake stands (Figure 6b), attributable to long residence time prolonging lake water exposure to solar radiation. The isotopic signature of water reservoirs is largely depleted in wet season, exhibiting a distinct isotopic signature derived from influx of non-evaporated local precipitation and rapid runoff from higher elevation headwaters. Water reservoirs are mostly in constant use, resulting in short residence times and limited exposure to solar radiation, hence experience minima evaporative fractionation. River isotopic signatures are largely influenced by evaporation in dry season (d = +6.3‰) than in wet season (d = +9.7‰), when depleted local precipitation dominates, coupled with mixing effect of river water with groundwater baseflow and lake water.

The spatial patterns of $\delta^{18}O$-$\delta^{2}H$ signatures correspond to altitude effect expectations, with enriched isotopic signatures predominant in lowlands relative to uplands (Figure 7). Statistical evidence reveals a modest inverse correlation of surface water $\delta^{18}O$ signatures and altitude. Though altitude exhibit a considerable effect on $\delta^{18}O$ variability, the correlation magnitude (Pearson correlation: $r = -0.4$) aligns with effects of other influential factors such as seasonality, mixing with lake water, and groundwater discharge to streamflow (Banda et al., 2019). The wet season isotopic enrichment of highland near-dambo and near-lake river sites exhibit unique isotopic characteristics that defy typical seasonal-altitude effects. This variability corresponds to the theorized recharge into, and delayed discharge of groundwater from upland dambo storage to streamflow, coupled with inflow of lake water predominant in wet season (Banda *et al*., 2019; Kelly *et al*., 2020). The convergence of highland-plateau river system and rift margin-consequent river system in the rift valley escarpments results in mixing of relatively enriched and depleted isotopic

signatures derived from these two river systems, respectively. As the highland-plateau rivers evolve from an old, senile state to a more active and rejuvenated state, they display an increasingly depleted isotopic signature likely due to inflow of isotopically depleted rift margin river system headwaters. This new isotopic insight highlights just how complex Lake Malawi basin hydrological system is.

3.4 Mixed isotopic and hydrochemical insights

Surface water mineral enrichment was assessed by coupling isotopic and hydrochemical signatures. High isotopic enrichment linked to high total dissolved salts (TDS) suggests influence of evaporation, while high isotopic enrichment with minimal TDS points to influence of factors apart from evaporation (Abass., *et al*., 2010; Atekwana *et al*., 2016). The high isotopic signature observed in Lake Malawi corresponds to moderate TDS, suggesting that evaporation plays a limited role in influencing its overall mineral signature. Instead, other influential factors such as water-rock reactions (of groundwater baseflow) and hydrochemical characteristics of river inflows likely contribute more substantially to the mineral enrichment signature of the lake water. Runoff from surrounding highlands, which introduces dissolved salts into the lake, can also influence the lake mineral signature. Overall, while there is an observable trend of high isotopic enrichment in surface waters of the Lake Malawi basin associated with low to moderate EC, it appears that evapo-concentration is not the sole factor driving surface water mineral enrichment; rather its effects are more localized (Figure S2). A subset of surface water sites, which includes Lake Chiwondo, Dwangwa, Limpimbi, Mtiti and Luweya Rivers, exhibit high isotopic enrichment associated with high EC (Table S3). This suggests predominant influence of evapo-concentration, highly noticeable in Lake Chiwondo which mimics inland drainage basin lake conditions. This phenomenon is a notable feature in Lake Chilwa, an inland drainage basin lake in south-eastern Malawi which has a high evapo-concentration signal (Rivett et al., 2020; Missi and Atekwana., 2020).

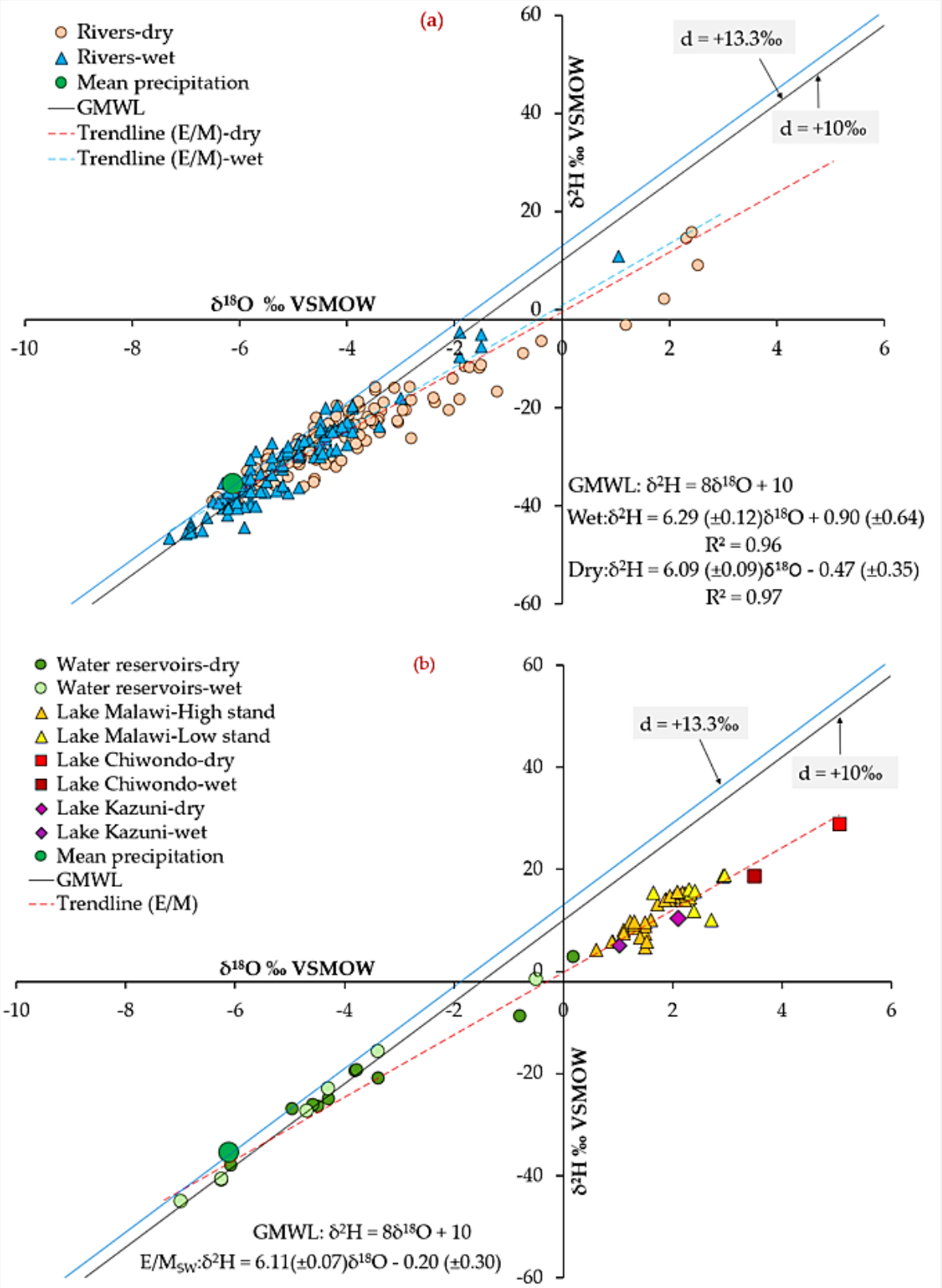


Figure 6. Scatter plots of seasonally variant δ^2H-$\delta^{18}O$ signatures of surface water samples from Lake Malawi basin. (**a**) Stream flow (rivers/streams) (**b**) Lakes and water reservoirs.

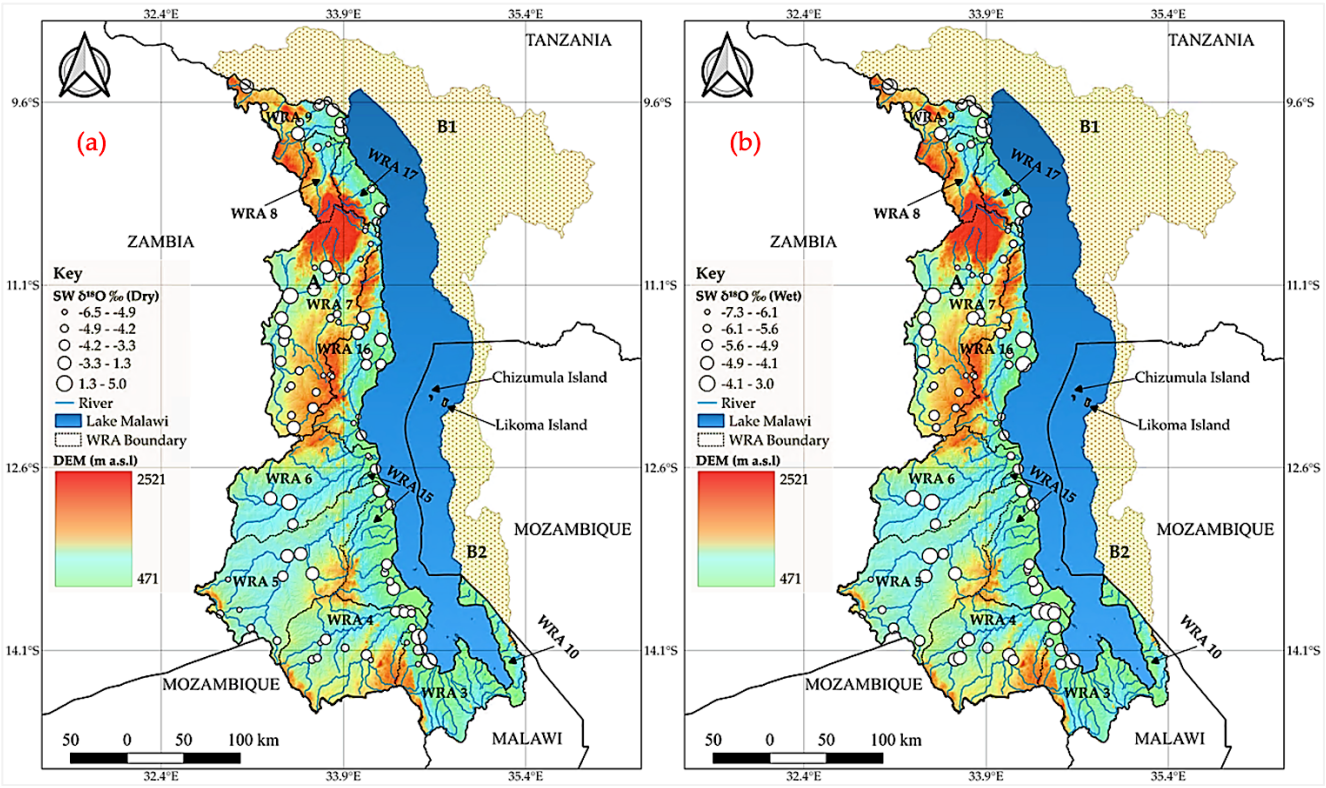


Figure 7. (a) Spatial and seasonal distribution of δ^2H-$\delta^{18}O$ signatures of surface waters across the Lake Malawi basin for (**a**) dry season and (**b**) wet season patterns.

3.6 Lake Malawi basin conceptual model: A lake basin perspective

The mixed isotopic and hydrochemical lines of evidence show that recent precipitation is the primary inflow source of surface water in the wet season, with no or minimal isotopic modification. The dry season is marked by an intense evaporation signal, isotopically enriching surface water, particularly in lakes, near-lake and near-dambo river water. During heavy rainfall events, surface runoff recharges into upland dambo storage zones (Banda *et al*., 2019), with gradual discharge of groundwater baseflow from the dambo storage zones into streamflow, predominant in drier periods. The streamflow-aquifer dynamics are pronounced in rift valley scarp gorges and along the rift valley cross-plains, with groundwater discharging into streamflow. The streamflow-aquifer dynamics reversals occur in permeable sandy zones and at the rift valley scarp foot where

streamflow leaks to the aquifer, especially under low water table conditions in drier periods (Banda *et al*., 2019; Kelly *et al*., 2019). These dynamics highlight a delicate balance of the dambo ecosystem within the Lake Malawi basin hydrology and emphasize the intricate interplay between surface water and groundwater systems, critical for integrated water resource management implementation. The mixed isotopic and hydrochemical evidence suggest possible indicators of surface water mineralization. These include water-rock reactions, precipitation, and evaporation processes. The hydrochemical evidence suggest that mineralization of most rivers is likely influenced by water-rock reactions (likely groundwater baseflow) and precipitation, with water reservoirs primarily influenced by precipitation. Highly localised spring discharges to streamflow is another factor contributing to mineralization of surface water in the Lake Malawi basin. The lake water mineral signature is mainly controlled by groundwater-rock reactions and evaporation. Overall, mineralization of surface water is not largely controlled by evaporation, pointing to other factors such as groundwater-rock reactions and runoff dissolution effect that contributes various dissolved salts and nutrients into the surface water system. The Lake Malawi basin complex topography and extended flow paths from headwaters to discharge zones facilitate prolonged surface flow, enhancing dissolution and transfer of mineral species into surface water bodies which may modify surface water mineral signatures. Thus, the hydrochemical and isotopic evidence underscores the complex and multi-faceted nature of surface water hydrochemical evolution along its flow paths from headwaters to discharge areas (Table S5). A basin-wide refined conceptual model is presented in Figure 8 with corresponding notes in Table 4 (after Banda et al., 2019).

Table 4. Explanatory notes for Lake Malawi basin hydrological conceptual model (Figure 10)

No.	System flow processes	No.	Hydrochemical signatures	No.	Isotopic signatures
1	Inflow to dambo storage by runoff, and baseflow discharge	14	Ca-Mg-HCO_3 – Fresh recharge water	16	Recent rainfall recharge, with no/minimal evaporative fractionation
2	Discharge (rapid/delayed) from dambo storage to river headwaters	15	Ca-Mg-SO_4-Cl – mixed water type depicting complex flow regime	17	High evaporation signal causing intense isotopic enrichment of surface water
3	River leakage (dry season) on permeable sand to groundwater			18	Spatially-temporally variant isotopic signatures highlighting process complexity
4	Modest groundwater flows and plateau aquifer recharge			19	Direct rainfall influx to surface water flows
5	Groundwater baseflow discharge to river in escarpment gorge			20	Isotopic enrichment of rivers predominant in dry season
6	Rivers incise into escarpment, rapids, falls, new streams				
7	River leakage/ recharge to aquifers at foot of escarpment				
8	Small streams leakage to ground, dry season cease to flow				
9	Baseflow groundwater discharge return to cross-plain rivers				
10	Wet season lakeshore plain flooding- high water tables				
11	Typical groundwater baseflow discharge to Lake Malawi				
12	Limited wet season – high level lake recharge to aquifer				
13	Dry season shallow phreatic groundwater evaporation				

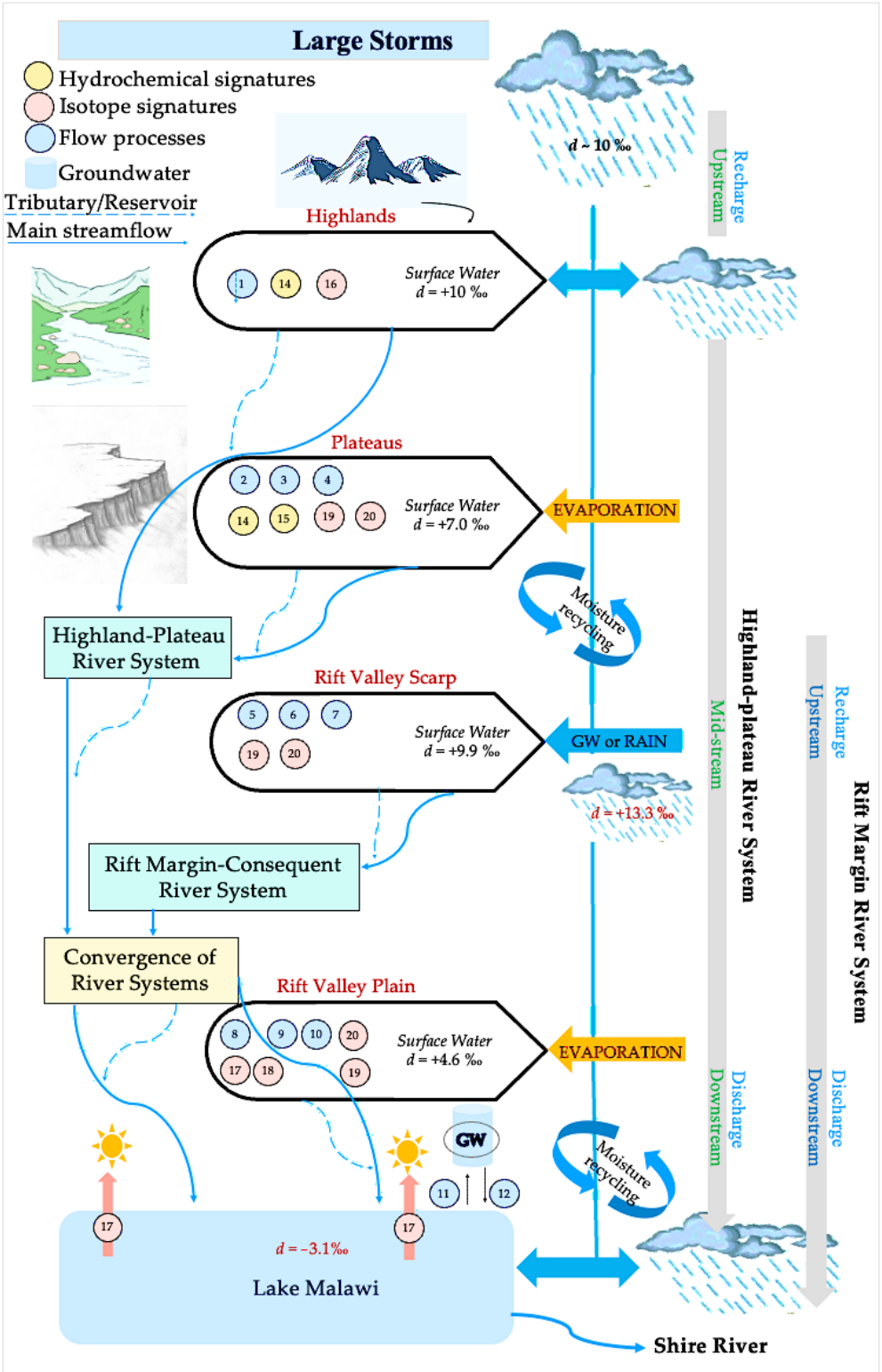


Figure 8. Refined conceptual model for Lake Malawi basin hydrology (after Banda et al., 2029)

3.7 Lake Malawi basin conceptual model: A wider-region perspective

Local precipitation is the primary source for replenishment of surface water flows in the Lake Malawi basin. The isotopic signatures of local precipitation significantly influence surface water characteristics, largely fingerprinted by distinct moisture sources. Key precipitation-bearing sources of moisture are of oceanic influences, such as tropical storms and trade winds that originate from the Indian Ocean (Figure 9). These moisture sources result in precipitation with excess deuterium similar to the global average of +10‰ (Banda et al., 2021). Besides, continental sources play a role, including large-scale evaporation from the African Great Lakes and seasonal shifts in the Intertropical Convergence Zone (ITCZ) in Central Africa. Notably, influence of moisture recycling from the African Great Lakes appears to enrich excess deuterium for local precipitation being higher than the global average of +10‰ (Banda et al., 2024). This isotopic effect seems to be masked in surface water of the Lake Malawi basin, suggesting that moisture recycling and subsequent re-precipitation do not contribute significantly to its overall hydrology. Broader climatic phenomena like the ITCZ and oceanic storms are essential for generating heavy precipitation events in the basin. Such heavy precipitation events are key to producing considerable surface runoff, which is vital for maintaining hydrological balance within the basin. This influence is reflected in wet season *d*-excess for rivers (d = +9.7‰) and reservoirs (d = +9.9‰), that aligns with moisture sources that are more extensive regionally (Banda et al., 2021). The *d*-excess during dry season show lower values of +6.3‰ for rivers and +8.0‰ for reservoirs. This reduction is attributed to lighter precipitation events, a phenomenon known as the amount effect, along with impacts of evaporation from rivers and reservoirs, and possible mixing of streamflow with already evaporated lake water near the lakes' estuaries. The stable isotopic signatures of Lake Malawi present a unique pattern in relation to evaporation and water level changes. The observed low *d*-excess of −3.4‰

during high lake stands and −2.9‰ during low stands indicated a consistent pattern in isotopic enrichment associated with varying water levels. This suggest that the lake retains a long-term memory of evaporation and its associated isotopic enrichment signal, allowing it to reflect historical climatic conditions. This relationship between lake water isotopic enrichment and evaporation underscores the importance of evaporation in shaping the lake's hydrology. noticeable in Lake Chiwondo which mimics inland drainage basin lake conditions. This phenomenon is a notable feature in Lake Chilwa, an inland drainage basin lake in south-eastern Malawi which has a high evapo-concentration signal (Rivett et al., 2020; Missi and Atekwana., 2020).

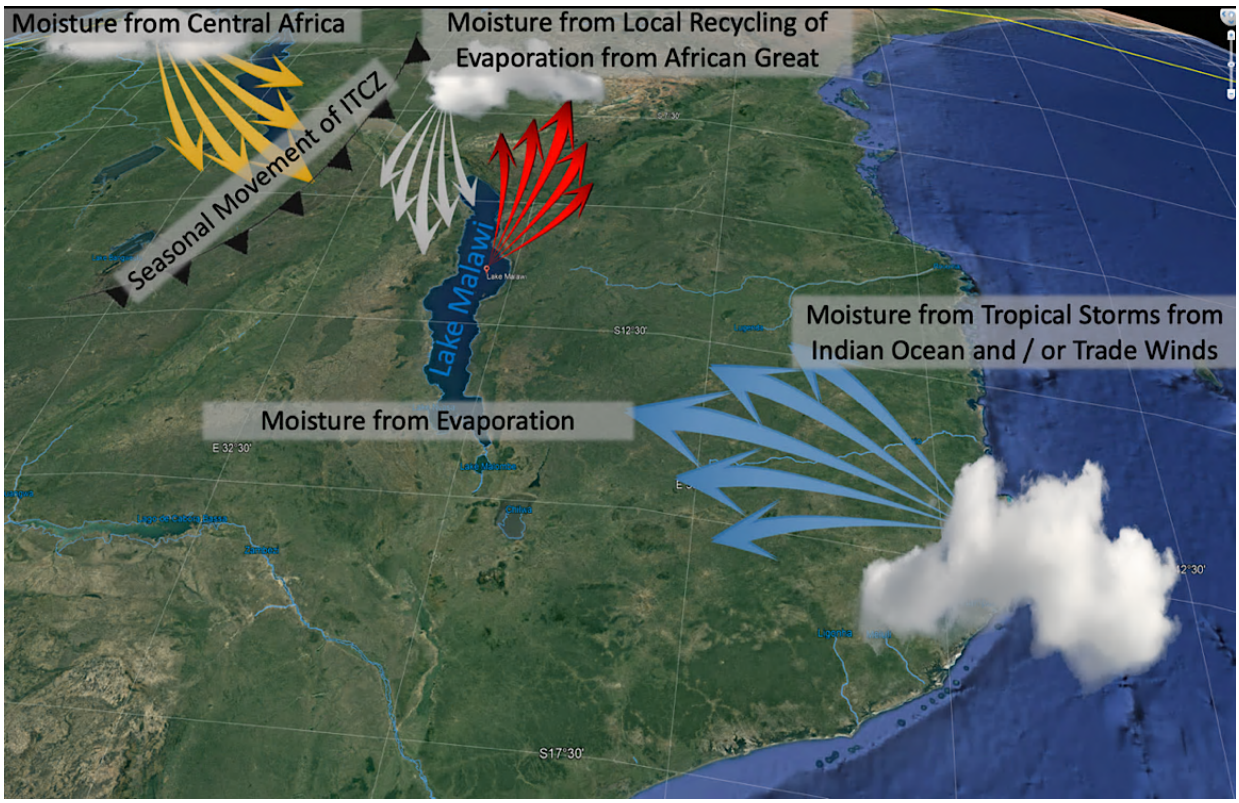


Figure 9. Origin of precipitation-bearing moisture in Lake Malawi Basin (Google earth, 2004)

3.8 Policy implications

Based on the comprehensive study of isotopic baselines and hydrochemical understanding of surface water in the Lake Malawi region, the following policy implications can be derived for effective water resource management and sustainable development:

a. Wetland ecosystems, such as the 'dambo' highlighted in the study, play a vital role in sustaining streamflow especially during dry periods. Protecting these ecosystems through effective conservation measures, land use planning, and wetland restoration is urgent and critical to manage surface water availability and quality.

b. The impact of land use and climate change on water resources in the basin is especially concerning, given the interconnectedness of water systems observed and anticipated in other Rift Valley basins. It is evident that modifications in land management around dambo areas can have considerable downstream effects, as these regions are crucial for maintaining river flow during the dry season.

c. Understanding how evaporation may affect surface water quality can encourage the creation of mitigation techniques. It may be necessary to implement policies aimed at reducing evaporation-related factors, such as controlling surface-water interactions or limiting land use activities.

d. The significance of continuous groundwater quality and quantity monitoring should be emphasized in policy initiatives. Based on identified hydrochemical features and isotopic markers, regulations governing land practices near recharge zones and protected groundwater areas could be put into place.

e. To effectively manage water resources and assess mineral enrichment, it is important to establish comprehensive water quality monitoring programs. These programs should include regular sampling and analysis of surface water and groundwater sources, focusing on key parameters that influence mineralization processes. By understanding the evolving water quality conditions, water authorities can make informed decisions regarding appropriate water treatment and management strategies.

f. Surface water and groundwater interactions are essential for understanding recharge dynamics and mineralization processes. Integrated water resource management approaches, which consider both surface water and groundwater as interconnected systems, should be adopted. This may involve coordinated planning, data sharing, and collaboration among relevant stakeholders, such as water management agencies, researchers, and local communities.

g. A crucial aspect of water resource management and environmental protection is ensuring public awareness and stakeholder involvement. Implementing educational campaigns, workshops, and awareness programs can help educate the public about the importance of responsible water resource management. Stakeholder involvement should be encouraged through participatory approaches, engaging local communities, and incorporating their traditional knowledge in decision-making processes.

By implementing these policy implications, water and environmental authorities can support sustainable management and preservation of water resources in the Lake Malawi Basin, safeguarding valuable surface water for future generations while protecting the environment.

4. Conclusion

The study developed a comprehensive isotopic baseline and hydrochemical understanding of surface water in the Lake Malawi region, establishing a vital reference for assessing future changes due to developmental pressures and climate change. It reveals that the $\delta^{18}O$–$\delta^{2}H$ signatures of surface water primarily originate from recent precipitation and groundwater contributions, varying by wet and dry seasons. These signatures depend on relative influence of precipitation, groundwater, and lake water inputs, as well as climatic factors, which include seasonal variations in precipitation from oceanic and continental moisture sources. Notably, the study finds greater variability in $\delta^{2}H$–$\delta^{18}O$ for river waters compared to lake and reservoir waters. The signatures of river waters exhibit distinctive spatial and seasonal precipitation characteristics, with depleted isotopic signatures predominant at higher elevations and more pronounced in wet season. During dry season, these river waters become isotopically heavier. The study also notes minimal impact from moisture recycling on isotopic signatures of surface water. The convergence of river systems from highland-plateau and rift margin areas, particularly in the escarpment zone, significantly influences isotopic signatures of surface water along their flow paths. This convergence reflects a transition of highland-plateau rivers from an older, more stable environment to a more dynamic, rejuvenated state, resulting in relatively depleted isotopic signatures. The hydrology of the Lake Malawi basin is complexly shaped by varied precipitation dynamics, which are crucial for replenishing surface water resources. The isotopic signatures of the basin are markedly influenced by different moisture sources, oceanic and continental, and are further affected by broader climatic phenomena, such as the Intertropical Convergence Zone (ITCZ) and tropical storms, which generate heavy rainfall events. These heavy precipitation occurrences lead to significant surface runoff and help sustain the hydrological balance of the basin. The study reports wet season *d*-excess for rivers and reservoirs at +9.7‰ and +9.9‰, respectively, highlighting the influence of regional

moisture sources. In contrast, the dry season *d*-excess show a noticeable decrease, suggesting that lighter precipitation, evaporation, and potential mixing with evaporated lake water considerably affect local hydrology. The isotopic evidence from Lake Malawi reinforces our understanding of how evaporation influences not only the lake's immediate hydrological responses but also its long-term behavioural patterns under changing climatic conditions. Overall, the research underscores the necessity of understanding complex interactions between precipitation sources, evaporation rates, and hydrological responses in Lake Malawi basin, especially in the context of changing climatic conditions. This understanding is essential for effective assessment and sustainable management of basin's water resources. The findings emphasize an urgent need for ongoing research to further elucidate the intricate hydrological processes at play in the basin.

CRediT authorship contribution statement

Limbikani Chitsundi Banda: Conceptualisation, methodology, validation, formal analysis, investigation, data curation, resources, writing—original draft preparation, writing—review and editing, project administration, funding acquisition**. Robert Michael Kalin:** Methodology, formal analysis, resources, writing—review and editing, project administration, funding acquisition**. Vernon Phoenix:** Resources, project administration, funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data Availability Statement

The research data provided in this study will be made available on reasonable request from the corresponding author.

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6.3 Research Article 3: Supplementary Materials

Isotopic and hydrochemical tracers reveal surface water dynamics in the Lake Malawi basin: A mixed-proxy approach for water resource conceptualization

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Table S1. Malawi-Network of Isotopes in Precipitation (MNIP) Stations in Lake Malawi Basin (n = 4)

Meteorological Station	Precipitation Station	District	UTM		Altitude (m asl)	Number of Monthly Samples
			Easting	Northing		
Mzuni	Mzuni	Mzimba	608577	8737419	1287	6
Chitedze	CWL	Lilongwe	583019	8454721	1046	18
Salima	Salima	Salima	671142	8478923	512	4
* Mzuni	Chiputula	Mzimba	637528	8574240	1292	1

*Provisional sampling site

Table S2. Descriptive statistics of surface water hydrochemical signatures in the LMB (n = 301)

Parameter	Unit	Min	Max	Mean	Median	StD Dev.	Range
pH	-	6.2	8.9	7.6	7.6	0.51	2.8
EC	μS/cm	26	1494	215	198	182	1468
TDS	mg/L	13	774	117	105	96	761
TEMP	°C	14.2	37.3	22.7	22.8	4.0	23.1
CO_3	mg/L	0.0	58	4.6	2.4	6.8	58
HCO_3	mg/L	7.0	350	73.7	60	57.7	343
Cl	mg/L	1.8	195	17.5	12.5	22.5	193
SO_4	mg/L	0.01	84.2	10.5	4.9	15.5	84.2
NO_3	mg/L	0.001	10.1	0.689	0.020	1.91	10.1
F^-	mg/L	0.001	2.51	0.30	0.16	0.37	2.51
Na	mg/L	1.1	118	14.5	10.3	16.0	117
K	mg/L	0.01	25	2.7	1.8	2.7	25
Ca	mg/L	1.57	122	16.5	13.4	15.2	120
Mg	mg/L	0.71	29	6.95	6.90	5.0	28.3
Fe	mg/L	0.001	8.60	0.711	0.547	0.856	8.59
Mn	mg/L	0.001	2.59	0.160	0.067	0.317	2.59
Total Alkalinity (as $CaCO_3$)	mg/L	8.2	292	68.1	62.6	50.7	292
Total Hardness (as $CaCO_3$)	mg/L	9.0	378	71	67	55.8	378

Table S3. Salinity concentration of surface water in Lake Malawi basin: Lows and highs

Water Body	Location	Low EC (μS/cm)	Relief
Compound dam	Outlet, Chikangawa	26	Highland
North Rumphi River	S103 Road Bridge	27	Highland
Kaziwiziwi River	S103 Road Bridge	30	Highland
Kambwiya River	M1 Road Bridge	35	Highland
Lunyangwa River	Chikangawa Forest	36	Highland
North Rumphi River	M5 Road Bridge	37	Highland
Water Body	Location	High EC (μS/cm)	Season
Limpimbi River	-	571	Lowland
Songwe River	Ipenza III Village	623	Lowland
Chikwidzi River	Near Mawira hot spring	630	Lowland
Linthipe River	M5 Road Bridge	634	Lowland
Luweya River	M5 Road Bridge	814	Lowland
Mtiti River	M1 Road Bridge	820	Lowland
Dwangwa River	M1 Road Bridge	872	Lowland
Lake Chiwondo	Lower Reach	1494	Lowland

Table S4: Descriptive statistics of stable isotopic signatures of surface in Lake Malawi basin

Surface water

Variable	Total Count	Mean	SE Mean	StD Dev	Minimum	Median	Maximum	Range
δ^2H	280	−21.6	1.03	17.3	−46.7	−26.9	28.9	75.6
$\delta^{18}O$	280	−3.5	0.17	2.8	−7.3	−4.5	5.1	12.4
D-excess	280	6.4	0.37	6.1	−13.1	8.6	16.7	29.8

Rivers

Variable	Total Count	Mean	SE Mean	StD Dev	Minimum	Median	Maximum	Range
δ^2H	220	−27.9	0.69	10.2	−46.7	−29.3	15.7	62.4
$\delta^{18}O$	220	−4.5	0.11	1.7	−7.3	−4.8	2.5	9.8
D-excess	220	8.2	0.33	4.9	−13.1	9.1	16.7	29.8

Water Reservoirs

Variable	Total Count	Mean	SE Mean	StD Dev	Minimum	Median	Maximum	Range
δ^2H	18	−24.3	3.10	13.2	−45.0	−25.6	2.9	47.9
$\delta^{18}O$	18	−4.1	0.48	2.0	−7.0	−4.4	0.2	7.2
D-excess	18	8.8	0.99	4.2	−2.4	10.4	13.0	15.4

Lakes

Variable	Total Count	Mean	SE Mean	StD Dev	Minimum	Median	Maximum	Range
$\delta^{2}H$	42	12.1	0.75	4.9	4.3	13.5	28.9	24.6
$\delta^{18}O$	42	1.9	0.12	0.8	0.6	1.9	5.1	4.5
D-excess	42	−3.1	0.46	3.0	−11.6	−2.3	2.4	14.0

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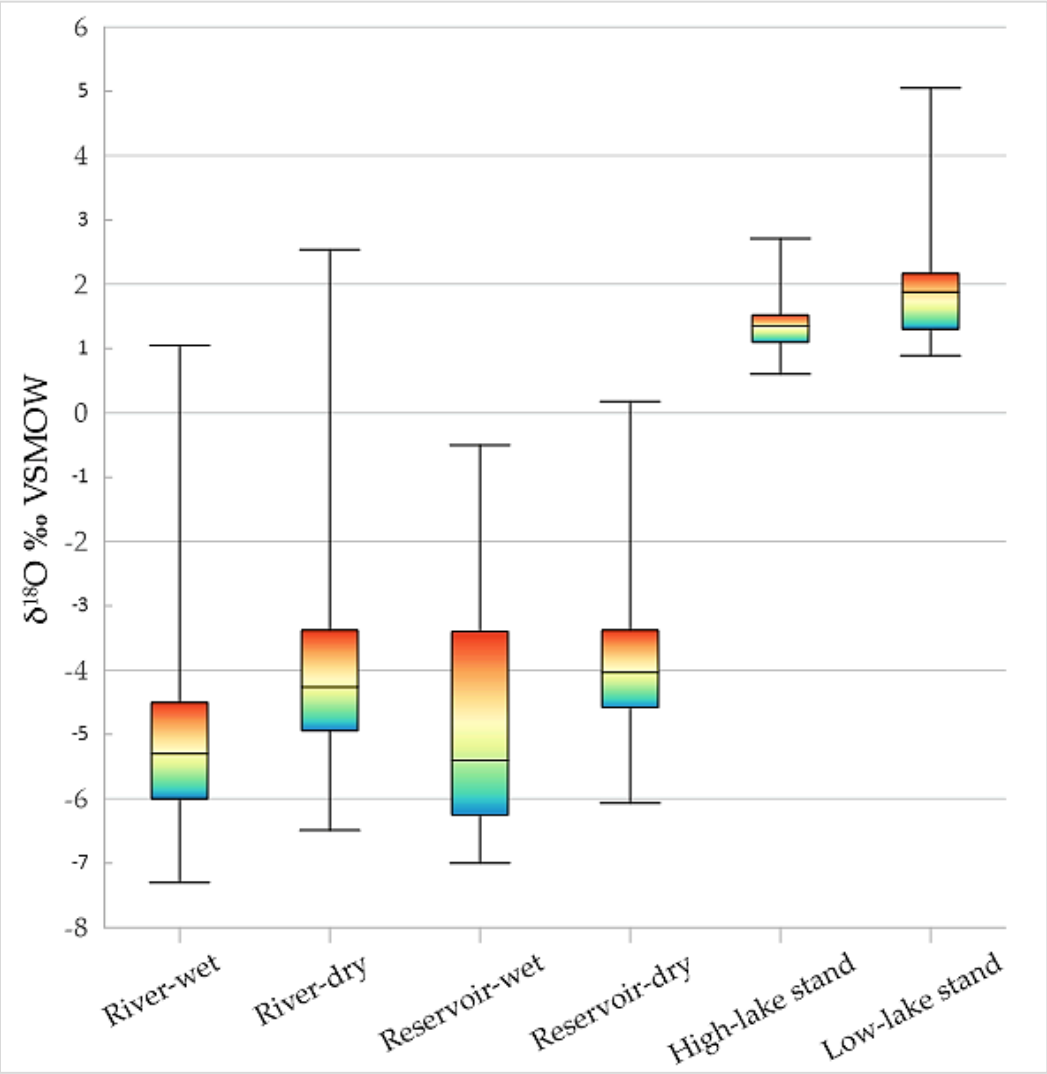

Figure S1. Plot of seasonally variant d $\delta^{18}O$ for rivers, reservoirs and lakes samples from Lake Malawi basin.

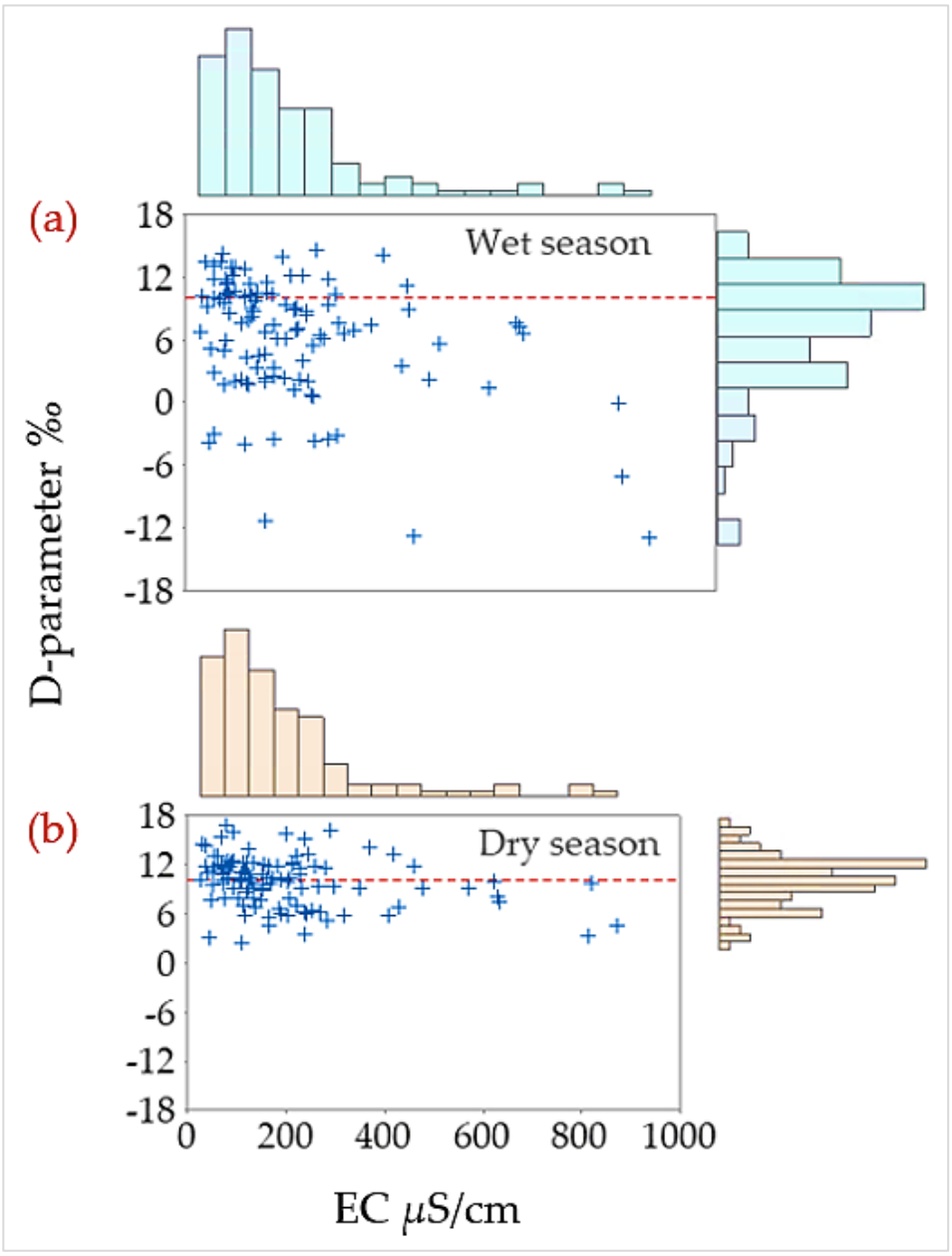

Figure S2. Scatter plots of seasonally variant d-excess and electrical conductivity for surface water samples from Lake Malawi basin for (**a**) wet season and (**b**) dry season.

Table S5. Mixed Isotopic and Hydrochemical lines of Evidence for Surface Water Resource Conceptualization in Lake LMB.

Hydrochemical line of evidence	Isotopic line of evidence	Mixed lines of evidence
Low mineralised and predominant water type Ca-Mg-HCO_3 indicate recent replenishment of most streamflow, with limited water-rock-mineral reactions.	Initial isotopic signature of local precipitation inflow to surface water is reflected in rivers (d = +8.1‰) and reservoirs (d = +8.8‰) but absent in lakes (d = −3.1‰).	Local precipitation contributes to water budget of Lake Malawi basin surface water, mainly during rainy period. Lake water reflect a high evaporation signal relative to river and reservoir waters.
Mixed water type (Ca-Mg-SO_4-Cl) characterised by mineral signature inhomogeneity, inferring notable inflow water contribution from multiple sources.	Seasonally-spatially heterogenous isotopic signatures for most streamflow, highlighting influence of multiple factors/processes.	The hydrogeological system of Lake Malawi is complex and requires high resolution investigations at catchment/sub-basin scale for refined conceptualisation of the water resource system.
Water reservoir mineral signature aligns with precipitation dominance influence (Gibbs diagram) attributable to precipitation influence, directly or via replenished riverine inflows.	Mixed isotopic signature from local precipitation and riverine inflows mostly visible in water reservoirs, highlighting their notable contribution to reservoir water budgets.	River and precipitation influx are principal controls of water reservoir isotopic-hydrochemical signatures, and critical to the water reservoir water budget.
Lake water mineral signature aligns with evaporation and water-rock reaction controls, suggesting their influence on lake water mineral enrichment. Lake Chiwondo high TDS depicts high mineralisation.	Lakes exhibit a high isotopic enrichment signature, highlighting a high degree of evaporative fractionation. Lake water mostly has long residence, hence prone to intense-progressive evaporation.	Lakes have a large evaporation signal which infers significant loss of evaporated moisture. This explains high mineral enrichment via evapo-concentration, which corresponds to high isotopic enrichment.

6.4 Postface

This chapter outlined results of the third phase of a PhD research study aimed at deepening our understanding of the hydrological complexities within the Lake Malawi basin. It specifically addressed research question 3: "How do the stable isotopic and hydrochemical signatures of surface water in the Lake Malawi basin enhance our understanding of hydrologic processes, climatic influences, and water provenance? Moreover, how can these insights predict the basin's hydrological responses to changing climatic conditions?

The pursuit of three distinct research objectives not only answered this research question but also enriched understanding of the interactions among various hydrological components in the basin. The first objective (RO 3.1) involved a detailed examination of the stable isotopic and hydrochemical signatures of Lake Malawi's surface waters, uncovering unique patterns and critical inputs vital for water replenishment. This analysis provided a foundational basis for subsequent findings. The second objective (RO 3.2) evaluated how isotopic signatures responded to climatic factors such as solar radiation and precipitation. The findings indicated a significant retention of isotopic enrichment in the lake water, suggesting a substantial impact of extended evaporative processes. The third and final objective (RO 3.3) was the development of a conceptual model that integrated the gathered data with prevailing climatic conditions. This model illuminated the interactions between atmospheric and hydrological patterns and offered a robust framework to forecast potential changes under different climate scenarios.

The synthesis of these objectives achieved the chapter's goals and added a deeper layer of understanding of the critical interactions between groundwater and surface water. These results support the recommendation for further detailed investigations within the nexus of these waters, potentially at a sub-basin level, to reveal more detailed data that could guide improved management

and conservation practices. By highlighting the enriched isotopic baselines and the dynamics of water sources across different seasons and locations, this research has strengthened the conceptual tools available to policymakers and environmental managers. It emphasizes the need for a coordinated water management approach that recognizes the essential hydrological zones and the interconnectedness of climatic, hydrological, and anthropogenic factors. The insights gleaned from this extensive analysis pave the way for effective preservation of the ecological and hydrological integrity of the Lake Malawi basin in the face of ongoing environmental changes. The foundational knowledge acquired through this research is crucial for future investigations and for enhancing strategies dedicated to maintaining the balance and health of this critical ecosystem. Furthermore, this study underscores the importance of integrated management of both groundwater and surface water resources to ensure sustainable environmental stewardship of the Lake Malawi basin. The preceding Chapter 7 constitutes phase four of the thesis, integrating insights from Chapters 4,5 and 6, and examining potential surface water and groundwater dynamics at sub-basin scale. The Chapter 7 explores spatial and seasonal interactions between groundwater and surface water and evaluates their implications for water policy and practical applications.

CHAPTER 7: GROUNDWATER AND SURFACE WATER DYNAMICS

7.1 Preface

Chapters 4, 5, and 6 of this thesis provided thorough analyses centred on the hydrological components of precipitation, groundwater, and surface water systems within the Lake Malawi basin, with each chapter examining these elements at an independent basin-wide scale. Chapter 7, the subsequent chapter, advances this research by examining these hydrological systems while adopting a more focused approach at the sub-basin level. This chapter aims to scrutinize the spatial and seasonal dynamics of groundwater and surface water, along with the implications for water resource management within these contexts.

This current chapter represents the fourth and final phase of the research, presenting results from extensive investigations conducted across three specific sub-basins: LM sub-basin I, which includes the Bua River, Dwangwa River, and Nkhotakota Lakeshore catchments; LM sub-basin II, consisting of the South Rukuru River and Nkhata Bay Lakeshore catchments; and LM sub-basin III, encompassing the Songwe River, Lufira River, and Karonga Lakeshore catchments. These investigations employed a mixed-methods approach, incorporating stable isotopic and hydrochemical tracers to deepen understanding of groundwater and surface water system dynamics within the Lake Malawi basin.

The chapter helps clarify the complex interactions among meteoric water inputs, surface water, and groundwater, focussing on spatial and seasonal variations in stable isotopic signatures in groundwater and surface water across these sub-basins. This approach provided a more nuanced understanding of the hydrological processes governing isotopic signal attenuation in these aquatic

systems. The findings from these sub-basin studies are set to make a significant contribution to the overall conceptualization of the Lake Malawi basin, providing valuable insights essential for the effective management and protection of this vital water resource. Results from these sub-basin studies have been compiled into research articles, each focusing on individual catchments and slated for publication in scholarly journals. The sequence of these articles begins with the results from sub-basin I, proceeds to sub-basin II, and concludes with sub-basin III, systematically articulating the complex hydrological interactions within the region.

7.2 Research Article 4: Main Paper

Dual-stable Isotopic Tracing of Meteoric Water Input Signal in Surface Water and Groundwater to Constrain Water Resource Conceptualisation: Implications for Groundwater-Surface Water Dynamics in Bua River, Dwangwa River and Nkhotakota Lakeshore Catchments

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Abstract: This study aimed to trace input isotopic signal of meteoric water in Bua River, Dwangwa River, and Nkhotakota Lakeshore catchments, to increase transformative understanding of surface water and groundwater dynamics. Water samples were collected from springs, boreholes, dug-wells, river, reservoir, and lake sites in wet and dry season, and were analysed for δD and $\delta^{18}O$ ratios using laser-mass spectrometry. The analysis results were evaluated using a local deuterium excess line and the Global Meteoric Water Line, alongside a suite of statistical methods. The results revealed a strong 'input isotopic signal' of meteoric water, predominant in wet-season surface water and groundwater sites. The input isotopic signal progressively attenuated between wet-dry season, with a higher seasonal attenuation observed in riverine flows relative to groundwater. A notable feature was retention of isotopic enrichment in lake water, which appeared to remain relatively unchanged despite considerable input of modern meteoric water in this Lake Malawi sub-basin. The study revealed significant spatial and seasonal inhomogeneity in δD and $\delta^{18}O$ signals of surface water

and groundwater. Surface water exhibited high variability in δD and $\delta^{18}O$ signals compared to groundwater, indicating varying input source contributions influencing surface water, while indicating a more defined and standardized input signal to groundwater. The results confirm complexity of hydrological interactions within the Lake Malawi sub-basin. The study underscores the need for Integrated Water Resource Management (IWRM) in managing this critical transboundary water resource. The study results are expected to enhance water-resource conceptualisation in the Lake Malawi basin and valuably inform water governance by contributing a new body of scientific knowledge and data towards Sustainable Development Goal 6 (SDG 6) objectives. Future research should focus on expanding the range and variety of isotopes to support high-resolution quantification of groundwater-surface water interactions, critical for refining the Lake Malawi basin's water balance model.

Key words: water isotope tracing, transboundary water resource, Lake Malawi, rivers, stable isotopes, integrated water resource management.

1. Introduction

Groundwater and surface water interactions play a critical role in maintaining hydrological balance and ecological health across various landscapes. These interactions are crucial for addressing challenges related to stream ecology, river management, agriculture, and ensuring a reliable supply of safe drinking water amidst anthropogenic-driven pollution (Blanc et al., 2024; Barthel and Banzhaf, 2016; Boano et al., 2014; Brunner et al., 2017; Poff and Zimmerman, 2010). Effective management of groundwater and surface water resources is increasingly important, particularly in regions experiencing water resource deficit (Jasechko et al., 2024a). The Lake Malawi basin, situated at the southernmost of the Great Rift Valley system, represents a vital

transboundary water resource for surrounding communities and ecosystems (Chavula et al., 2023; Kalin et al., 2022; Banda et al., 2024). The basin's main hydrologic feature, Lake Malawi, is of great socio-economic importance, accounting for around 80-82% of total Shire River flows, key for primary-national electrical power production (Kumambala et al., 2024). The lake offers nutritional security, providing approximately 70% of animal protein and 40% of total protein consumed in Malawi, with fisheries value chain contributing ca. 7.2% to Malawi's GDP, underpinning food security and economic growth (Hara et al., 2016). The complexity of groundwater-surface water dynamics in the basin is notable and paramount for Integrated Water Resource Management (IWRM) (Banda et al., 2019a; Kelly et al., 2020; Kelly, et al., 2019). Key features of groundwater-surface water interactions theorized in the basin include delayed, slow release of water from dambo systems that sustain riverine flows especially during the dry season, occurrence of both influent and effluent river reaches across the plateau and lakeshore plains, with evidence of seasonal reversals and also prominent groundwater baseflow-dominated exchanges with surface water systems, all these critical insights requiring further clarification (Kelly et al., 2020; Banda et al., 2019a; Banda et al., 2019).

Isotopic signals, particularly those of meteoric waters, provide valuable and unique insights into water resource origin, pathways, and interactions within the water cycle (Cole & Boutt, 2021a; Yoshimura, 2015). These isotopic signals are reliable in clarifying contribution of meteoric water inputs to surface water flows and groundwater recharge (Cai & Ofterdinger, 2016; Gupta et al., 2016; Jasechko & Taylor, 2015; Kotchoni et al., 2018; Taylor et al., 2012; Banda et al., 2019b, 2020a, 2024; Rivett et al., 2020; Banda et al., 2024b). Groundwater-surface water interactions have been widely explored using various methods. Groundwater contributions to streamflow have been quantified using baseflow index method (Kelly et al., 2019; Kelly et al., 2020; Kumambala et al., 2024; Madlala et al., 2019; Singh et al., 2019), geochemical trace methods (Lott & Stewart, 2016;

Mei et al., 2024; Pellerin et al., 2008) and environmental isotopes (Jung & Lee, 2020; Klaus & McDonnell, 2013). Some have used heat signatures to clarify surface and groundwater origin in a water system (Roshan et al., 2012). The breadth of research on this topic underscores the critical role of groundwater and surface water interactions, with critical implications for IWRM practices.

In Malawi, groundwater and surface water interactions studies have been previously conducted using baseflow index method (Banda et al., 2019b; Kelly, Bertram, et al., 2019a, 2019b; Kelly et al., 2020; Kelly et al., 2019; Kumambala et al., 2024). To date, there still remains striking research gaps for meteoric water input signals constraints on groundwater and surface water dynamics, particularly using isotopic techniques (Banda et al., 2019a, 2024). While water isotope tracing techniques represent a unique and reliable methodology for constraining groundwater and surface water dynamics (Lewandowski et al., 2020; Ma et al., 2024; Madlala et al., 2019; Modie et al., 2022; Pham et al., 2024), their local application remains underexplored (Banda et al., 2019, 2024). While the integrative nature of groundwater and surface water is widely acknowledged (Boano et al., 2014; Brunke and Gonser, 1997; Winter et al., 1998), development of water resources in many least developing countries occur in isolation, often neglecting the convoluted linkage between these hydrological components. This is particularly evident in rural Africa, where primary focus has been on groundwater resource development, typically through hand-pumped production boreholes, with insufficient recognition of the need for an understanding of broader water resource sustainability through detailed scientific research (McDonald et al., 2012; Kalin et al., 2022; Truslove et al., 2019). Previous water research mainly focused on surface water or groundwater dynamics in isolation (Banda et al., 2024; Smith-Carington & Chilton, 1983). The status quo underscores a critical need for improved knowledge and understanding of the groundwater and surface water relationships in the basin. Therefore, this study is part of a series of catchment-wide studies aimed at clarifying groundwater and surface water relationships, critical for holistic water

resource conceptualisation of the Lake Malawi basin. This study addresses the following research question: How do stable isotopic signals of meteoric water constrain groundwater-surface water dynamics? The study tackles the research question by addressing the following objectives: 1) characterizing input stable isotopic signals of meteoric water in groundwater and surface water; 2) investigating spatial and temporal variations in stable isotopic signals between groundwater and surface water systems; and 3) assessing implications of isotopic variations on groundwater-surface water dynamics. To meet the stated aim and objectives, this study used a novel mixed-method approach that integrated stable isotopic and hydrochemical tracers with spatial-temporal analysis. The study outcomes are expected to yield significant insights into the dynamics of groundwater and surface water interactions, with critical implications for water-resource conceptualisation in the Lake Malawi basin.

2. Study area description

The study area covers the Bua and Dwangwa River catchments, and the Nkhotakota lakeshore catchment (Figure 1). These catchments are situated at the far southern stretch of the Great Rift Valley System, covering an area of ca. 23,228 km² (GoM., 2017). Collectively, they form a transboundary water resource shared by Malawi, Tanzania, Mozambique, and Zambia, highlighting its importance in the context of shared surface water and aquifer resources (Banda et al., 2024; Kalin et al., 2022; Fraser et al., 2020).

2.1 Riverine drainage network

The Bua River, Dwangwa River, and Nkhotakota lakeshore catchments form a complex and interconnected drainage network, predominantly influenced by the study area's unique physiographic and geological context (Figure 1). The Bua River catchment occupies most of the

south-western front, covering an area.10,658 km² (Figure 1). This catchment is mainly drained by the Bua River and its network of tributaries (e.g., Namitete, Lusa, Mphelele, Ludzi, Liwelezi, Mtiti), which traverse steep rift valley slopes before converging onto the lakeshore rift valley plains. Topographical gradients in the Bua River catchment result in significant alluvial sediment deposition, fostering diverse ecosystems and enhancing agricultural productivity. The Dwangwa River catchment occupies the north and north-western fronts of the study area, covering an area of about 7,751 km² (Figure 1). It is characterised by a dual drainage system consisting of the Dwangwa River and its network of tributaries (e.g., Rupashe, Lingadzi, Liziwazi, Chitete, Luwelezi, Mchenda). This catchment is characterised by both youthful geomorphic features, including broad, grassy landscapes, with gently meandering channels and steep, incised valleys typical of youthful Rift Margin rivers. The catchment's distinct drainage patterns converge along the Kasungu Plain and Nkhotakota Scarp Zones, exhibiting geological diversity that significantly influences hydrological characteristics.

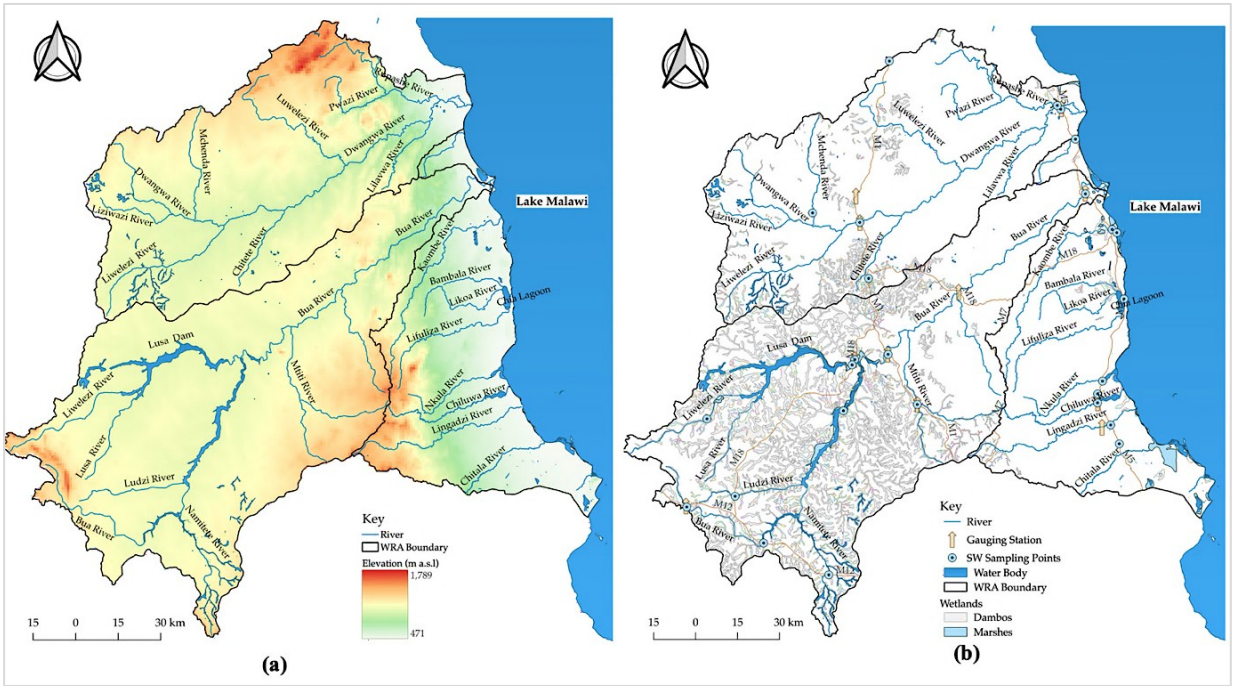

Figure 1. Study area extent (a) Topographic spread (SRTM elevation data: USGS), Water resource areas (WRAs) and major rivers. (b) Surface water sampling network.

The Nkhotakota lakeshore catchment largely occupies the eastern front of the study area, covering approximately 4,819 km² (Figure 1). This catchment primarily features rivers stemming from the Rift Valley Scarp that flow through the Rift Valley lakeshore plains and drain into Lake Malawi. The hydrological behaviour within this catchment reflects varying tectonic activities characterised by a mix of youthful steep valleys, mature meandering and braided patterns across the rift valley lakeshore plains. Recent geological faulting, notably the Mphalanyongo fault, disrupted traditional drainage patterns, and resulted in formation of marshy areas.

2.2 Topography

The study area exhibits a varied topography that significantly impacts its hydrology. The Bua River catchment, predominantly a flat plateau, spans elevations from 472 to 1,755 meters above sea level (m asl), with approximately 90% of the area situated between 1,000 and 1,300 m asl. The Mchinji Highlands represent the highest point at an elevation of 1,755 m asl. Contrastingly, elevations in the Dwangwa River catchment range from 500 to 1,500 m asl. This catchment includes the Kasungu plain in eastern and central regions, characterized by gently rolling terrain shaped by both ancient geological activities and more recent rift-fault movements. The Nkhotakota Lakeshore catchment combines elements of the Great Rift Valley and Central African Plateau. This area is distinguished by significant escarpments alongside the low-altitude shoreline of Lake Malawi at 474 m asl. The catchment's landscape shows a striking contrast between highlands in the west, including the Ntchisi Mountains at 1,700 m asl, and lowlands extending toward the Lake Malawi shoreline. Geological processes such as faulting and erosion play crucial roles in shaping the catchment's topography, leading to flat terrains that gradually slope towards Lake Malawi and various degrees of landscape dissection.

2.3 *Geology and hydrogeology*

The study area is characterized by three primary geological units: Weathered Basement, Fractured Basement, and Unconsolidated Sedimentary formations. These units constitute two main aquifer groups (Kalin et al., 2022). The first aquifer group (Group 1) comprises the Weathered Basement located beneath Unconsolidated Sedimentary units (Figure 6). In contrast, the second aquifer group (Group 2) features the Weathered Basement overlaying Fractured Basement. The Aquifer Group 1 is defined by colluvium, shallow alluvium, fluvium, and lacustrine formations, where transmission of groundwater mainly occurs through intergranular pore spaces (Kalin et al., 2022). Aquifer Group 2 comprises a diverse array of rock types including charnockitic gneiss, hornblende-biotite gneiss, marble, perthite gneiss, quartzo-feldspathic psammite, ultrabasic and basic igneous intrusive rocks, amphibolite, quartz reef, biotite-muscovite and graphite gneiss, schist, and quartzite (Kalin et al., 2022). Groundwater transmission in this aquifer group mainly

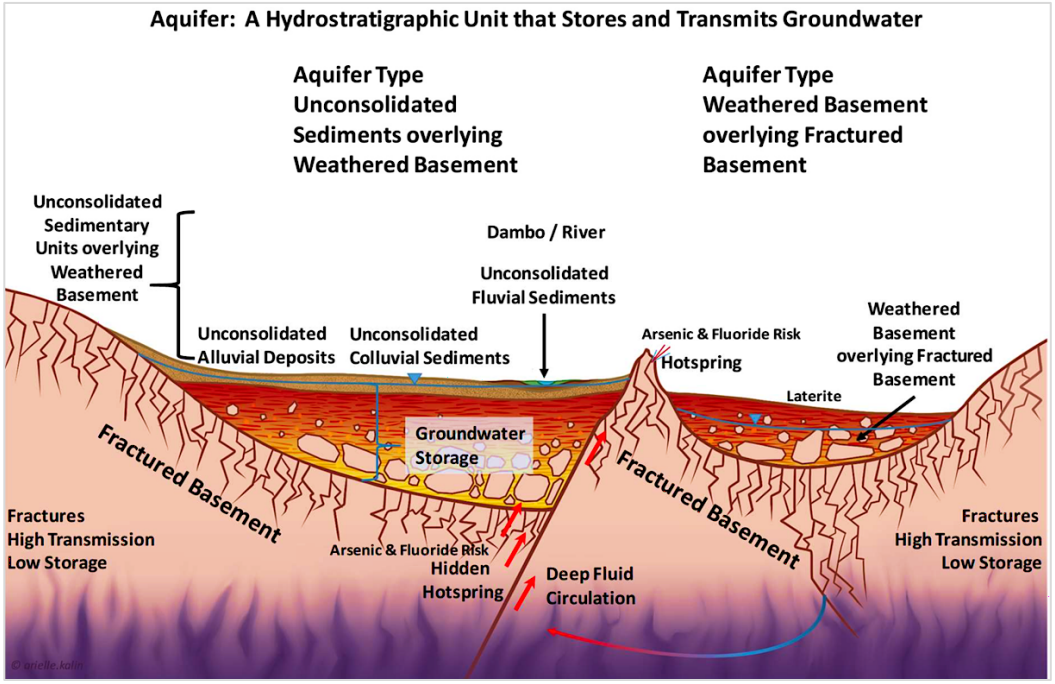

Figure 2. Idealised cross-section of the hydrostratigraphic aquifer units in the study area (after Kalin et al., 2022).

occurs through intergranular pore spaces, fissures, fractures, and joints (Kalin et al.,2022). These lithological formations originate from the Precambrian to Lower Paleozoic periods and include some folded syenite whose age remains undetermined. Isolated outcrops of basement lithologies are present within the catchment area, particularly along the Malawi-Zambia border and a small segment of the rift escarpment in the east, where the Bua River flows into the Lake Malawi Rift Valley Plain (Kalin et al., 2022). The flood plains of the Lake Malawi Rift valley are composed of unconsolidated fluvial, colluvial, and alluvial sediments that lie above the Weathered Basement (WB) units. Groundwater resources are essential for water supply, especially in rural areas where communities predominantly depend on alluvial aquifer formations for their drinking water (Kalin et al., 2019; Smith-Carington and Chilton, 1983; Upton et al., 2018). The yield from Group 1 aquifers in production boreholes can reach up to 20 L/s. In contrast, Group 2 aquifers typically have a lower yield, around 2 L/s (Smith and Carrington, 1983: Groundwater Resources of Malawi). Geographically, Aquifer Group 1 predominantly covers the western portion of the study area, whereas Aquifer Group 2 is the primary group found on the eastern side, especially along the Rift valley scarp zones.

2.4 Climate

The climate of the study area is classified as tropical-continental, characterized by clearly defined wet (November to April) and dry (May to October) seasons. According to the revised Köppen-Geiger classification system, which draws on extensive global data from long-term monthly precipitation and temperature records, the climate of the study area is designated as Aw, or Savannah (Peel et al., 2007). This classification adheres to the following specific criteria: “Not Af and Pdry < 100 – MAP/25”, where Af is “not rainforest” and Pdry is “precipitation of driest month” and MAP is “mean annual precipitation”.

Rainfall patterns are predominantly influenced by the Intertropical Convergence Zone (ITCZ), tropical storms, and trade winds (Peel, et al., 2007; Ngongondo et al., 2011). The rainfall distribution varies significantly depending on topography and altitude of the study area. The northeastern highlands receive up to 1,525 mm of rain annually, rendering these areas relatively humid, whereas the western regions, including parts of the Dwangwa River catchment and the Kasungu Plain, receive about 890 mm, hence, relatively semi-arid. Areas near the Rift valley escarpments and along the Lake Malawi shoreline receive moderate to high rainfall, while the interior areas experience relatively drier conditions. Another factor influencing rainfall distribution is distinct seasonality of the area, with most of the rainfall received during wet season.

Mean annual temperature of the study area ranges between 18 and 21 °C, with the northeastern part typically registering slightly higher temperatures. There are notable seasonal temperature fluctuations; in November, maximum temperatures in the eastern parts can reach between 32 and 35 °C, while in July, minimum temperatures can drop to between 4 and 7 °C. These climatic conditions have a profound influence on the study area's hydrology (Kalin et al., 2022). The peak of the wet season associated with heavy storms, tends to experience localised flooding and sediment deposition, particularly in low lying areas of the study area.

2.5 Land-use and economic context

The study area is predominantly used for extensive agriculture, which includes both irrigated and rain-fed farming (Kalin et al., 2022). This significantly influences land use patterns and water resource management. In the Bua River catchment, irrigated agriculture is particularly crucial as it accounts for 97% of total surface water abstractions. This heavy reliance on irrigation supports cultivation of staple crops like maize and tobacco, which are vital for local sustenance and economic

activity. The Bua River irrigation initiative exemplifies this, drawing large volumes of water from the Bua River to sustain agricultural production, especially during the dry season. The Dwangwa River catchment primarily depends on rain-fed agriculture, with tobacco and maize being the predominant crops. However, increasing demand for farmland has escalated pressures on forest resources, leading to significant deforestation and soil erosion. This situation underscores vulnerabilities of rain-fed agriculture in face of escalating climatic variability and highlights the need for sustainable land management practices. The Nkhotakota lakeshore catchment presents a more diverse picture, combining rain-fed agriculture and fisheries. Agriculture here significantly contributes to local livelihoods, particularly along the lakeshore where rice irrigation is prevalent. This catchment is recognized for its rich aquatic resources, which provide essential dietary and economic benefits to the local population.

The plateau is largely inhabited by smallholder farmers dependent on rain-fed maize as their major crop. The catchment's wetlands are cultivated, though much of the lakeshore areas are well known for irrigated sugarcane cultivation. Although there is smallholder cultivation of sugarcane in the catchment, most of the land is estate agriculture, under ownership of the Illovo Sugar (Malawi) Ltd. Almost all the sugarcane cultivated in the area is sold to Illovo, which remains the only sugar milling entity in the area and a dominant one in the country, followed by Salima Sugar Limited. Most land resources are devoted to woodlands and rain-fed agriculture, followed by grasslands and dimba cultivation. Rain-fed agriculture is dominated by tobacco and maize cultivation, while woodland settings dominate Kasungu National Park and Nkhotakota Game Reserve. In the lower reaches of the Dwangwa River and along the eastern reaches of Lake Malawi, dimba cultivation is extensively dominated by sugar cane plantations by Illovo Sugar Corporation and smallholder farmers. The growing need for farmland for intensive rain-fed cultivation has

contributed to the accelerated eradication of forests and the degradation of catchments due to the rapid erosion of woodlands.

3. Materials and Methods

3.1 Sample collection

Water isotope samples were collected from surface water points, including rivers, lakes, and reservoirs, and groundwater points, including springs, dug-wells and boreholes fitted with handpump. Water samples were collected during the peak of both the dry and wet seasons to capture seasonal changes. To maintain integrity and accuracy of the water samples, stringent protocols were followed. Water samples were collected using 50-mL High-Density Polyethylene (HDPE) bottles, acid-washed prior to sampling. The sampling bottles were completely filled to eliminate any headspace, reducing the potential for gas exchange. Each sampling bottle was tightly sealed using a waterproof tape to avoid isotopic fractionation through leakage, evaporation and biological activity. Consistent quality control measures, including keeping the water samples at a steady temperature of 4°C, away from direct sunlight, were adhered to during transportation and storage. Pre-sampling procedures involved thorough rinsing of HDPE bottles with sampled water eliminate any possible contaminants and residues. For rivers, water samples were collected from main flow channels. Grab samples were collected from minor river-main channels as they were deemed to be well mixed, whereas, structured interval sampling was used in major river systems, performed from easily accessible road and railway bridges, considering potential differences in water composition across their cross-sections. In lakes, water sampling was conducted from boats, approximately 1 km from the shorelines using specialized depth samplers. Reservoir inflows and outflows, areas with presumed homogenous mixing, were sampled using simple grab technique. Additionally, composite sampling in central parts of reservoirs was employed to achieve sample

representativeness. Groundwater samples were collected from active community water supply boreholes, utilizing effective purging to ensure freshwater turnover before sampling. Boreholes that were not in used at the time of sampling were thoroughly purge for 5 minutes to remove the stagnant water column and collect a representative water sample. This was critical in establishing an accurate representation of the current hydrological state of the sampled water resource. Springs were sampled directly at/or near primary discharge points, avoiding any adjacent stagnant water that may be prone to isotopic changes due to evaporation and atmospheric exchanges. The described rigorous methodology and strategic selection of sampling points were intended to yield robust, high-resolution isotopic data crucial for hydrological assessment and modelling. These strict procedures highlight the critical role of careful preparation and precise execution to ensure high integrity results.

Hydrochemical and isotopic samples were concurrently collected using similar techniques. Hydrochemical analysis required use of two acid-washed 1L HDPE screw-capped bottles for each sampling site. To ensure stability of cations and avert precipitation during transit and storage, one sampling bottles for each site was preserved using 2 ml of concentrated hydrochloric acid (HCl) to reduce pH to 2. The low pH tends to suppress biological activities and keeps cationic species in solution. Before sample collection, the non-acidified sampling bottles were rinsed thrice with sampled water to guarantee representativeness. The sampling bottles were filled to capacity to eliminate atmospheric gas exchanges that could potentially disrupt water samples' chemical equilibrium. Water samples from rivers were collected from active flow channels to for sample homogeneity, while those from springs were collected from primary discharge sites. Each water sample was carefully labelled and kept at 4°C while being transported and stored prior to laboratory analysis. The low temperature tends to suppress chemical or biological activities, thus preserving integrity of water samples. The water samples were filtered through Whatman glass fiber filters

with a 0.45 μm pore size to eliminate insoluble particulates that could interfere with analytical instruments. The field procedures for hydrochemical sampling adhered rigorously to the International Standard Procedures (APHA, 2005).

3.2 Sample analysis

In situ measurements of fluctuating parameters such as temperature, electrical conductivity (EC), total dissolved solids (TDS), and pH were performed at the sampling sites using a carefully calibrated portable multi-meter (Model: HI-98194, Hanna Instruments, Woonsocket, RI, USA). Before recording any measurement, the multi-meter readings were allowed to stabilize for 2 to 5 minutes for consistent results. For surface water, the multi-meter probe was submerged at least 100 mm deep in areas of continuous water flow, avoiding stagnant water zones. For springs, measurements were taken right at/or near primary outflow points. For pumped or bailed groundwater samples, field measurements were conducted immediately after sampling, with the multi-meter probe placed in a polyethylene 250-ml beaker. The field measurement results provided initial insights into the water conditions and helped assess any physicochemical changes that might occur during transportation and storage.

Stable isotope samples were analysed using a Picarro 2140i CRDS laser spectrometer (Model: L2140-i, Picarro Inc., Santa Clara, CA, USA), with a precision of 2σ of ±0.2 ppm or better for oxygen-18 and ±2.0 ppm or better for deuterium, at the IAEA isotope hydrology laboratory in Vienna, Austria. The initial step involved creating a sample list for batches of 10 samples in the laboratory information management system (LIMS), where each batch included calibration and quality control standards and water samples for quality control objectives. A 1 ml water sample was sucked through a 0.45 μm filter into a 2 ml glass vial, which was then transferred onto an autosampler

tray for the Picarro laser spectrometer. The analysis run was performed in high-precision mode, involving three autoruns and using dry synthetic air as a carrier gas. The Picarro laser spectrometer was prepared by running two vials of deionized water, achieving a required range of concentration peaks between 19,000 and 21,000 ppm. A mean 60-minute stabilization period for the Picarro laser spectrometer was implemented prior to water sample analysis. Each water sample was auto-sucked from the auto-sampler unit and injected six times into the Picarro laser spectrometer's vapourizer unit. Reference materials used during the analysis included Lake Kyoga (enriched) and Standard-09 (Greenland Ice, depleted) which encompassed anticipated range of isotopic compositions of the samples. Control standards, Standard-11 (Monaco Lagoon) and Standard-06 (Heidelberg tap water), were used to maintain stringent QA/QC of the analysis process.

Upon completing the isotopic analysis, data files for analytical runs were retrieved from the analyzer and transferred into the LIMS, where they were merged and given unique identifiers prior to normalization and validation. Results from initial three injections for each sample were disregarded to prevent potential memory effect of the analyzer, with the remaining injections' results processed as raw data using residual memory correction techniques in LIMS. Data normalization was carried out referencing the Vienna Standard Mean Ocean Water (VSMOW) and Standard Light Antarctic Precipitation (SLAP) scales, utilizing dual reference points for accuracy objectives. The processed data was then integrated and assigned additional identifiers, and uploaded to LIMS for further processing and final validation. The water sample chain of custody, covering all steps, from onsite measurements and sample collection to transportation, storage, preparation, and analysis, strictly adhered to International Standard Procedures (ISP, IAEA, 2009).

Water isotope analysis results were reported as delta (δ) values, considering relative deviations in isotopic ratios between the sample and a standard (Coplen., 2011).

$$\text{Delta } (\delta) = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) \text{x } 1000 \text{ ‰}$$

In the equation above, "R" represents a dimensionless isotopic ratio, whereas "R_{sample}" and "$R_{standard}$" are isotopic ratios of sample and standard, respectively. Specifically, for hydrogen isotopes, R is expressed as ratio $^{2}H/^{1}H$, and for oxygen isotopes, it is expressed as $^{18}O/^{16}O$. The delta notation (δ) is a measure deviation of R_{sample} from $R_{standard}$. Considering these deviations are typically small, they are presented in parts per thousand, or per mil (‰), allowing for accurate measurement of minor isotopic differences (Rozanski et al., 1993; Coplen, 2011; IAEA, 1981). The VSMOW standard values for δD and $\delta^{18}O$ set at zero. Thus, a positive δ value indicates isotopic enrichment of heavier isotopes relative to the VSMOW standard, while a negative δ value indicates isotopic depletion. Deuterium excess (*d*-excess or d), as described in Equation (3) (Dansgaard, 1964), is a proxy indication of source of precipitation-bearing air moisture and provides critical information about origin of air moisture (Rozanski et al., 1993; Merlivat and Jouzel, 1979; Gat et al., 1970). The d-excess is largely influenced by atmospheric relative humidity over ocean surfaces (Clark and Fritz, 1997). Where average global relative humidity is approximately 85%, the resulting d-excess value for average global precipitation is ~ 10‰ (Merlivat and Jouzel, 1979; Gonfiantini, 1986). A d-excess value around 10‰ is primarily associated with precipitation derived from air moisture originating from oceanic source. D-excess value exceeding 10‰ offers evidence of air moisture recycling associated with large-scale evaporation and low atmospheric humidity in the source region according (IAEA, 2005). Additionally, the *d*-excess is influenced by secondary processes including the Evaporation of raindrops below clouds and the evaporation from terrestrial water bodies (Rozanski, 1993; Froehlich et al., 2002). Such processes can either decrease or increase *d*-excess values, thereby enabling it to act as an indicator of varying moisture sources.

$$\delta D = \delta^{18}O + 10$$

$$d = \delta D - 8\delta^{18}O \text{ ‰ VSMOW}$$

Hydrochemical analyses were carried out at both the Environmental Analytical Laboratory at the University of Strathclyde in Glasgow, United Kingdom and the Central Water Laboratory of the Ministry of Water and Sanitation in Lilongwe, Malawi. These analyses involved measuring dissolved anionic and cationic species according to the International Standard Methods (APHA, 2005). Engaging two laboratories facilitated timely analysis and promoted intra-laboratory quality control. The ions fluoride (F^-), chloride (Cl^-), nitrate (NO_3^-), and sulphate (SO_4^{2-}) were quantified using ion chromatography (Model: 850 Professional IC, Metrohm, Switzerland). Metals such as iron (Fe^{2+}), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), and manganese (Mn^{2+}) were assayed using an inductively coupled plasma spectrometer (Model: iCAP 6000 Series, Thermo Scientific, Waltham, MA, USA). Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) species were determined through standard titration methods, while alkalinity ($CaHCO_3$) was measured using a photometric analyser (Model: KONE Aquakem V.7.2.AQ2, Skalar, Breda, Netherlands). Ionic balance error (IBE) was calculated for each sample to ensure accuracy of the hydrochemical analysis, with results indicating an acceptable IBE within ±5%. Overall, the field measurements and laboratory analyses were conducted with strictly adherence to International Standard Procedures (APHA, 2005).

3.0 Results

3.1 Stable isotopic signatures

3.1.1 Stable isotopic characteristics of surface water

Surface water samples (n = 54) revealed a wide range of $\delta^{18}O$ and δD signatures. The $\delta^{18}O$ signatures vary from –6.9 to +2.2‰, with a mean of –3.6‰ (Table 1). Correspondingly, δD signatures range from –45.2 to –15.6‰, with a mean of –23.1‰. River water samples (n = 44) exhibit a broader $\delta^{18}O$ range of –6.9 to +2.2‰, with a mean of –4.2‰. The d-excess values for rivers range from –15.7 to +16.1‰, averaging +6.0‰. Reservoir water samples (n = 6) exhibit $\delta^{18}O$ signatures ranging from –5.5 to +0.2‰, with a mean of –2.3‰, and δD signatures that span from –35.0 to +2.9‰, averaging –14.4‰. In contrast, lake water samples (n = 4) showed a narrower range for $\delta^{18}O$ signatures, between –1.3 to +2.1‰ and a mean of +0.9‰. The δD signatures for Lake water range from +4.8 to +15.6‰, with a mean of +9.0‰. The findings indicate significant stable isotopic enrichment of lake water relative to river and reservoir water, suggesting distinct hydrological influences on lake water. The findings also highlight clear stable isotopic distinction between the surface water bodies, underscoring variability due to different hydrological processes. When plotted alongside meteoric water lines, most of the surface water samples align with the Global Meteoric Water Line (GMWL), described as $\delta D = 8\delta^{18}O + 10$ (Craig, 1961) (Figure 3). This pattern indicates substantial input of recent meteoric water into the surface water system through such processes as direct precipitation, surface runoff and interflow, with minimal stable isotopic fractionation. A subset of the surface water samples deviated from the GMWL, conforming to a trendline modelled as $\delta D = 5.96\ (\pm 0.25)\ \delta^{18}O - 1.79\ (\pm 1.05)$ ($R^2 = 0.79$, n = 54) (Figure 3). This trendline suggests that surface water, while primarily replenished by recent meteoric water input, experience certain degree of isotopic fractionation presumably through evaporation and/or mixing

of multiple water sources. The $\delta^{18}O$-δD signatures of lake water form a distinct endmember cluster signaling pronounced isotopic enrichment ascribed to intense evaporation associated with long residence times within lake systems.

Table 1. Descriptive Statistics of Surface water $\delta^{18}O$-δD and *d*-excess signatures

Isotopic Tracer	**N**	**Mean**	**SE Mean**	**Std Dev**	**Min**	**Median**	**Max**	**Range**
$\delta^{18}O$ ‰ VSMOW	54	–3.6	0.33	2.4	–6.9	–4.4	2.2	9.1
δD ‰ VSMOW	54	–23.1	2.06	15.1	–45.2	–27.1	15.6	60.8
d-excess ‰	54	5.5	0.89	6.6	–15.7	6.8	16.1	31.8

Isotopic Tracer	**Source Type**	**N**	**Mean**	**SE Mean**	**Std Dev**	**Min**	**Median**	**Max**	**Range**
$\delta^{18}O$ ‰ VSMOW	Lake	4	0.9	0.75	1.51	–1.3	1.4	2.1	3.4
	Reservoir	6	–2.3	0.92	2.25	–5.5	–2.1	0.2	5.7
	River	44	–4.1	0.31	2.0	-6.9	–4.5	2.2	9.1
δD ‰ VSMOW	Lake	4	9.0	2.44	4.88	4.8	7.9	15.6	10.8
	Reservoir	6	–14.4	6.11	14.96	–35.0	–12.1	2.9	37.9
	River	44	–27.2	1.72	11.4	–45.2	–30.2	1.9	47.1
d-excess ‰	Lake	4	1.8	4.65	9.3	–6.3	-0.9	15.2	21.5
	Reservoir	6	4.0	2.14	5.3	–2.4	2.3	11.7	14.1
	River	44	6.0	0.97	6.5	–15.7	7.4	16.1	31.8

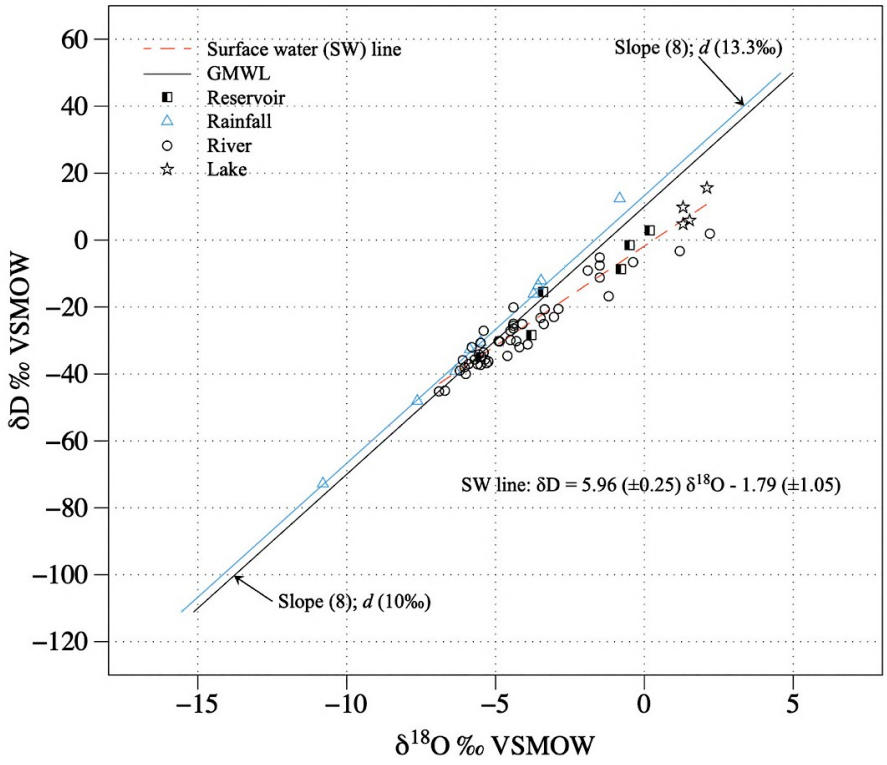

Figure 3. Distribution of δ^{18}O-δD and *d*-excess (*d*) signatures for surface water sources: river, reservoir, and lake.

3.1.2 Stable isotopic co-variability of surface water

Co-variability and distributional analysis of stable isotopic signatures of surface water revealed distinct isotopic gradients in δ^{18}O-δD and *d*-excess (d) signatures across river, reservoir, and lake samples, hinting that each type of surface water source has unique stable isotopic (Table 1; Figure 3 & 4). River water exhibits a broad spectrum of isotopic signatures, predominantly characterized by depleted δ^{18}O-δD signatures (Figure 4). This variability is likely influenced by several factors, including evaporation, baseflow contributions, local rainfall dynamics, runoff processes, and potential infiltration from adjacent lake waters (Kelly et al., 2019; Banda et al., 2019; Banda et al., 2024). The mean δ^{18}O-δD signatures for river water are relatively lower than those for both reservoirs and lakes, indicating a relative stable isotopic depletion. The wider range of *d*-excess

signatures for river water suggests that riverine flows are shaped by a combination of diverse source contributions, evaporation, and mixing dynamics of multiple source water. Reservoir water displays a more constrained spread of δ^{18}O-δD signatures, with a mean value slightly higher than that of river water but lower than that of lake water. This pattern reflects a balance between riverine inflows and evaporative processes, leading to more consistent isotopic signatures over time. Thus, reservoirs exhibit a moderate co-variability response. Lake water shows a rather most limited spread of δ^{18}O-δD and d signatures, indicating least variability relative to rivers and reservoirs. Lake water recorded highest mean δ^{18}O-δD signatures and lowest *d*-excess, indicating significant isotopic enrichment due to intense evaporative fractionation. Prolonged lake water tends retention fosters more uniform isotopic profiles over time.

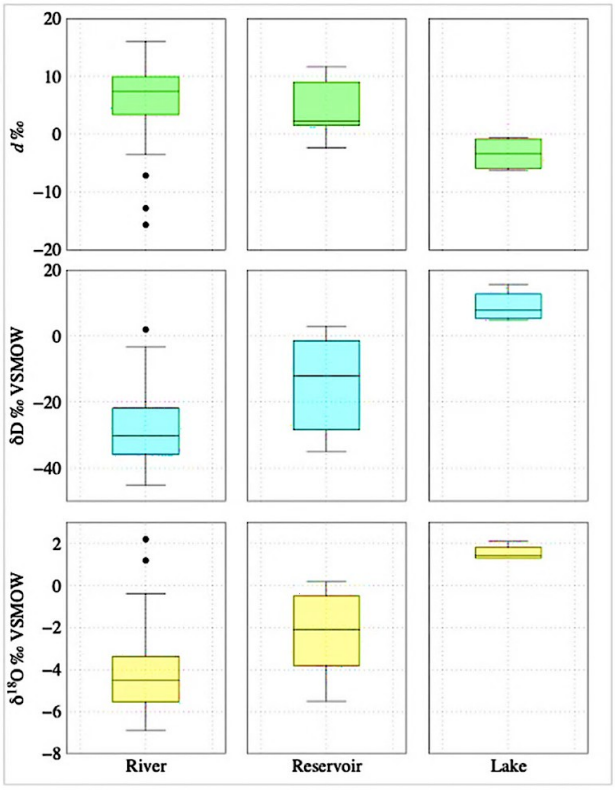

Figure 4. Co-variability of δ^{18}O-δD and *d*-excess (d) signatures for rivers, reservoirs and lakes.

3.1.3 Spatial distribution of stable Isotopes of surface water

The stable isotopic analysis of surface and groundwater across diverse terrains provided significant insights into hydrological processes in highland-plateau and lowland rift valley lakeshore plain sites. For highland-plateau sites (n = 28), $\delta^{18}O$ values range from –6.7 to +2.2‰, with a mean of –2.9‰, while δD values average –24.1‰ (Table 2). In comparison, lowland lakeshore plain sites *(*n = 26) exhibit $\delta^{18}O$ values with a mean of –22.0‰. These variations suggest that differential terrain and topography influence stable isotopic fractionation dynamics. Notably, certain surface water samples from upstream sites, particularly around dambo areas, plot below the meteoric water lines, contrasting with some lowland sites that align with these lines. Most highland groundwater samples plot along the meteoric water lines, although a subset plot above the meteoric lines, indicating potential water vapor condensation processes that produce isotopically depleted atmospheric precipitation in the highlands. Spatially, surface water displays increased isotopic depletion in upper reaches compared to middle reaches, ranging from –6.9 to +2.1‰ and from –45.2 to +15.6‰, respectively, an indication of progressive isotopic enrichment toward discharge zones. Localized isotopic enrichment in highland-plateau sites could be due to discharge of baseflow from surrounding dambo storage (Banda et al., 2024). The surface water *d*-excess demonstrates considerable spatial variation, with lower values in low-elevation areas correlating with higher evaporation rates. Higher *d*-excess values observed are predominantly associated with wet season and highland sites, while lower *d*-excess values correspond to dry season conditions, particularly in lowland areas. This observation highlights a seasonal isotopic gradient, where upland dry season sites exhibit higher isotopic values, contrasted by lower values in lowland wet season sites.

Table 2. Spatial Distribution of $\delta^{18}O$-δD and *d*-excess signatures in surface water.

Variable	Relief	N	Mean	SE Mean	Std Dev.	Min	Median	Max	Range
$\delta^{18}O$ ‰ VSMOW	Highland	28	–3.6	0.44	2.3	–6.7	–4.3	2.2	8.9
	Lowland	26	–3.6	0.50	2.6	–6.9	-4.5	2.1	9.0
δD ‰ VSMOW	Highland	28	–24.1	2.51	13.3	–45.0	-29.3	1.9	46.9
	Lowland	26	–22.0	3.34	17.1	–45.2	-26.4	15.6	60.8
d-excess ‰	Highland	28	4.3	1.41	7.5	–15.7	5.9	15.1	30.8
	Lowland	26	6.7	1.03	5.3	–6.3	7.9	16.1	22.4

3.1.4 Seasonal variability of stable isotopes of surface water

Surface water (SW) stable isotopic signatures exhibit notable variations between wet and dry seasons. During the wet season (n = 27), $\delta^{18}O$ signatures range from –6.9 to +1.5‰, with a mean value of –4.2‰, while δD signatures vary from –45.2 to 9.8‰, with a mean of –25.7‰ (Table 3; Figure 5). In contrast, during the dry season (n = 27), $\delta^{18}O$ signatures range from –6.0 to +2.2‰, with a mean of –2.9‰, and δD values extend from –38.0 to +15.6‰, averaging +20.4‰. These differences suggest that SW is relatively more enriched during the dry season compared to the wet season. The SW line for the wet season is described as $\delta D = 6.50\ (\pm 0.27) + 1.81\ (\pm 1.30)$, exhibiting a slope that, while larger than that for the dry season, remains smaller than for local, regional, and global precipitation. The consistently lower slopes observed in both wet and dry seasons, compared to those for meteoric water lines, indicate isotopic enrichment influence likely from evaporation. The wet season exhibits a narrow interquartile range (IQR = +4.1‰) for SW *d*-excess compared to dry season IQR of +7.5. This wet season low isotopic variability suggest a predominance of precipitation input with minimal isotopic fractionation influence (Table SM5; Figure 6b). The dry season is characterized by a significantly wider d-excess distribution, along with notable outliers, pointing to influence of diverse inflow sources coupled with enhanced evaporation processes

affecting the SW system. This pattern is further corroborated by the isotopic signatures of δ^{18}O-δD, which reveal a narrower IQR and lower median values during the wet season compared to the dry season IQR values (Table SM 5). These observations imply that wet season isotopic signatures of SW are largely influenced by depleted input meteoric waters, but with limited evaporative effects, while during the dry season, the SW isotopic signatures are largely influenced by a complex mix of evaporation and contributions from multiple water sources. The elevated medians and broader IQR for δ^{18}O-δD signatures observed in the dry season reinforce evidence of substantial variability, likely driven by intense evaporation and diverse water inputs. These findings underscore contrasting hydrological dynamics between wet and dry seasons. The wet season is characterized by consistent stable isotopic profiles and reduced variability, indicative of consistent source water inputs. In contrast, the dry season is marked by pronounced variability, particularly in δ^{18}O values, reflecting increased evaporation rates and multiple source water inputs.

Table 3. Seasonal variability of surface water δ^{18}O-δD and *d*-excess (d) signatures.

Isotopic Tracer	Season	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
δ^{18}O ‰ VSMOW	Dry	27	–2.9	0.46	2.4	–6.0	–3.5	2.2	8.2
	Wet	27	–4.2	0.44	2.3	–6.9	–5.2	1.5	8.4
δD ‰ VSMOW	Dry	27	–20.4	2.83	14.7	–38.0	–25.1	15.6	53.6
	Wet	27	–25.7	2.94	15.3	–45.2	–30.2	9.8	55.0
d-excess ‰	Dry	27	2.8	1.37	7.1	–15.7	2.2	15.2	30.9
	Wet	27	8.2	0.90	4.6	–6.3	8.9	16.1	22.4

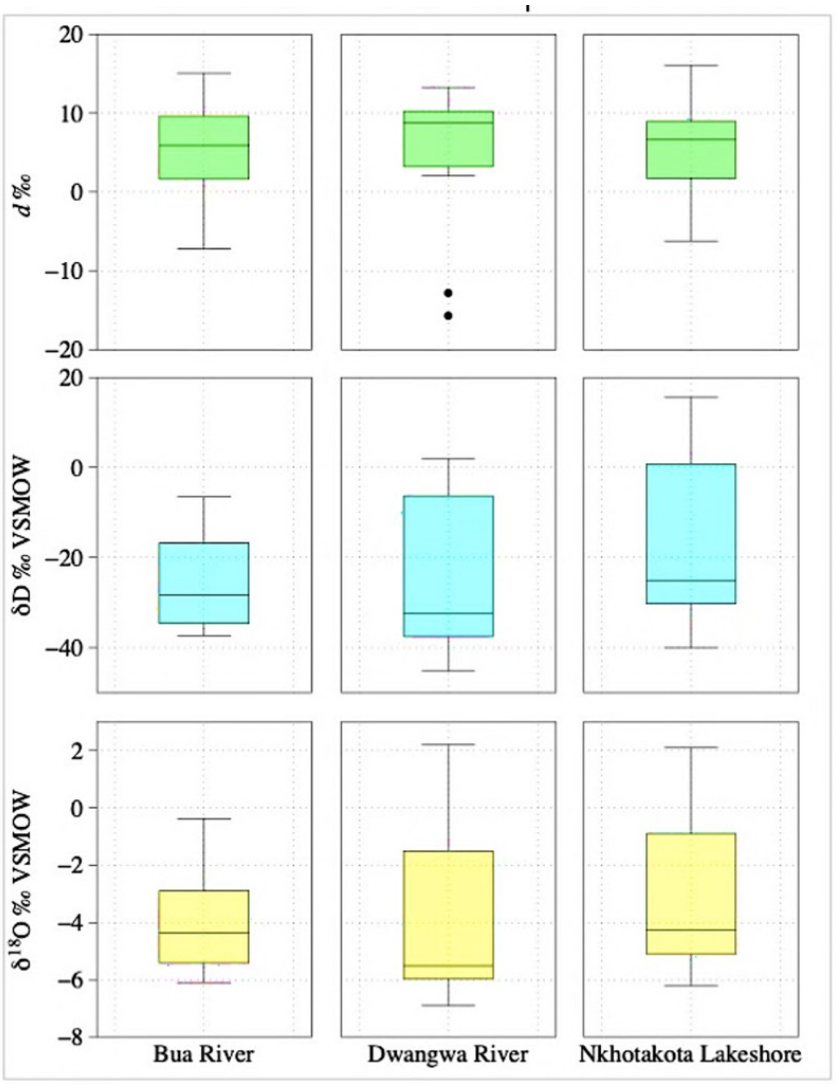

Figure 5. Spatial distribution δ^{18}O-δD and *d*-excess (*d*) signatures across different catchments.

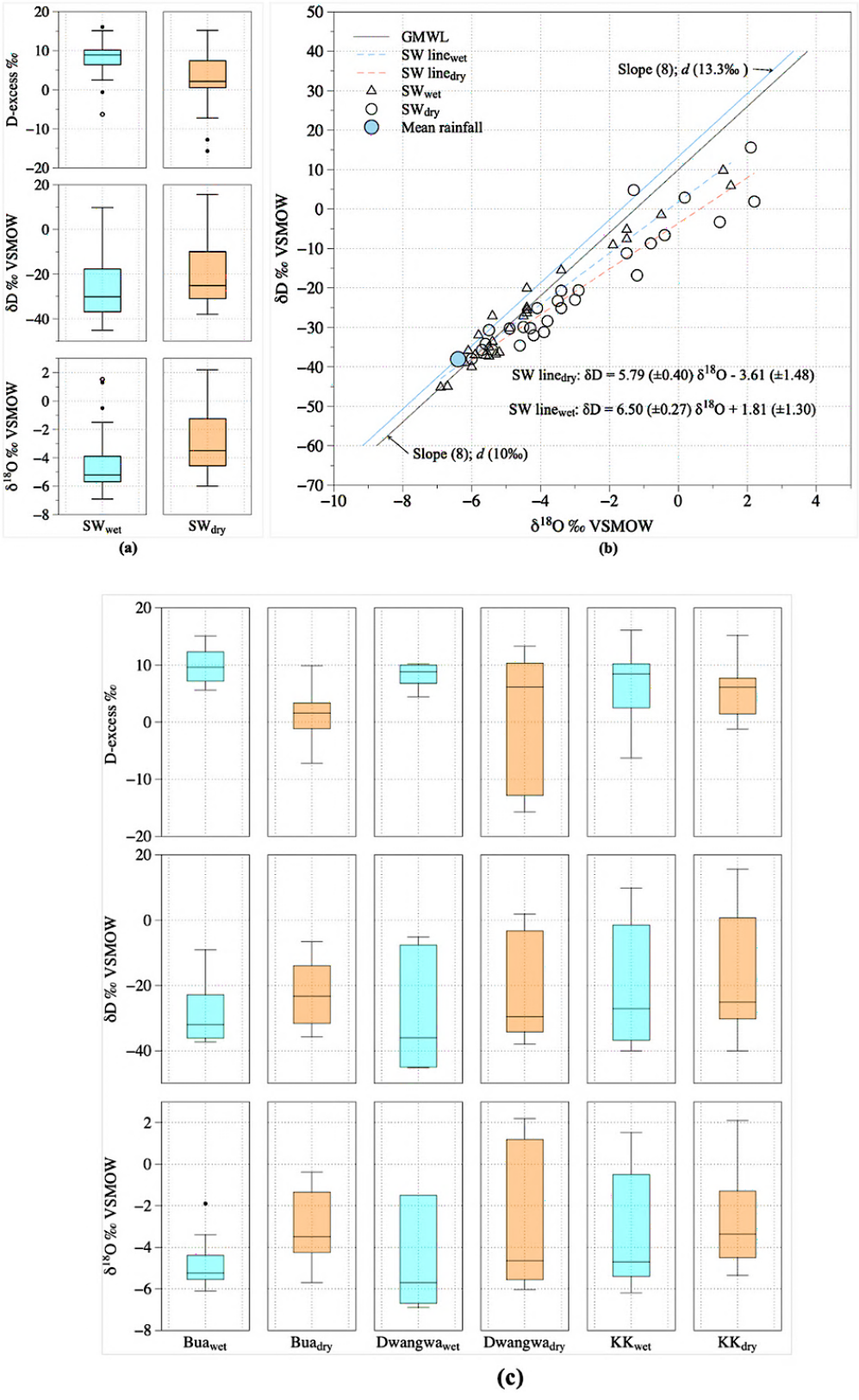

Figure 6. Seasonal variation of surface water $\delta^{18}O$-δD and *d*-excess signatures

3.1.5 Stable isotopic characteristics of groundwater

The stable isotopic signatures of $\delta^{18}O$ and δD for groundwater (GW) samples (n = 89) show considerable variability, with δD ranging from –45.2 to -18.3‰ (mean: –34.7‰) and $\delta^{18}O$ from –6.9 to –4.0‰ (mean: –5.6‰) (Figure 7a; Table 4). The δD range spans +26.9‰, while $\delta^{18}O$ varies by +2.9‰, suggesting GW recharge occurring through distinct meteoric water inputs over varying time scales. GW mean *d*-excess is +10.3‰, closely aligning with the global precipitation average of +10‰, indicating that the sampled GW is predominantly of meteoric origin, mainly influenced by modern precipitation recharge. The outliers in GW d-excess values suggest that local precipitation may influenced by condensation effect before recharging GW, a pattern typical of highland environments with cool climates (Figure 7a). This could also imply GW recharge events influenced by historical climate variations. The relationship between $\delta^{18}O$ and δD for GW, determined through least squares linear regression, is defined as: $\delta D = 7.0 (\pm 0.4) \delta^{18}O + 4.6 (\pm 2.2)$, with an R^2 value of 0.79 (Figure 7b). While the slope is close to 8 for GMWL, mean *d*-excess for GW is less than the GMWL intercept of 10‰. This deviation indicates that, although the GW is primarily of meteoric origin, it has experienced evaporation and mixing influences, resulting in a slope slightly less than 8.

Table 4. Descriptive statistics of groundwater $\delta^{18}O$-δD and *d*-excess signatures

Isotopic Tracer	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
$\delta^{18}O$ ‰ VSMOW	89	–5.6	0.08	0.71	–6.9	–5.8	–4.0	2.9
δD ‰ VSMOW	89	–34.7	0.59	5.6	–45.2	–35.9	–18.3	26.9
D-excess ‰	89	10.3	0.29	2.7	1.6	10.4	18.6	17.0

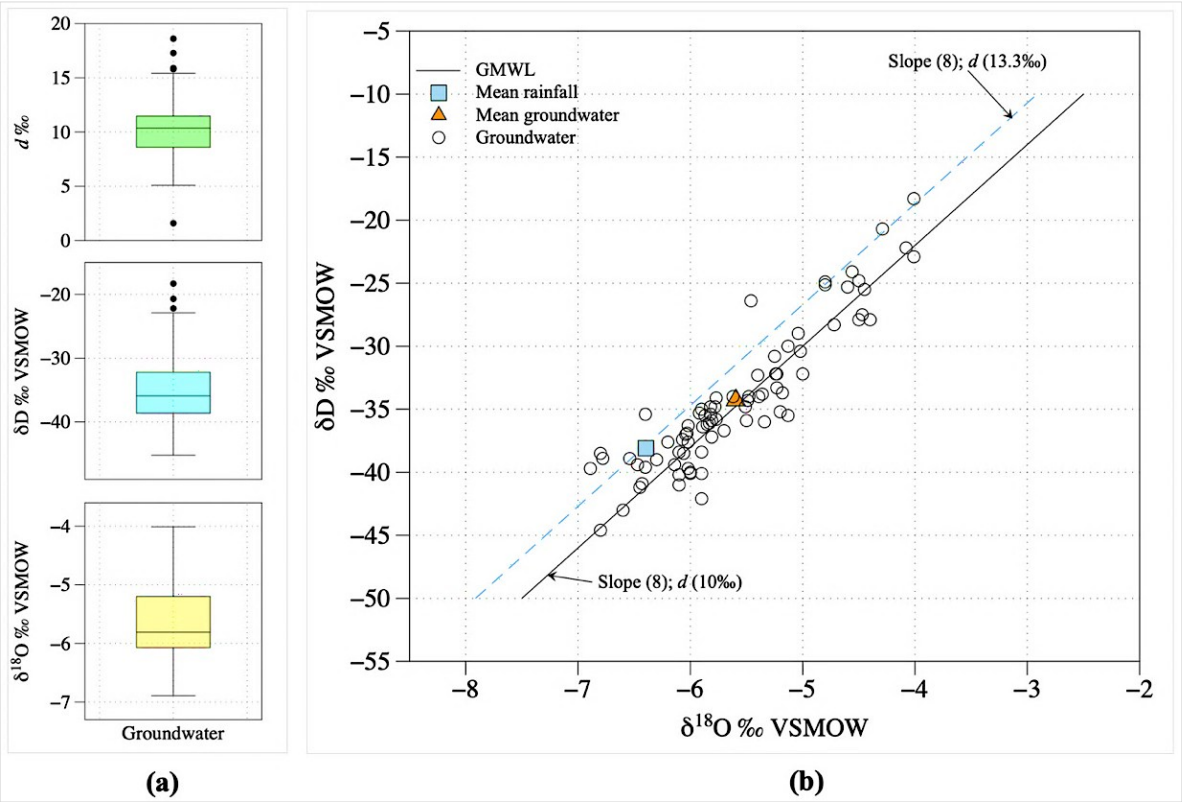

Figure 7. (a) Distribution of δ^{18}O-δD and *d*-excess (*d*) signatures in groundwater and (b) Bi-variate plot of δ^{18}O-δD signatures in groundwater across the Lake Malawi sub-basin II.

3.2 Groundwater and surface water dynamics

The SW line modelled as δD = 5.96 (±0.25) δ^{18}O – 1.79 (±1.05), while the GW line is modelled as δD = 7.0 (± 0.4) δ^{18}O + 4.6 (± 2.2), with nearly identical slopes, but lower than 8 for GMWL. This observation suggests isotopic attenuation of initial input meteoric water prior and/or post recharge process. The SW line slope greater than GW line slope indicate intense evaporation effect on SW compared to the GW. Furthermore, the evaporation and/or mixing lines, characterizing SW samples, demonstrate that the dry season slope (5.8) is smaller than that during the wet season (6.5) (Figure 8b). This differential slopes reinforce the idea of intensified evaporation during the dry season compared to the wet season, and also a close relationship between wet season

SW and SW. Also, clustering of groundwater δD and $\delta^{18}O$ along the meteoric water lines imply that groundwater primarily derives from modern precipitation recharge, with minimal influences from evaporation or condensation processes. Overall, the findings provide critical evidence of pronounced evaporation effect on surface water, while highlighting consistent recharge isotopic signal in groundwater.

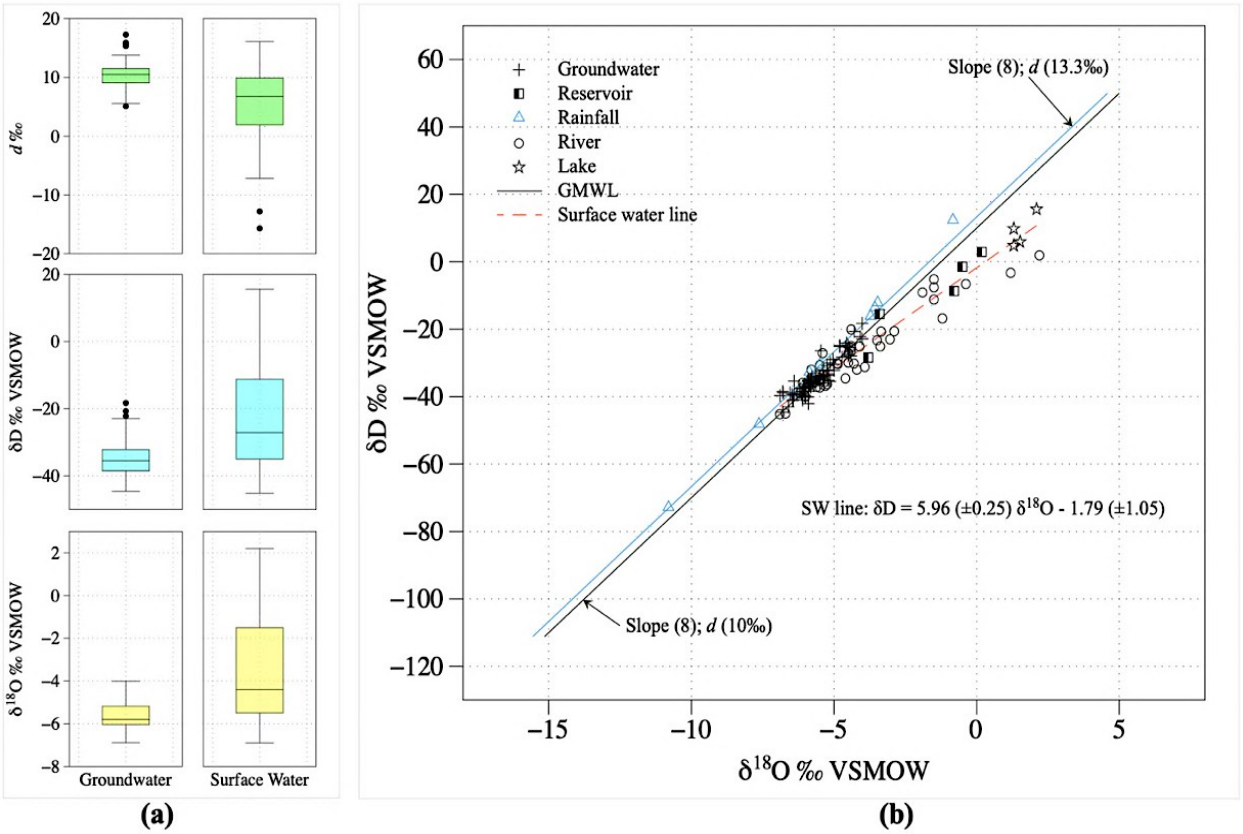

Figure 8. (a) Distribution of $\delta^{18}O$-δD and *d*-excess signatures in for groundwater and surface water, and (b) Bi-variate plot of $\delta^{18}O$-δD signatures in groundwater and surface water across the Lake Malawi sub-basin II

3.3 Hydrochemical results

The hydrochemical results and their descriptive statistics for groundwater in the study area are presented in Table 5; Tables SM 7-9, respectively. The results presented are on the hydrochemical characteristics and classification of hydrochemical facies.

3.3.1 Hydrochemical characteristics

Groundwater (GW) pH (n =147) ranged from 4.5 to 9.4, with a mean value of 7.0 and median of 7.0 (Table 5). A total of 79 GW samples (53.7%) were alkaline, while 68 GW samples (46.3%) were acidic. Spatially, the mean pH values across different WRAs and physiographical zones are predominantly alkaline (Table 5; Table SM 8&9). Of the total 147 GW samples, 119 are within the World Health Organisation (WHO) recommended guidelines limits of 6.5-8.5 for drinking water quality, while 28 GW samples did not comply, representing 81% compliance rate (WHO chronicle., 2011). The groundwater noncompliance with the WHO Guidelines was mainly due to elevated acidity (n = 26) relative to alkalinity (n = 2). Electrical conductivity (EC), a proxy indicator of total dissolved salts TDS, range from 48 to 4,009 μS/cm, with a mean of 847 μS/cm and a median of 712 μS/cm. A total of 94 GW samples recorded measured TDS values < 600 mgL^{-1}, falling within the WHO recommended guidelines for drinking water of good taste, while 53 GW samples recorded measured TDS values > 600 mgL^{-1} (WHO chronicle., 2011). Out of the 147 GW samples analysed, only 11 recorded measured TDS values > 1000 mgL^{-1} which might cause objectionable taste, especially when consumed for the first time.

Analysis of mean concentration of the GW hydrochemistry showed the following major ionic dominance trend HCO_3^- (4.796 $meqL^{-1}$) > Cl^- (1.884 $meqL^{-1}$) > SO_4^{2-} (1.519 $meqL^{-1}$) for anions and Ca^{2+} calcium (3.300 $meqL^{-1}$) > Na^+ (2.970 $meqL^{-1}$) > Mg^{2+}) (1.970 $meqL^{-1}$) for cations (Figure 9a). Spatial distribution of GW concentration indicates progressive mineral enrichment

from highland-recharge areas through the plateaus onto the rift valley escarpment, slightly decreasing along the rift valley plain where evidence of groundwater-surface water mixing is reported (Table SM 9). This conventional geochemical evolution trend is disrupted with convergence of highland plateau and rift margin hydrologic system, with potential mixing of headwaters-recharging water in the rift valley escarpment (Banda et al, 2024-in review). At catchment-scale, GW samples from the Nkhotakota lakeshore catchment (WRA 15) are more mineralized, followed by Dwangwa River catchment, and then Bua River catchment (Table SM 8).

Table 5. Descriptive statistics of groundwater hydrochemistry in Lake Malawi sub-basin II.

Variable	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range	IQR
pH	147	7.0	0.06	0.74	4.5	7.0	9.4	4.9	0.93
EC, μS/cm	147	847	60.0	727	48	712	4009	3961	864
TDS, mgL^{-1}	147	480	34	414	25	380	2389	2364	541
HCO_3^-, mgL^{-1}	147	293	21	254	9.0	245	1900	1891	345
Cl, mgL^{-1}	147	66.8	8.1	97.8	2.7	37.0	896	893	58.8
SO_4^{2-}, mgL^{-1}	147	72.9	10.1	123	0.1	21.8	790.0	790	59.9

3.3.2 Hydrochemical facies

A Piper plot was utilized to investigate the hydrogeochemistry of groundwater, revealing distinct hydrogeochemical facies based on the dominant cations and anions (Piper., 1944). This analysis provided insights into the hydrogeochemical profiles of groundwater in the study area and highlighted role of minerals in surrounding rock matrix on groundwater chemistry along GW flow bath flow path. The hydrogeochemical facies analysis identified five groundwater types: (1) Ca-Mg-HCO_3, (2) Ca-Mg-SO_4, (3) Na-Cl, (4) Ca-Mg-SO_4-Cl, and (5) Na-HCO_3-Cl (Figure 8b).

The most common type, Ca-Mg-HCO_3, represented 80.8% of the samples, whereas the mixed water types (Groups 4 and 5) accounted for 14.4%. This dominance indicates that groundwater chemistry evolves during recharge through interactions with primary silicate minerals and secondary carbonates, as well as with high-Mg Dolomitic carbonate rocks. Occurrence of mixed groundwater type (Ca-Mg-SO_4-Cl and Na-HCO_3-Cl) suggest that groundwater chemistry is influenced by mixing dynamics.

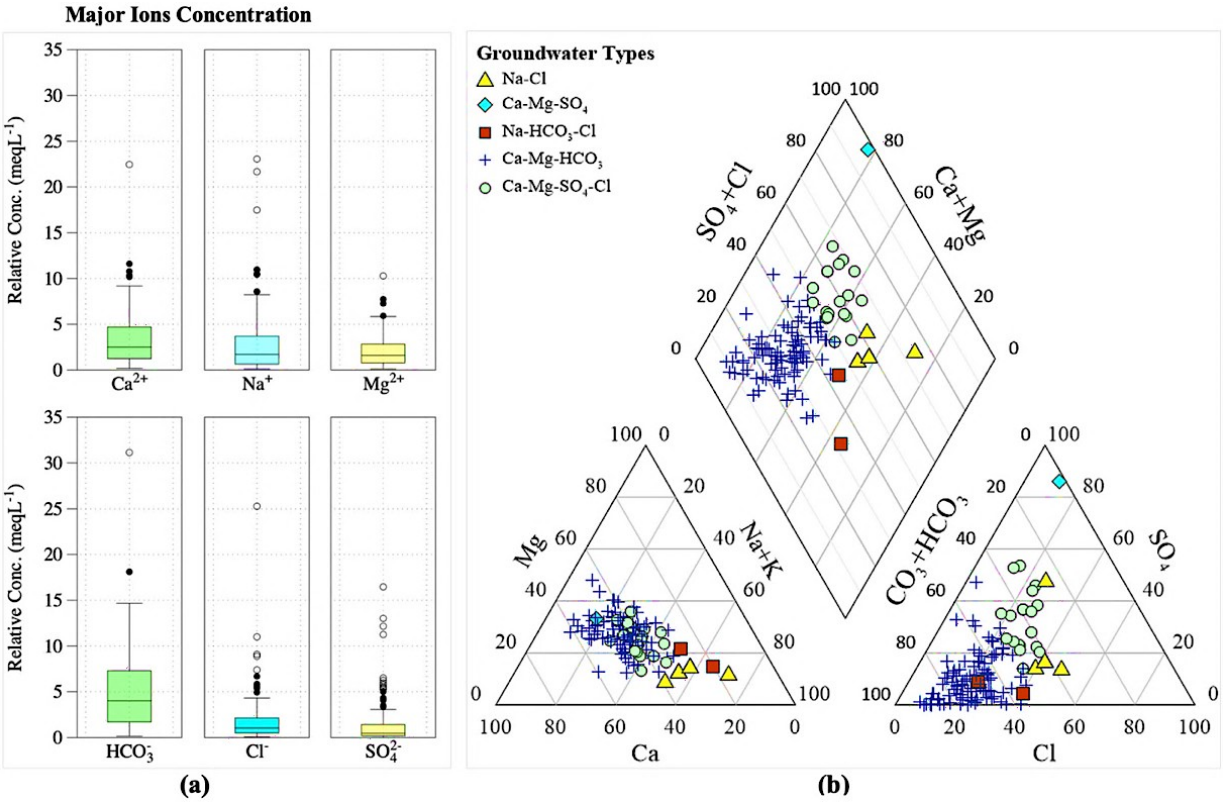

Figure 9. Relative abundance of major ions concentration and classification of hydrochemical facies of groundwater.

4. Discussion

The significant isotopic enrichment in lake water (higher $\delta^{18}O$ and δD values) suggests prolonged evaporation and longer residence times. This is typical for closed or semi-closed water bodies where evaporation exceeds inflow, leading to higher isotopic ratios (Wu et al., 2015;

Gibson., 2002). Reservoirs and rivers show broader isotopic ranges, indicating a mix of sources and processes. Reservoirs, with intermediate enrichment, likely experience both evaporation and inflow from various sources (Dasgupta et al., 2024; Yang et al., 2019). Rivers, with the widest range, reflect diverse contributions from precipitation, runoff, and possibly groundwater inputs (Nan et al., 2019; Halder et al., 2015). The alignment of most surface water samples with the GMWL and LMWL indicates that recent local precipitation is a major contributor to these water bodies. This suggests minimal isotopic fractionation during processes like direct precipitation, runoff, and interflow (Banda et al., 2019, 2020). The subset of samples deviating from the meteoric water lines (following a different trendline) suggests isotopic fractionation due to evaporation or mixing of multiple water sources. This deviation highlights the complexity of hydrological processes affecting surface water isotopic composition (Banda et al., 2024; Brady et al., 2019; Kendall and J. J. McDonnell., 1998). The distinct isotopic signatures across different water bodies underscore the influence of various hydrological processes. For instance, lakes show significant evaporation effects, reservoirs reflect mixed influences, and rivers capture a broad spectrum of hydrological inputs. Understanding these isotopic distinctions can aid in water resource management, helping to identify sources of water, track changes in hydrological processes, and manage the impacts of climate variability on water resources (Cole and Boutt., 2021).

5. Policy implication

1. Monitor isotopic enrichment in lake waters to gauge evaporation rates and residence times. Use this data to manage lake water levels and quality, particularly during dry seasons.

2. Align river and reservoir isotopic signatures with meteoric water lines to confirm substantial groundwater recharge. Implement protective measures for recharge areas to maintain groundwater levels.
3. Use isotopic data to understand how water bodies respond to changes in precipitation and temperature. Develop strategies to mitigate the impacts of climate change on water availability and quality.
4. Analyse isotopic deviations to detect potential contamination sources. This can help identify areas where pollution might be entering the water system.
5. Differentiate between water sources and their contributions to allocate resources sustainably. Prioritize river water use during wet seasons and rely on reservoirs during dry periods.
6. Use detailed isotopic data to support decision-making in water policy and planning. Develop regulations for water extraction, protect critical water sources, and plan for future water needs.
7. Educate the community about the importance of water conservation and the impacts of human activities on water resources. Engage local communities in water management practices for more sustainable outcomes.
8. Establish a routine isotopic monitoring program to track changes in water sources and hydrological processes over time. Implement land-use policies to protect critical groundwater recharge areas from development and pollution.

By implementing these recommendations, local water management authorities can enhance the sustainability and resilience of water resources, ensuring their availability for future generations.

6. Conclusion

This study investigated the isotopic signals of meteoric water in the Lake Malawi sub-basin to elucidate the interactions between surface water and groundwater. The isotopic analysis revealed significant seasonal variations, highlighting distinct sources and processes that influence these water bodies. These findings emphasize the necessity of integrated water resource management (IWRM) in transboundary basins like Lake Malawi. By understanding isotopic signals, policymakers can develop more effective strategies for sustainable water management, addressing both environmental and socio- economic challenges. The study advances our understanding of surface water and groundwater interactions in the Lake Malawi sub-basin, contributing to the broader goal of sustainable water management in transboundary lake basins, aligning with the Sustainable Development Goals. It highlighted the co-variability in isotopic signatures across different hydrologic boundaries and topographic zones, providing a benchmark for further research in isotopic hydrology.

Key findings include:

i. Isotopic Enrichment in Lake: Lake water samples show significant isotopic enrichment, indicating prolonged residence times and substantial evaporation effects.

ii. Variability in Rivers and Reservoirs: River and reservoir samples exhibit broader isotopic ranges, reflecting the dynamic integration of various water sources and hydrological processes.

iii. Seasonal Differences: Wet season samples are relatively depleted in heavy isotopes, dominated by recent precipitation with minimal evaporative effects. In contrast, dry

season samples are enriched, suggesting increased evaporation and contributions from older water sources.

iv. Spatial Variations: Highland sites generally show more depleted isotopic values due to higher precipitation rates and lower evaporation, while lowland sites exhibit more enriched signatures, indicative of higher evaporation rates.

These findings underscore the complex interplay of precipitation, evaporation, and mixing processes in shaping the isotopic composition of surface water. The study highlights the importance of isotopic analysis in understanding regional water cycles and their responses to climatic and environmental changes.

CRediT authorship contribution statement

Limbikani Chitsundi Banda: Conceptualisation, methodology, validation, formal analysis, investigation, data curation, resources, writing—original draft preparation, writing—review and editing, project administration, funding acquisition**. Robert Michael Kalin:** Methodology, formal analysis, resources, writing—review and editing, project administration, funding acquisition**. Vernon Phoenix:** Resources, project administration, funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data Availability Statement

The research data provided in this study will be made available on reasonable request from the corresponding author.

7.3 Research Article 4: Supplementary Materials

Table SM 1. Surface Water Sampling Points

Sampling Site ID	Coordinates (Decimal degrees)		Altitude	WRA	Geographic relief
	Latitude	Longitude	m a.s.l	No.	Physiographic zone
R1	-12.787883	34.196412	504	5	Rift Valley Plain
R2	-13.918427	33.137225	1064	5	Plateau
R3	-13.470136	33.644513	1123	5	Plateau
R4	-13.802061	32.882981	1185	5	Plateau
R5	-13.490846	33.400668	1053	5	Plateau
R6	-13.433667	34.24013	523	15	Rift Valley Plain
R7	-13.462794	34.239766	525	15	Rift Valley Plain
R8	-12.882692	33.453267	963	6	Plateau
R9	-12.51549	34.114115	496	6	Rift Valley Plain
R10	-12.902546	34.285067	478	15	Rift Valley Plain
R11	-13.594501	34.312161	532	15	Rift Valley Plain
R12	-13.533856	34.283297	524	15	Rift Valley Plain
R13	-12.611465	34.16262	483	15	Rift Valley Plain
R14	-13.517332	32.949825	1082	5	Plateau
R15	-13.767368	33.043031	1082	5	Plateau
R16	-12.502933	34.10264	492	6	Rift Valley Plain
R17	-12.361137	33.549695	1440	6	Highlands
R18	-12.852144	33.298	1012	6	Plateau
R19	-13.308482	33.5477	1041	5	Plateau
R20	-14.020776	33.352958	1110	5	Plateau
R21	-13.392356	34.255749	505	15	Rift Valley Plain
R22	-13.325522	33.437603	1045	5	Plateau
D1	-13.0557	33.4692	1057	6	Plateau
D2	-13.325522	33.437603	1045	5	Plateau
D3	-13.1268	34.32518	478	15	Rift Valley Plain
L1	-12.912877	34.300357	477	15	Rift Valley Plain
L2	-13.716	34.629	475	15	Rift Valley Plain
MNIP2	-13.75402	34.58439	513	15	Rift Valley Plain
MNIP4	-11.415204	33.995268	1287	8	Plateau

Table SM 2: Surface Water $\delta^{18}O$-δD and *d*-excess signatures of Wet-Dry Seasons

Sampling Site ID	$\delta^{18}O$ ‰ VSMOW		δD ‰ VSMOW		*d*-excess (*d*) ‰	
	Wet	Dry	Wet	Dry	Wet	Dry
R1	-4.4	-2.9	-25.6	-20.6	9.6	2.5
R2	-5.5	-4.3	-37.3	-30.2	6.7	4.2
R3	-4.4	-1.5	-20.1	-11.2	15.1	0.8
R4	-5.6	-4.6	-37.1	-34.6	7.7	2.2
R5	-4.4	-3.5	-26.4	-23.3	8.8	4.6
R6	-6.0	-5.4	-40.0	-35.7	8.0	7.1
R7	-6.2	-4.9	-39.0	-30.3	10.6	8.6
R8	-1.5	2.2	-7.6	1.91	4.4	-15.7
R9	-6.9	-5.5	-45.2	-30.7	10	13.3
R10	-4.4	-3.4	-25	-20.7	10.2	6.1
R11	-4.5	-3.0	-27.1	-23	8.9	1.3
R12	-5.3	-4.5	-36.8	-29.9	5.6	6.1
R13	-5.4	-4.1	-27.1	-25.1	16.1	7.7
R14	-6.1	-5.7	-35.9	-35.7	12.9	9.9
R15	-5.8	-3.9	-32	-31.2	14.4	0.2
R16	-5.9	-5.6	-37	-34.2	10.2	10.3
R17	-6.7	-6.0	-45	-38	8.6	10.3
R18	-1.5	1.2	-5.2	-3.3	6.8	-12.8
R19	-5.4	-1.2	-33.6	-16.8	9.6	-7.2
R20	-5.2	-4.2	-36.3	-32	5.6	1.6
R21	-4.9	-3.4	-30.2	-25.1	9	1.9
R22	-1.9	-0.4	-9.1	-6.6	6.1	-3.6
D1	-5.5	-3.8	-35	-28.4	9	2.0
D2	-3.4	-0.8	-15.5	-8.7	11.7	-2.4
D3	-0.5	0.2	-1.5	2.9	2.5	1.5
L1	1.3	2.1	9.8	15.6	-0.6	-1.2
L2	1.52	-1.3	5.9	4.8	-6.3	15.2

Surface Water – Descriptive Statistics

Table SM 3

Variable	N	Mean	SE Mean	StD Dev	Max	Median	Min	Max
$\delta^{18}O$ ‰ VSMOW	54	-3.567	0.331	2.429	2.200	-4.400	-6.900	2.200
δD ‰ VSMOW	54	-23.06	2.06	15.11	15.60	-27.10	-45.20	15.60
d-excess ‰	54	5.478	0.892	6.556	16.100	6.750	-15.690	16.100

The data contain at least five mode values. Only the smallest four are shown.

Table SM 4

Variable	Source Type	N	Mean	SE Mean	StD Dev	Median	Min	Max	Range	IQR
$\delta^{18}O$ ‰ VSMOW	Dam	4	-3.373	0.974	1.948	-3.600	-5.500	-0.790	4.710	3.633
	Lagoon	2	-0.16	0.340	0.481	-0.160	-0.500	0.180	0.680	*
	Lake	4	0.905	0.754	1.508	1.410	-1.300	2.100	3.400	2.605
	River	44	-4.146	0.305	2.025	-4.500	-6.900	2.200	9.100	2.188
δD ‰ VSMOW	Dam	4	-21.90	5.98	11.96	-21.95	-35.00	-8.70	26.30	22.95
	Lagoon	2	0.70	2.20	3.11	0.70	-1.50	2.90	4.40	*
	Lake	4	9.03	2.44	4.88	7.85	4.80	15.60	10.80	9.07
	River	44	-27.16	1.72	11.41	-30.20	-45.20	1.91	47.11	14.57
d-excess ‰	Dam	4	5.07	3.22	6.45	5.50	-2.40	11.70	14.10	12.32
	Lagoon	2	1.980	0.520	0.735	1.980	1.460	2.500	1.040	*
	Lake	4	1.79	4.65	9.30	-0.90	-6.26	15.20	21.46	16.24
	River	44	6.009	0.976	6.472	7.400	-15.690	16.100	31.790	7.035

Table SM 5

Variable	Season	N	Mean	SE Mean	StD Dev	Variance	Min	Median	Range	IQR
$\delta^{18}O$ ‰ VSMOW	Dry	27	-2.9	0.462	2.4	5.769	-6.0	-3.490	8.2	3.400
	Wet	27	-4.2	0.444	2.3	5.316	-6.9	-5.240	8.4	2.400
δD ‰ VSMOW	Dry	27	-20.4	2.83	14.7	216.31	-38.0	-25.10	53.6	22.50
	Wet	27	-25.7	2.94	15.3	233.96	-45.2	-30.20	55.0	21.50
d-excess ‰	Dry	27	2.8	1.37	7.1	50.67	-15.7	2.20	30.9	7.54
	Wet	27	8.2	0.895	4.6	21.608	-6.3	8.900	22.4	4.100

GROUNDWATER DESCRIPTIVE STATISTICS

Table SM 6

Variable	N	Mean	SE Mean	StD Dev	Min	Median	Max	Range
δD ‰ VSMOW	89	-34.748	0.593	5.593	-45.200	-35.900	-18.300	26.900
$\delta^{18}O$ ‰ VSMOW	89	-5.6285	0.0751	0.7089	-6.8900	-5.8100	-4.0100	2.8800
d-excess ‰	89	10.282	0.285	2.684	1.600	10.400	18.600	17.000

Table SM 7: Descriptive Statistics: GW Chem

Variable	N	Mean	SE Mean	StD Dev	Min	Median	Max	Range	IQR
pH	147	7.0318	0.0608	0.7377	4.5000	7.0300	9.4200	4.9200	0.9300
EC	147	847.0	60.0	727.2	48.0	712.0	4009.0	3961.0	864.0
TDS	147	480.1	34.1	414.0	25.0	380.0	2389.0	2364.0	541.0
HCO_3	147	292.6	21.0	254.3	9.0	245.0	1900.0	1891.0	345.0
Cl	147	66.81	8.07	97.81	2.70	37.00	896.00	893.30	58.80
SO_4	147	72.9	10.1	122.7	0.1	21.8	790.0	789.9	59.9
pCO_2	147	1.12	1.08	13.06	0.00	0.02	157.84	157.84	0.03

Table SM 8: Descriptive Statistics: GW Chem

Variable	WRA		Mean	SE Mean	StD Dev	Min	Q1	Median	Max	Range	IQR
pH	5	57	7.016	0.127	0.962	4.500	6.485	6.890	9.420	4.920	1.155
	6	45	7.0462	0.0860	0.5770	5.7800	6.6300	7.0600	8.4600	2.6800	0.8550
	15	45	7.0376	0.0810	0.5436	5.7900	6.7300	7.0400	8.3000	2.5100	0.6950
EC	5	57	800	121	911	71	249	434	4009	3938	532
	6	45	866.6	76.7	514.2	48.0	466.0	766.0	2486.0	2438.0	801.5
	15	45	887.3	97.7	655.4	73.0	193.0	1046.0	3380.0	3307.0	996.5
TDS	5	57	437.1	66.5	501.8	36.0	138.0	234.0	2389.0	2353.0	283.0
	6	45	499.6	46.3	310.4	25.0	248.0	428.0	1505.0	1480.0	514.0
	15	45	515.1	57.3	384.7	39.0	112.0	605.0	2028.0	1989.0	597.0
HCO_3	5	57	255.2	43.1	325.1	9.0	76.0	173.0	1900.0	1891.0	189.5
	6	45	316.9	26.5	177.9	21.0	161.5	292.0	750.0	729.0	287.5
	15	45	315.7	31.8	213.2	17.0	94.0	399.0	745.0	728.0	373.5
Cl	5	57	69.6	18.1	136.5	6.2	17.1	26.6	896.0	889.8	35.0
	6	45	70.05	9.50	63.71	2.70	32.95	47.30	322.16	319.46	62.35
	15	45	60.06	9.30	62.37	3.77	12.35	52.00	315.00	311.23	67.65
SO_4	5	57	74.7	17.4	131.7	0.1	10.6	19.8	625.0	624.9	55.4
	6	45	57.3	11.5	77.3	0.1	7.0	25.6	266.6	266.5	74.1
	15	45	86.2	21.8	146.5	0.4	10.4	44.1	790.0	789.6	63.1
pCO_2	5	57	2.81	2.77	20.90	0.00	0.00	0.02	157.84	157.84	0.03
	6	45	0.04409	0.00798	0.05352	0.00116	0.01020	0.02873	0.22717	0.22601	0.04238
	15	45	0.02136	0.00425	0.02816	0.00004	0.00318	0.00845	0.11397	0.11393	0.02739

Table SM 9: Descriptive Statistics: GW Chem

Variable	Physio- Zone	N	Mean	SE Mean	StD Dev	Min	Q1	Median	Max	Range	IQR
pH	Highlands	2	7.255	0.565	0.799	6.690	*	7.255	7.820	1.130	*
	Plateau	96	7.0381	0.0843	0.8256	4.5000	6.5200	7.0300	9.4200	4.9200	1.0600
	Rift Valley Scarp	10	7.277	0.136	0.430	6.760	6.848	7.255	7.900	1.140	0.845
	Rift Valley Plain	39	6.9418	0.0876	0.5474	5.7900	6.5900	6.9500	8.3000	2.5100	0.8100
EC	Highlands	2	531	232	329	298	*	531	763	465	*
	Plateau	96	822.6	79.1	775.3	48.0	310.8	590.0	4009.0	3961.0	758.3
	Rift Valley Scarp	10	1083.6	16.6	52.5	1014.0	1038.0	1079.5	1162.0	148.0	88.0
	Rift Valley Plain	39	863	114	710	73	160	990	3380	3307	1121
TDS	Highlands	2	270	113	161	156	*	270	383	227	*
	Plateau	96	459.8	44.5	435.6	25.0	160.3	317.0	2389.0	2364.0	462.8
	Rift Valley Scarp	10	613.3	12.9	40.9	556.0	578.5	620.5	673.0	117.0	67.0
	Rift Valley Plain	39	506.8	66.9	417.8	39.0	96.0	605.0	2028.0	1989.0	673.0
HCO_3	Highlands	2	226	150	211	76	*	226	375	299	*
	Plateau	96	278.8	28.0	274.2	9.0	106.3	211.5	1900.0	1891.0	302.8
	Rift Valley Scarp	10	405.3	32.8	103.9	265.0	270.0	432.5	550.0	285.0	207.4
	Rift Valley Plain	39	301.3	36.7	229.5	17.0	48.0	292.0	745.0	728.0	438.0
Cl	Highlands	2	23.0	12.8	18.0	10.2	*	23.0	35.7	25.5	*
	Plateau	96	71.6	11.5	113.1	2.7	19.3	35.0	896.0	893.3	64.5
	Rift Valley Scarp	10	74.5	11.3	35.7	24.5	43.6	73.4	124.0	99.5	63.6
	Rift Valley Plain	39	55.3	10.3	64.4	3.8	11.6	37.0	315.0	311.2	58.4
SO_4	Highlands	2	26.5	19.7	27.9	6.8	*	26.5	46.2	39.4	*
	Plateau	96	66.5	11.6	113.2	0.1	8.3	19.8	625.0	624.9	59.7
	Rift Valley Scarp	10	95.5	25.8	81.5	19.9	44.8	58.5	241.0	221.1	108.5
	Rift Valley Plain	39	85.2	24.6	153.9	0.4	8.7	36.5	790.0	789.6	58.5
pCO_2	Highlands	2	0.0381	0.0369	0.0522	0.0012	*	0.0381	0.0750	0.0738	*
	Plateau	96	1.69	1.64	16.11	0.00	0.01	0.02	157.84	157.84	0.04
	Rift Valley Scarp	10	0.0049	0.00162	0.00487	0.00080	0.0021	0.0035	0.0171	0.0163	0.0033
	Rift Valley Plain	39	0.0287	0.00506	0.03160	0.00004	0.0054	0.0198	0.1140	0.1139	0.0307

7.4 Research Article 5: Main Paper

Seasonal and Spatial Dynamics of Surface Water and Groundwater in South Rukuru/North Rumphi River and Nkhata Bay Lakeshore Catchments: Implications for Integrated Water Resource Management.

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Abstract: This study characterised seasonal and spatial changes in δD-δ^{18}O and *d*-excess of surface water and groundwater in a Lake Malawi sub-basin covering the South Rukuru-North Rumphi Rivers and Nkhata Bay lakeshore catchments. Sampled water sources include rivers, lakes, reservoirs, springs, dug-wells and boreholes. The study found remarkable differences in δD-δ^{18}O signatures, largely in surface water compared to groundwater. For surface water, river water showed a broad spectrum of δD-δ^{18}O signatures, while mirroring contributions from fresh meteoric water input. Lake water, followed by reservoir water, show strong evidence of evaporative enrichment, highly retained both in wet and dry seasons. The δD-δ^{18}O signatures in GW show a limited spread that corresponds to defined groundwater recharge input. The δD-δ^{18}O signatures in surface water-groundwater mostly align with global meteoric water signal, suggesting of recent meteoric water input with minimal evaporation rate. The *d*-excess signal for

surface water-groundwater derived from meteoric water input indicate influence of mixed and contrasting air moisture origin, predominantly oceanic source, but with notable contribution from recycled air moisture. Seasonal shift in SWL isotopic gradients for surface water-groundwater indicate progressive evaporative enrichment occurring from wet to dry seasons. The wet season is highly characterised by isotopic depletion alongside a high *d*-excess signal, while the dry season is highly characteristic of isotopic enrichment and a low *d*-excess signal. Spatial shift in isotopic gradients occurring from west-east of the basin depict progressive enrichment, but with localised isotopic disparities. This study has successfully developed, for the first time, a transformative isotopic baseline critical for water resources monitoring and future isotope-based water research in the Lake Malawi basin and the wider region.

Key words: stable isotopes; *d*-excess; Lake Malawi; seasonal-spatial variability, groundwater-surface water interaction.

1. Introduction

The Lake Malawi sub-basin, which includes the South Rukuru River and Nkhata Bay Lakeshore catchments, is crucial for the socio-economic development of Malawi and has become a key centre for hydrological research. In recent times, this sub-basin has experienced mounting environmental pressures, mainly due to intensified agricultural practices that involve excessive fertilizer use, coupled with a rapidly growing population. These factors have heightened concerns about water quality, particularly nitrate contamination in groundwater .

On a global scale, the unsustainable extraction of groundwater has led to significant reductions in aquifer volumes, posing serious threats to water security. This issue is acutely critical in Malawi, where about 65% of the population depends heavily on groundwater for their

daily needs (Jasechko & Perrone, 2021). The challenge of overexploitation, often exceeding natural recharge rates, highlights an urgent need for a more profound understanding of how water systems interact considering, considering abstraction and recharge mechanisms. Recent studies have underscores significant research gaps on water systems replenishment and how they vary at spatial and temporal scales (Jasechko et al., 2024; Banda et al., 2024). The erratic nature of precipitation patterns and unpredictability in surface water trends are exacerbated by climatic effects, presenting major challenges in managing water resources, especially when it comes to large-scale irrigated agriculture and rural gravity-fed water supply schemes (Kalin et al., 2022).

It is essential to have a thorough understanding of hydrological processes across different catchments, as highlighted by extensive previous research (Monjerezi, 2012; Monjerezi et al., 2011, 2012; Monjerezi & Ngongondo, 2012; Rivett et al., 2018). Building on this foundational knowledge, this study aims to enhance transformative understanding that not only clarifies conceptual perspectives on water resource systems but also informs water policy through integrated water resources management (IWRM). Specifically, this research seeks to establish a for the first time, a baseline characterisation of $\delta^{18}O$-δD signatures for both groundwater and surface waters within the Lake Malawi sub-basin III. By analysing variability of these signals across various catchments, this study seeks to identify source and process controls, thereby improving management of water resources in response to increased land-use changes and climatic variability. This effort is crucial for developing future strategies in water resource management, supporting sustainability of the sub-basin's vital water resource under changing climatic conditions.

2. Study area description

The study area encompasses the South Rukuru/North Rumphi River and Nkhata Bay Lakeshore catchments. These catchments collectively form what is referred to as Lake Malawi sub-basin III, covering ca. 18,252 km². This area lies within the Malawian territory of the broader Lake Malawi basin (GoM, 2017). Located within the East African Rift System (EARS), Lake Malawi sub-basin 2 serves as a transboundary water resource shared by Malawi, Tanzania, Mozambique, and Zambia (Banda et al., 2024; Fraser et al., 2020; Kalin et al., 2022).

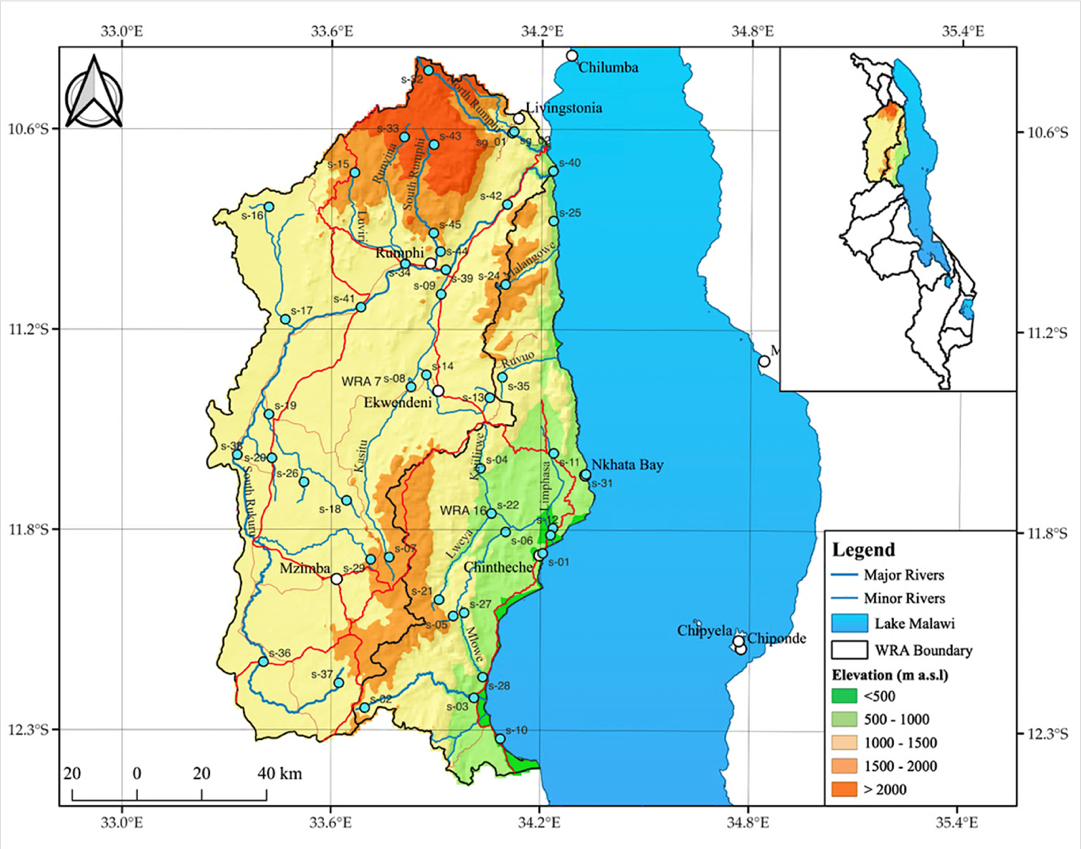

Figure 1. Study area extent of Lake Malawi sub-basin III (WRA 7 and WRA 16) depicting topographic spread (SRTM elevation data: USGS), water resource areas (WRAs), major rivers and associated sampling points.

2.1 Riverine drainage network

The Lake Malawi sub-basin's is a complex and compelling matrix of river systems, primarily characterised by the Plateau and Rift Margin Consequent River systems. The former exerts a significant hydrological influence over the western section of the basin, while the latter predominates eastwards. This dual structure encapsulates an intricate drainage network, including the South Rukuru, Kasitu, Luweya-Limphasa, and Dwambadzi River systems, and an array of Consequent Rivers flowing from the escarpment zones. The South Rukuru River system, a critical hydrological component of the Plateau system, originates near the Zambian border and flows toward a drainage divide demarcated by rolling hills that separate it from the Kasitu River basin. This river system exhibits characteristics of a mature drainage basin, mainly impeded by eastward and northward uplifting topography, creating narrow marshy belts through which the river meanders slowly. Its bifurcated inflows, comprising predominantly westerly tributaries including the Njoka, Mirara, and Luweya Rivers, and southward flowing tributaries that drain the East Nyika Plateau and adjacent escarpments, are worth noting.

The Kasitu River's flow path from the Viphya Escarpment to its confluence with the South Rukuru River highlights its trajectory through fault-influenced terrains, creating broad marsh zones and contributing significantly to the hydrology of the Viphya Mountains' western slopes. This river's maturity is evidenced by its extensive dambo formations, a significant indicator of geomorphological evolution within fluvial contexts. On the other side of the topographical spectrum, the Rift Margin Consequent River system, exemplified by the Luweya River, presents a contrasting drainage pattern. The Luweya River carves through the eastern Viphya Plateau landscape in a deep, fault-defined gorge, extending northeast for 28 km. Supported by substantial precipitation, ranging from 1370 to 2000 mm annually, this river

system features one of the highest discharges in the region, a testament to its vigorous hydrological dynamics. Also, the Dwambadzi River, a south-eastward flowing waterbody that incises deeply into the Rift Escarpment, showing the geomorphological aggression of youthful stream systems on steep escarpments. This area's drainage pattern is further complicated by several short, rejuvenated, and largely fault-controlled streams that exemplify the dynamic interaction between geological structures and hydrological processes. This comprehensive analysis of the region's drainage systems not only underscores the complexity of its hydrological network but also showcases the profound impact of geological formations on river path and behaviour. Such insights are instrumental for advancing our understanding of riverine systems in similar plateau and rift margin settings, thereby contributing valuable knowledge to the field of geomorphological and environmental studies.

2.2 Water resources

Within the context of northern Malawi, particularly in the Lake Malawi sub-basin 3, water resources consist predominantly of multiple reservoirs such as Lunyangwa, Ruvuo, and Chikangawa, alongside a network of rivers described in section 2.1 (Banda et al., 2024; Kalin et al., 2022). These water bodies of water are strategically situated amidst expansive forested regions, playing a pivotal role in supplying water for domestic and agricultural irrigation purposes. Notably, the Lunyangwa Reservoir, located along the Lunyangwa River, serves as the principal water source for urban populations in Mzuzu City, a critical area administered by the Northern Regional Water Board (NRWB) (Banda et al., 2019a, 2024; Kalin et al., 2022). The NRWB is tasked with managing this vital resource to align the supply of water with the escalating demands of the urban populace. Beyond the Lunyangwa Reservoir, the region's water

infrastructure is supported by the Mzimba River, which caters to water needs of the Mzimba Central Business District (GoM., 2017). The Ministry of Water and Sanitation has been proactive in harnessing these resources through the implementation of gravity-fed water schemes and the installation of community boreholes within the rural districts. This strategic framework has significantly improved water access, embodying a vital community resource management model (GoM., 2017). Furthermore, various Non-Governmental Organizations (NGOs) are instrumental in enhancing water availability in rural areas by constructing additional community boreholes and protected shallow wells. These efforts are pivotal in promoting of sustainable water usage practices within these communities.

Despite these multifaceted interventions, the Northern Regional Water Board confronts formidable challenges including a deficit in water supply. The current infrastructure yields approximately 1,200 cubic meters per day, which falls short of the requisite 1,400 cubic meters per day needed to adequately meet the needs of the growing population. The situation is further exacerbated by substantial environmental concerns such as pronounced siltation in both the Mzimba and Lunyangwa Rivers, primarily attributed to riverbank cultivation and the degradation of catchment areas. This environmental degradation significantly impairs both the quality and availability of water resources, necessitating urgent enhancement of water supply infrastructures and the implementation of strategic catchment conservation measures. In addressing these acute challenges, a comprehensive integrated water resource management approach grounded in transformative water resources monitoring data and information, is imperative.

2.3 Topography

This region exhibits a rich tapestry of topographical features that delineate a clear contrast between its extensive peneplains to the west and rugged escarpments to the east. A detailed examination from the shorelines of Lake Malawi to the elevated terrains of the Nyika Plateau Scarp reveals an elevation range from 474 to 2425 m above sea level (asl). Prominently, the western frontier of the Nyika Plateau manifests a noticeable transition into the dissected highlands of the Nyika Plateau Foothills, augmenting the area's geological diversity. To the east, the arc of the Nyika Scarp converges with the South Karonga Scarp Zone, creating a delineation along the western periphery of the region. Hydrologically, this area is distinguished by significant river systems, including major watercourses that have carved profound gorges through the Nyika and South Karonga scarps. Additionally, these rivers are accompanied by smaller consequent streams, forming deeply incised channels marked by cascading waterfalls. The southern section of the scarp plunges dramatically into the Henga Valley, where the South Rukuru River makes its northeastern journey. Following the river, Uzumara Hill stands in 1942 m asl, signifying the northward extension of the dissection patterns observed in the Nyika Plateau. Complementarily, the Livingstonia hills north of South Rukuru persist in embellishing the region's high relief.

In stark contrast to the elevated terrains, the western lakeshore plains are characterized by predominantly flat lands interspersed with swamps and modest hill ridges, seldom rising above 600 m asl. This variance is pivotal in understanding the geomorphological processes at play. Further accentuating the region's topography are notable landscapes such as the South Rukuru Valley, the Mzimba Hills along the Kasitu Valley, and the Viphya Plateau, culminating in the Viphya scarp zone. These geographical entities ascend from approximately 100 m up to

around 1820 m asl from the upper reaches of the Kasitu valley to the domains of the Viphya Plateau. The Mzimba Hills, positioned along the watershed between the South Rukuru and Kasitu basins, encapsulate a hilly terrain spread between 1370 and 1590 m wide. Crucial relief elements within the Mzimba Hills are typified by Mt. Hora and Mazozo Hill, both of which are incised by tributaries feeding into the South Rukuru River. These topographical intricacies pivotal in this region suggest profound implications for ecological stratification, water resource management, and geographical delineation. The topographical diversity not only fosters unique ecosystems but also challenges human interactions and adaptations within these dynamic landscapes. As such, a comprehensive understanding of such topographic features is indispensable for informed environmental stewardship and sustainable regional planning.

2.4 Geology and hydrogeology

The aquifer system within the Lake Malawi basin is delineated by a complex arrangement of hydrostratigraphic units that include a weathered and fractured basement, alongside both consolidated and unconsolidated sedimentary units. These delineations form three principal aquifer categories: consolidated sedimentary rock, unconsolidated sedimentary units atop a weathered basement, and weathered basement units above a fractured basement (Figure X). The primary aquifers composed of consolidated sedimentary rock principally consist of sandstone and shale, furnishing a robust framework for groundwater reserves. Conversely, the aquifers comprising unconsolidated sedimentary units overlying the weathered basement are predominantly characterized by colluvium and alluvium materials, creating favourable conditions for the storage and transmission of groundwater due to their significant intergranular pore spaces. Similarly, the

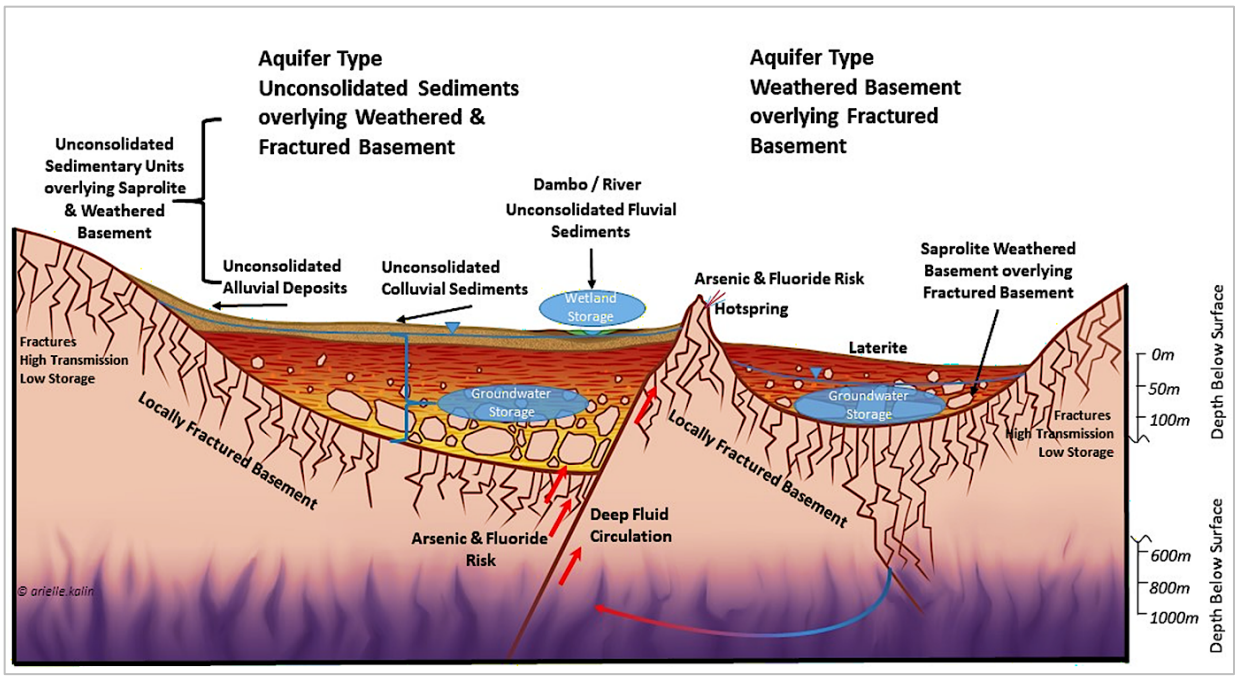

Figure 2. Idealised cross-section of the hydrostratigraphic aquifer units in the study area (after Kalin et al., 2022).

weathered basement super jacent to the fractured basement aquifers is predominantly made up of charnockitic gneiss and hornblende-biotite-gneiss, which support groundwater flow through their intergranular spaces, fissures, fractures, and joints. The chemical composition and quality of groundwater in these aquifers are heavily influenced by the mineralogical characteristics of the underlying rocks. Dominant minerals such as plagioclase, pyroxenes, feldspars, amphiboles, and biotite contribute various chemical species to the groundwater. During the process of weathering, plagioclase minerals - notably more calcium-rich in this region - release calcium and sodium into the groundwater. Additionally, the dissolution of mafic minerals introduces magnesium, iron, and other ions, some of which are compounded with fluoride ions. Geographically, the distribution of these aquifers varies within the basin. Consolidated sedimentary aquifers are predominantly found in the northern sector, albeit sparsely. The unconsolidated sedimentary units that overlie the weathered basement predominantly occupy the western areas of the basin. In contrast, the eastern

regions, particularly along the rift scarp zones, are mostly composed of weathered basement units atop the fractured basement. Notably, the Lake Malawi shoreline and adjacent rift valley plains feature substantial deposits of unconsolidated fluvial, colluvial, and alluvial sedimentary units overlying weathered basement units. Hydrogeologically, these settings play a critical role in defining the availability and the sustainability of groundwater resources in the Lake Malawi basin. The estimated potential yield of the aquifer with unconsolidated sedimentary units overlying the weathered basement can reach up to 20 litres per second. In juxtaposition, the water supply from boreholes tapping into the weathered basement overlying the fractured basement aquifer yields significantly less, up to a maximum of 2 litres per second. These hydrogeological nuances emphasize the intricate relationship between geological formations and groundwater dynamics, pivotal for water resource management and planning in the region. Understanding these interactions is essential for developing effective strategies to harness and safeguard this vital resource in light of both current demand and future climate variability challenges.

2.5 Climate

The study area, characterized by a tropical continental climate, features diverse climates influenced by varying topographies and elevations. This region, with its dual season pattern of wet and dry seasons, shows significant climatic variations over short distances, crucial for understanding local agricultural and ecological systems. In the Mzimba-South Rukuru Plains on the western Viphya Plateau, conditions are warm and dry with temperatures ranging from 18.3°C to 21.1°C and annual rainfall between 635 mm and 1,370 mm. The East Viphya Scarp has warmer temperatures up to 23.9°C and higher rainfall between 1,370 mm and 2,000 mm. The Viphya Plateau itself is cooler and wetter, with temperatures from 12.8°C to 15.6°C, and similar

rainfall to the Scarp zone. Higher areas like the Viphya Mountains and Chimaliro Hills experience even colder and wetter conditions. Conversely, the southern Mzimba Plains and Kasungu Hills are warmer and drier. The Nkhata Bay region near Lake Malawi receives a lot of rain (1,520 mm to 2,290 mm annually) with temperatures in parts reaching up to 35°C. The western areas are drier with mild consistent temperatures. The Dwambadzi Valley and the rift valley escarpment are notably wet areas, with rainfall reaching up to 2,030 mm and temperatures from 15.6°C to 23.9°C. In summary, elevation and geographic relief are major factors that lead to varied climatic conditions such as temperature and precipitation throughout the region, with effects critical for local management practices.

3. Materials and Methods

3.1 Sample collection

Water isotope samples were systematically collected from a range of surface and groundwater sources, including rivers, lakes, reservoirs, springs, dug-wells, and boreholes equipped with handpumps, during both dry and wet seasons. The sampling strategy commenced at a surface water location, followed by an examination of adjacent groundwater points to assess potential interactions between the two water types. Samples were collected using 50-ml pre-cleaned High-Density Polyethylene (HDPE) bottles, filled to capacity to eliminate headspace. Each bottle was sealed with paraffin film and secured with waterproof tape to prevent contamination and minimize isotopic changes attributable to leakage, evaporation, or chemical and biological processes. During transport and storage, samples were maintained at a temperature of 4°C and shielded from direct sunlight until analysis. Prior to collection, the HDPE bottles were thoroughly rinsed three times with the water being sampled. For river samples,

collection points were chosen along primary flow channels to capture representative water. Simple grab sampling was adequate for smaller rivers due to their narrow width. In contrast, larger rivers necessitated the collection of samples at specified intervals across the river's cross-section to create composite samples, employing bridges for access when possible. Lake samples were collected from estuarine zones located 1 km offshore, utilizing a boat with a customized depth sampler. Reservoir sampling involved collecting water from both main inflow and outflow points, alongside grab samples from central locations, to ensure comprehensive representation. Groundwater samples were taken from community boreholes that were actively in use, ensuring thorough purging before sampling. In the case of inactive boreholes, a minimum purging duration of five minutes was enforced to eliminate any standing water. Additionally, groundwater was sampled from springs located near principal discharge points while deliberately avoiding stagnant pools to reduce the risk of isotopic alterations induced by evaporation and atmospheric interactions.

3.2 Sample analysis

Temperature, electrical conductivity (EC), total dissolved solids (TDS), and pH, were measured in the field using a calibrated portable multi-meter (Model: HI-98194, Hanna Instruments, Woonsocket, RI, USA). These water quality constituents can easily be modified by environmental factors between the field and the laboratory, hence the need to measure them while onsite for good representativeness. When measuring these water quality constituents, the readings were allowed to stabilise, which mostly took between 2 and 5 minutes, before recording the measurements for consistent measurements. To achieve optimum functionality of the multi-meter when conducting the measurements in the field, its probe was submerged at a minimum

depth of 100 mm in flowing water, deliberately avoiding stagnant areas, in the case of surface water. Onsite measurements for spring water were conducted directly at the main discharge points for representativeness. Borehole and dug-well samples were transferred into a 250 ml measuring beaker after pumping and bailing. Onsite measurements for these groundwater sources was conducted from the beaker immediately after sampling. The water quality constituents measured onsite provided informative insights and preliminary data for understanding onsite conditions at the time of sampling. They also acted as a benchmark to check if at all there were any quality changes in the samples during transport and storage prior to laboratory analysis.

Stable isotope samples were measured using a Picarro 2140i CRDS Isotopic Water Analyser (IWA) (Model: L2140-i, Picarro Inc., Santa Clara, CA, USA), with precision of ± 0.2 ppm for oxygen-18 and ± 2.0 ppm for deuterium (2σ). The isotopic analyses were conducted by the IAEA at the Isotope Hydrology Laboratory in Vienna, Austria, an internationally recognised institution when it comes to isotopic analysis. The following is a brief protocol that was adhered to during sample preparation, analysis and results processing. The water sample analysis list was prepared in IWA specific Laboratory Information Management System (LIMS) software, in batches of 10 samples. Each batch included prescribed calibration and control standards for quality control and assurance. A 1 ml portion of sample was filtered through into a 2 ml a 0.45 μm filter into a glass vial, which was then loaded onto an autosampler unit of the IWA. The IWA was then warmed up for 60-minutes, running deionized water until concentration peaks equilibrated within the recommended range of 19,000 to 21,000 ppm for optimum performance. The IWA was run in high-precision mode that involved three autoruns, using dry synthetic air serving as a carrier gas. Water sample injection was set at a frequency of 6, enough to mitigate

any interreferences during the analysis process. Prescribed reference materials were to keep the analysis in check including the Lake Kyoga (enriched) and Standard-09 (Greenland Ice, depleted). Standard-11 (Monaco Lagoon) and Standard-06 (Heidelberg tap water), as control standards, were incorporated as part of a rigorous quality assurance and control protocol. Post-analysis, raw data from the auto-runs were merged and tagged unique identifiers and exported to the LIMS software for normalization and validation. Raw data from the first three injections for each water sample were discarded to eliminate any memory interference. The raw data for the remaining injections were then processed using residual memory correction method. Data normalization employed the Vienna Standard Mean Ocean Water (VSMOW) and Standard Light Antarctic Precipitation (SLAP) scales as two reference points. After this process, the resulting data were assigned additional identifiers further processing, normalization, and validation. All these step-wise laboratory protocols, alongside the field measurements, sample collection, transportation, holding where conducted in line with International Standard Procedures (ISP) (IAEA, 2009). The final processed isotopic data were expressed as delta (δ) values (Equation 1), illustrating relative differences in isotopic ratios of water samples and standards (Coplen, 2011).

$$\text{Delta } (\delta) = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) \text{x } 1000 \text{ ‰} \quad (1)$$

In equation 1, R is a unitless isotopic ratio, where R_{sample} and $R_{standard}$ are isotopic ratios ($R = {}^{2}H/{}^{1}H$ and $R = {}^{18}O/{}^{16}O$) of sample and standard, respectively. The delta notation (δ) quantifies the deviation of the sample's isotopic composition from the standard, reflecting relatively minor isotopic expressed in parts per thousand (‰) (Rozanski et al., 1993; Coplen, 2011; IAEA, 1981). A positive δ value indicates isotopic enrichment of heavy isotope relative to Vienna Standard Mean Ocean Water (VSMOW), while a negative δ value denotes isotopic depletion of the heavy

isotopes. By definition, the VSMOW values for δD and $\delta^{18}O$ are calibrated to zero. The *d*-excess (d), defined in Equation 2 (Dansgaard, 1964), serves as an indicator of the meteorological conditions in the source region of precipitation-bearing moisture (Rozanski et al., 1993; Merlivat and Jouzel, 1979; Gat et al., 1970). The *d*-excess is significantly influenced by atmospheric relative humidity above oceanic bodies (Clark and Fritz, 1997). Under conditions where the mean global humidity is approximately 85%, the average global *d*-excess value for global precipitation hovers around 10 ‰ (Merlivat and Jouzel, 1979; Gonfiantini, 1986). A *d*-excess value close to 10 ‰ implies that precipitation is predominantly derived from oceanic moisture. Conversely, *d*-excess values exceeding 10 ‰ indicate processes involving moisture recycling via large-scale evaporation, typically linked to lower atmospheric humidity in the source region (IAEA, 2005). Additionally, the *d*-excess is influenced by secondary processes including raindrop evaporation beneath clouds and the evaporation of terrestrial water bodies (Rozanski, 1993; Froehlich et al., 2002), which can modify the *d*-excess values in a manner that reflects varying moisture sources.

$$d - \text{excess} = \delta D - 8\delta^{18}O \text{ ‰ VSMOW} \quad (2)$$

4. Results

4.1 Isotopic characteristics of different surface water sources

Analysis of surface water $\delta^{18}O$, δD and *d*-excess signatures (n = 106) exhibit a distinct distribution range: δD varies by 61.4‰ and $\delta^{18}O$ by 9.8‰ (Table 1; Figure 2a). The $\delta^{18}O$ signatures range from −7.3 to +2.5‰, with a mean of −4.4‰, while δD signatures range from −46.7 to +14.7‰ with a mean of −27.7‰. D-excess values range between −11.4‰ and +16.7‰, averaging +7.6‰. For river water, δD signatures range from −46.7 to +8.9‰, with a mean of

−30.9‰, and $\delta^{18}O$ values range from −7.3 to +2.5‰, averaging −4.9‰. Reservoir water $\delta^{18}O$ signatures span from −7.0 to −3.8‰, averaging −5.1‰, while δD signatures fall between −45.0 and −19.3‰, with a mean of −29.3‰ (Table SM 1). Lake water $\delta^{18}O$ values from +0.9 to +2.1‰, averaging +1.6‰, while δD signatures range from +5.0 to +14.7‰, with a mean of +10.0‰. These mean values for lake water $\delta^{18}O$ and δD suggest substantial isotopic enrichment due to intense evaporation, while the reservoir and river water mean $\delta^{18}O$ and δD signatures suggest a predominant input of meteoric water, where the isotopic signal is largely retained.

Cluster A, composed of reservoir and river samples, aligns with both local *d*-excess line (Banda et al., 2024) and the Global Meteoric Water Line (GMWL) as described as $\delta D = 8\delta^{18}O + 10$ by Craig (1961) (Figure 2b), indicating a significant input of non-evaporated meteoric water into these bodies. Clusters **B** and **C**, primarily comprising river and lake samples respectively, deviate from the meteoric water lines and follow a unique Surface Water Line (SWL) defined as $\delta D = (6.0 \pm 0.1)\ \delta^{18}O - (1.1 \pm 0.7)$ (Figure 2b). The slope of SWL_{slope} $(6.0 \pm 0.1) < GMWL_{slope}$ (8), indicating influence of intense evaporation and subsequent isotopic enrichment, with lake water samples (Cluster **C**) acting as an end-member due to intense evaporation. The SWL_{slope} also hints at dual influence of evaporation and mixing with groundwater baseflow during periods of reduced river flow (Banda et al., 2019a, 2020a; Kelly et al., 2019a; Kelly et al., 2020; Kelly et al., 2019b).

Table 5. Descriptive statistics of $\delta^{18}O$-δD and *d*-excess signatures in surface water points

Isotope tracer	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
δD ‰ VSMOW	106	–27.7	1.37	14.1	–46.7	–30.6	14.7	61.4
$\delta^{18}O$ ‰ VSMOW	106	–4.4	0.221	2.27	–7.3	–5.0	2.5	9.8
D-excess ‰	106	7.6	0.538	5.53	–11.4	9.90	16.7	28.1

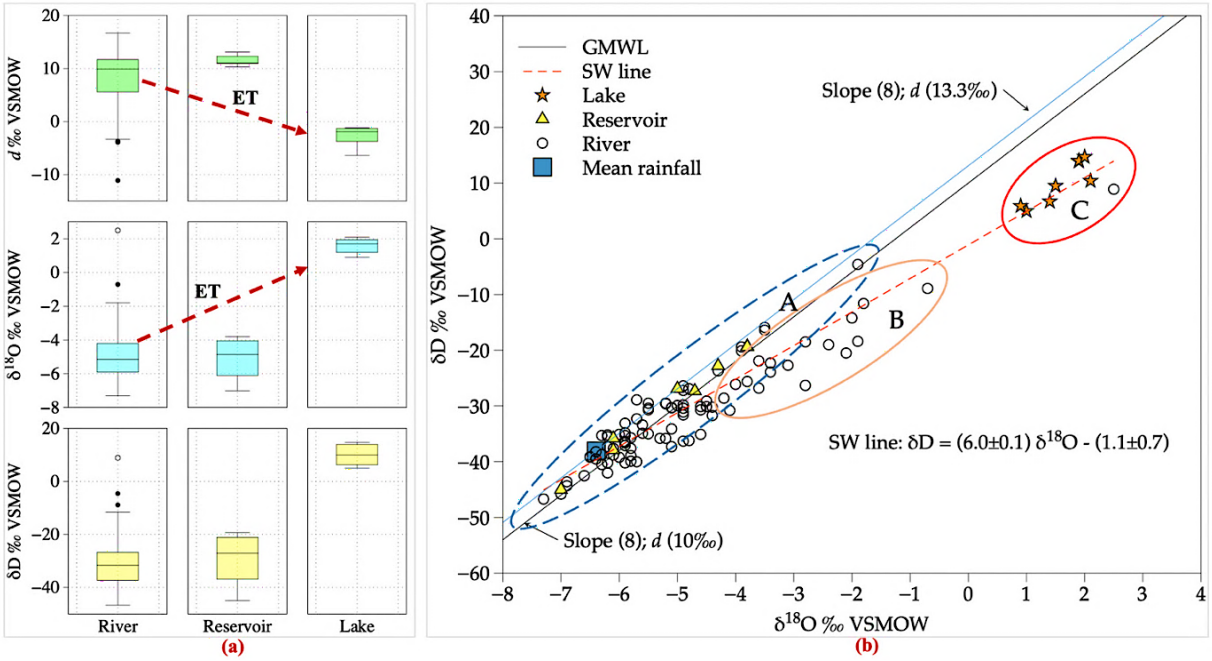

Figure 3. (a) Box and whisker plots of $\delta^{18}O$, δD and *d* (*d*-excess) signatures, and **(b)** bi-variate plot of $\delta^{18}O$-δD signatures for different surface water sources.

4.2 Isotopic characteristics of groundwater sources

Analysis of groundwater isotopic data (n = 83) shows that δD signatures range from –47.4‰ to –21.2‰, with a mean of –36.9‰. The $\delta^{18}O$ signatures vary from –8.9‰ to –2.5‰, with a mean of –5.7‰ (Table 2 and Figure 3a). The *d*-excess signatures span from –10.5‰ to +28.6‰, averaging 8.9‰. A significant subset of groundwater samples, designated as Cluster **A**, aligns with the local *d*-excess line and the Global Meteoric Water Line (GMWL) (Figure 3b). This suggests that groundwater recharge primarily occurs through non-evaporated modern meteoric water, likely from the Indian Ocean monsoon (Banda et al., 2019b, 2020a, 2024). Cluster **B** samples deviate from the meteoric water lines, indicating localized isotopic enrichment in aquifer groups 2 and 3 (Figure 3b). This enrichment can be attributed to excess $\delta^{18}O$ resulting from secondary evaporation, mixing of ancient and fresh meteoric waters on different time

scales, and interactions between rock minerals and water. Such processes may occur in specific areas, including near lake sites and dambo or marshy environments, either during surface runoff before groundwater infiltration or through shallow groundwater evaporation within the aquifer. Cluster **C** samples are plotted above the meteoric water lines, indicating a mix of old and fresh meteoric waters from different time scales. This suggests input from meteoric water originating from high altitudes, potentially affected by condensation effects.

Table 6. Descriptive statistics of δ^{18}O-δD and *d*-excess signatures in groundwater points

Variable	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
δD ‰ VSMOW	83	–36.9	0.600	5.47	–47.4	–37.5	–21.2	26.2
δ^{18}O ‰ VSMOW	83	–5.7	0.116	1.06	–8.9	–5.80	–2.5	6.40
D-excess ‰	83	8.9	0.682	6.21	–10.5	9.62	28.6	39.1

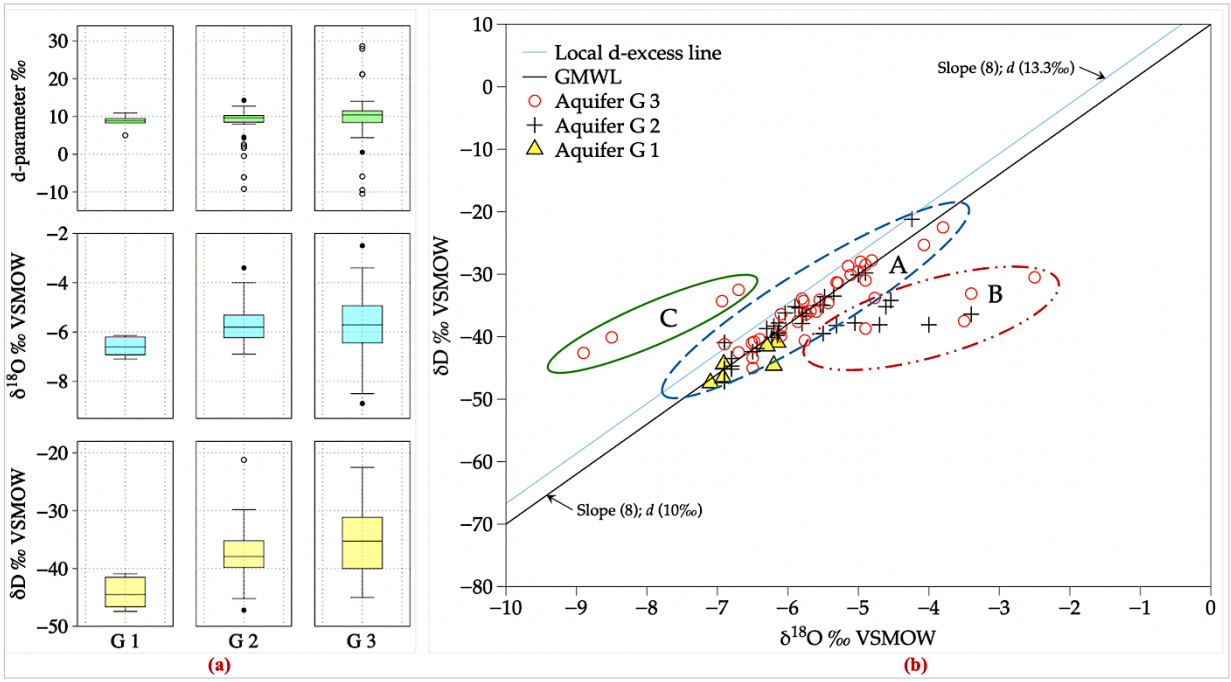

Figure 3. Box and whisker plots of δ^{18}O, δD and d-parameter (*d*-excess) signatures for groundwater from different aquifer groups.

4.3. Spatial variability of stable isotopes in surface water

The $\delta^{18}O$ and δD signatures of surface water exhibit remarkable spatial variability across both the South Rukuru River catchment (WRA 7) and the Nkhata Bay lakeshore catchment (WRA 16). In WRA 7, $\delta^{18}O$ signatures ranged from –7.0 to +2.5‰, with an interquartile range (IQR) of +1.7‰, while δD signatures varied from –45.8 to +10.4‰, showing an IQR of +11.3‰ (Table 3: Figure 4). The WRA 16 exhibited $\delta^{18}O$ signatures ranging from –7.3 to +2.0‰, with an IQR of +2.8‰, while δD signatures ranged from –46.7 to +14.7‰, corresponding to an IQR of +18.5‰. The findings show that WRA 16, located in the eastern section of the study area, is relatively more isotopically enriched than WRA 7, positioned in the western section. This indicates a pronounced west-to-east attenuation in the meteoric water isotopic signal, aligning with Lake Malawi sub-basin's prevailing hydrological flow patterns.

Table 7. Spatial variability of $\delta^{18}O$-δD and *d*-excess signatures in SW across different catchments

Isotope tracer	WRA	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
$\delta^{18}O$ ‰ VSMOW	7	70	–4.7	0.23	1.93	–7.0	–5.1	2.5	9.5
	16	36	–3.9	0.46	2.79	–7.3	–4.9	2.0	9.3
δD ‰ VSMOW	7	70	–29.8	1.38	11.5	–45.8	–31.7	10.4	56.2
	16	36	–23.6	2.91	17.5	–46.7	–27.9	14.7	61.4
D-excess ‰	7	70	7.5	0.62	5.21	–11.4	9.3	14.4	25.8
	16	36	7.8	1.03	6.19	–4.5	11.1	16.7	21.2
Isotope tracer	Topography	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
δD ‰ VSMOW	Lowland	26	-19.9	3.70	18.9	-43.6	-26.6	14.7	58.3
	Upland	80	-30.2	1.24	11.1	-46.7	-31.7	10.4	57.1
$\delta^{18}O$ ‰ VSMOW	Lowland	26	-3.4	0.60	3.03	-6.9	-4.3	2.0	8.9
	Upland	80	-4.7	0.21	1.88	-7.3	-5.1	2.5	9.8
D-excess ‰	Lowland	26	7.5	1.25	6.36	-4.5	10.1	16.7	21.2
	Upland	80	7.6	0.59	5.28	-11.4	9.9	14.4	25.8

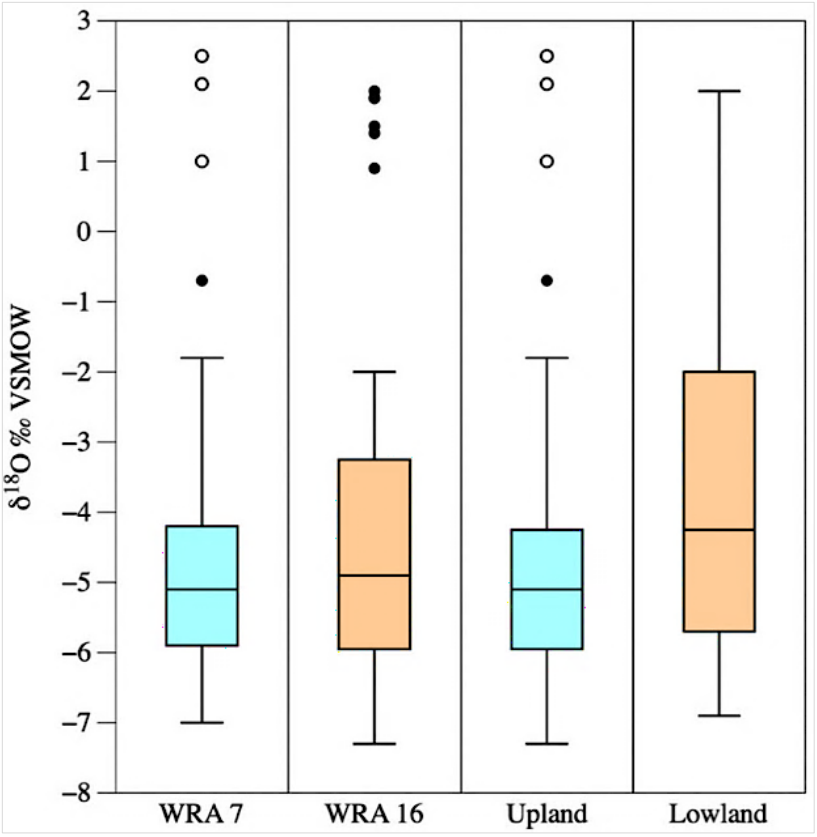

Figure 4. Box and whisker plots for spatial variability of $\delta^{18}O$ signatures in surface water across different catchments and topographic zones.

The hydrological dynamics of the study area are primarily influenced by riverine flows that originate in highland-escarpment zones, traverse plateau regions and rift valley lakeshore plains, and ultimately discharge along the shores of Lake Malawi. The $\delta^{18}O$ and δD signatures of surface water exhibit significant variability between upland and lowland landscapes. Upland $\delta^{18}O$ signatures range from –7.3‰ to +2.5‰, with an interquartile range (IQR) of +1.8‰, whereas lowland $\delta^{18}O$ signatures range from –6.9‰ to +2.0‰, with an IQR of +4.5‰ (Table 3). Notably, surface water from lowland sites is more isotopically enriched, with an average δ18O of –3.4‰, compared to –4.7‰ in upland regions. This indicates a more pronounced isotopic signal from meteoric water inputs in uplands than in lowlands. This spatial isotopic

heterogeneity, characterized by localized enrichment in uplands and depletion in lowlands, can be attributed to various factors, including groundwater baseflow contributions in dambo areas, marshy regions, and lakeshore floodplains, where there is evidence-based theorised hydraulic connectivity between groundwater and surface water (Banda et al., 2019c, 2020b, 2024; Kelly, Bertram, et al., 2019b; Kelly et al., 2020; Kelly, Kalin, et al., 2019; Kumambala, 2010; Kumambala et al., 2024).

4.4. Spatial variability of stable isotopes in groundwater

Groundwater $\delta^{18}O$-δD signatures show distinct spatial variability across the South Rukuru River catchment (WRA 7) and the Nkhata Bay lakeshore catchment (WRA 16). In WRA 7, $\delta^{18}O$ signatures vary from –8.9 to –2.5‰, with an interquartile range (IQR) of +1.2‰, while δD signatures vary from – 47.4 to –21.2‰, with an IQR of +7.6‰ (Table 4: Figure 5a). In WRA 16, $\delta^{18}O$ signatures vary between – 6.9 and –3.5‰, with an IQR of +0.9‰, whereas δD signatures range from – 47.2 to –28.5‰, with an IQR of +3.7‰. This indicates that groundwater in WRA 16 is isotopically enriched relative to groundwater in WRA 7.

Groundwater $\delta^{18}O$-δD signatures also vary across distinct aquifer groups (Figure 3c; Table 9). Groundwater sub-samples for aquifer Groups 2 and 3 in Cluster C exhibit evidence of isotopic enrichment trend (Cluster C; Figure 5b), whereas Group 1 exhibit high meteoric water input signal. Group 3 plots across all clusters (A-C) suggesting complex interactions within the local hydrological processes. Alignment of the three distinct clusters relative to meteoric water lines indicate that groundwater is predominantly of meteoric origin but experience local isotopic attenuation either during runoff phase before infiltration or the aquifer system due to phreatic due to factors such as evaporation, mixing with deep-seated hydrothermal waters, or recharge

input from closed-basin moisture sources (Banda et al., 2024; Tuinenburg et al., 2020; Vystavna et al., 2021). The spatial isotopic inhomogeneity, characterized by localized enrichment and depletion relative to the meteoric water lines, can be attributable to multiple input sources into the aquifer system. The aquifer group-based spatial distribution indicate that aquifer Group 2 has a higher δD mean value (–37.7‰), with a larger range (+26.0‰), Group 3: Highest δD mean value (–35.1‰) with a range of +22.5, whereas Group 1 registered a lowest δD mean value (–44.2‰) with a relatively small range (+6.5), (Table 5). This suggest that consolidated sedimentary rock group has more consistent isotopic signatures, while the unconsolidated sediments/weathered basement group exhibits greater variability.

Table 8. Spatial variability of $\delta^{18}O$-δD and *d*-excess signatures in GW across different catchments

Isotopic Tracer	WRA	N	Mean	SE Mean	Std Dev	Min	Median	Max	IQR	Range
δD ‰ VSMOW	7	59	–37.0	0.77	5.92	–47.4	–36.7	–21.2	7.6	26.2
	16	24	–36.7	0.87	4.27	–47.2	–37.6	–28.5	3.7	28.7
$\delta^{18}O$ ‰ VSMOW	7	59	–5.9	0.15	1.13	–8.9	–6.1	–2.5	1.2	6.4
	16	24	–5.4	0.15	0.75	-6.9	–5.5	–3.5	0.9	3.4
D-excess ‰	7	59	9.9	0.84	6.43	–10.5	10.1	28.6	2.8	39.1
	16	24	6.4	1.01	4.94	–9.5	8.7	11.2	6.7	20.7

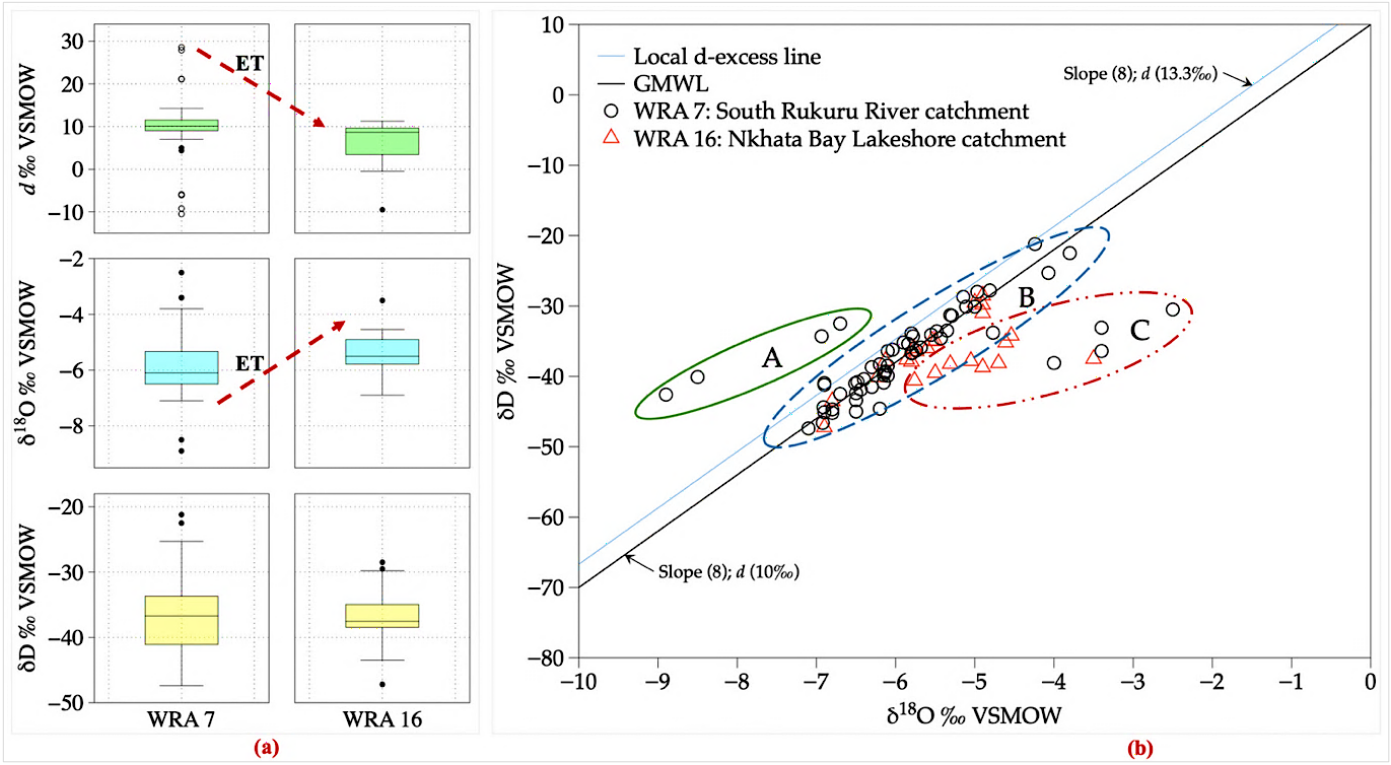

Figure 5. Distribution of δ^{18}O-δD and *d (d*-excess*)* signatures in GW across different catchments.

Table 9. Distribution of δ^{18}O-δD and *d* (*d*-excess) signatures in GW across different aquifer groups

Tracer	Aquifer-Group	Mean	SE Mean	Std Dev	Min	Median	Max	Range
δD ‰	Consolidated sedimentary rock (*Group* 1)	–44.2	1.07	2.62	–47.4	–44.5	–40.9	6.50
	Weathered basement/Fractured basement (*Group 2*)	–37.7	0.79	4.82	–47.2	–37.9	–21.2	26.0
	Unconsolidated sediments/Weathered basement *(Group 3)*	–35.1	0.85	5.34	–45.0	–35.3	–22.5	22.5
δ^{18}O ‰	Consolidated sedimentary rock (*Group* 1)	–6.6	0.17	0.42	–7.1	–6.6	–6.2	0.95
	Weathered basement/Fractured basement (*Group 2*)	–5.7	0.14	0.86	–6.9	–5.8	–3.4	3.50
	Unconsolidated sediments/Weathered basement *Group 3)*	–5.6	0.19	1.23	–8.9	–5.7	–2.5	6.40
d ‰	Consolidated sedimentary rock (*Group* 1)	8.5	0.80	1.95	5.0	8.8	10.9	5.88
	Weathered basement/Fractured basement (*Group 2*)	8.0	0.82	4.98	–9.2	9.6	14.3	23.5
	Unconsolidated sediments/Weathered basement *Group 3)*	9.8	1.18	7.49	–10.5	10.4	28.6	39.1

4.5. Seasonal variability in surface water stable isotopes

The isotopic signatures of surface water (SW) show distinct seasonal variability across the study area. In dry season, $\delta^{18}O$ signatures varied from – 6.5 to +2.5‰, with a mean of – 3.8‰ and a median of – 4.4‰, while δD signatures varied from – 42.0 to +9.5‰, with a mean of –24.2‰ and a median of – 26.9‰ (Table 6; Figure 6a). In wet season, $\delta^{18}O$ signatures varied from –7.3 to +2.1‰, with a mean of –5.0 ‰ and a median of –5.8‰, while δD signatures varied from – 46.7 to +14.7‰, with a mean of –31.0‰ and a median of – 35.4‰. Both δD and $\delta^{18}O$ signatures more depleted in heavy isotopes in wet season but relatively enriched in the dry season. The SWL_{dry} slope of 5.7±0.2 shows that the original meteoric water input that replenished the SW experienced isotopic fractionation which resulted in lowering of the SWL_{wet} relative to slope of 8 for the GMWL (Craig, 1961). Though most SW samples plotted along the meteoric water lines, the SWL_{wet} slope of 6.4±0.2 exhibits evaporative effects. This could be ascribed to high retention of isotopic enrichment signal for lake water samples in wet season which lowers the SWL_{wet}. The wet season recorded high *d*-excess values than the dry season, suggesting seasonally-variant isotopic fingerprinting by different air moisture sources or hydrological processes such as evaporation and its associated isotopic fractionation. In wet season, the *d*-excess mean value was +9.2‰, consistent with fresh meteoric water input isotopic signal, while in the dry season, a *d*-excess mean value of +5.9‰ highlights influence of evaporation and its associated isotopic enrichment (Table 6). The δD and $\delta^{18}O$ standard deviation and range values were greater in wet season than in dry season, indicating greater intra-seasonal variability during the former season.

At catchment scale, δD and $\delta^{18}O$ signatures across WRA 7 and WRA 16 show distinct seasonal variability consistent with the seasonal trend observed across the entire study area.

Particularly, SW $\delta^{18}O$ mean values for WRA 7 and WRA 16 show that SW in WRA 16 is isotopically enriched in dry season relative to SW in the WRA 7 (Figure 6: Table SM 4). In wet season, SW $\delta^{18}O$ signatures show more depletion in WRA 7 relative to SW $\delta^{18}O$ signatures in WRA 16.

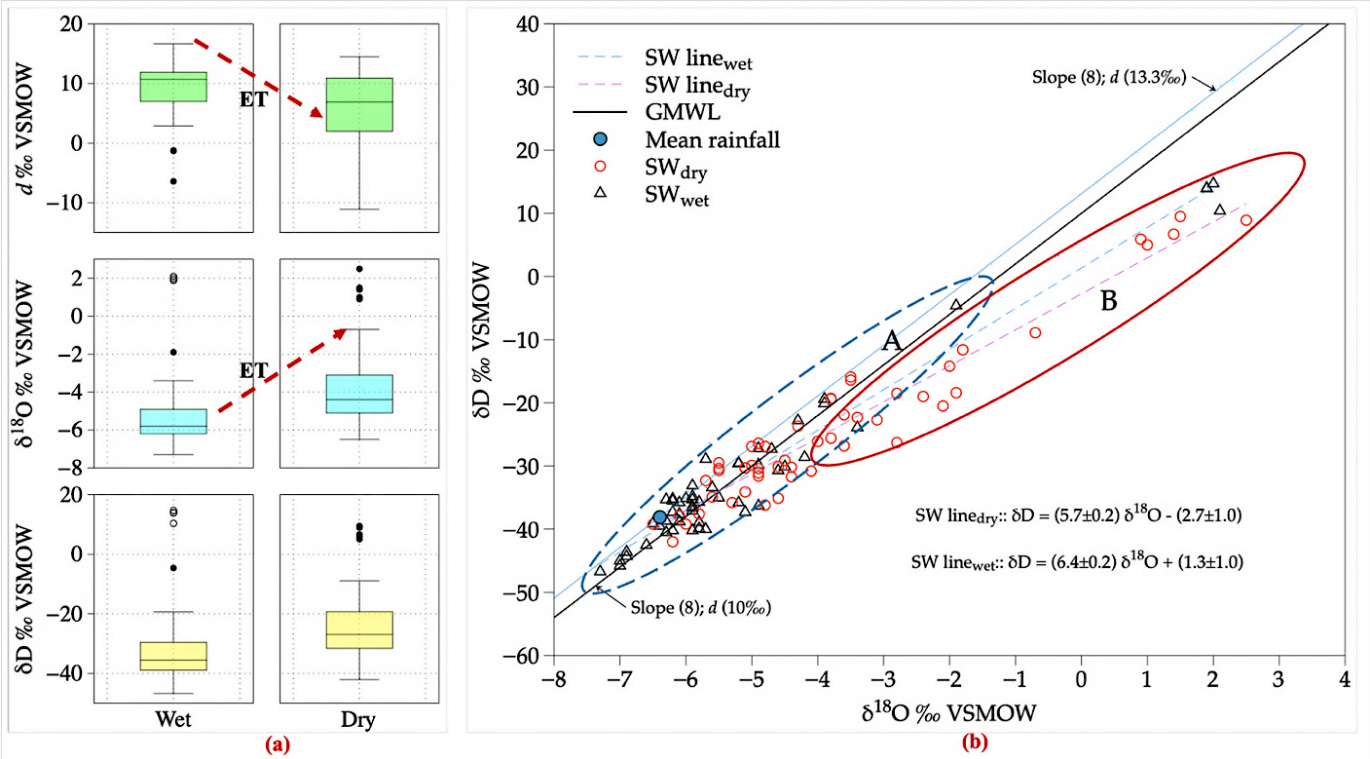

Figure 6. Seasonal variability of surface water $\delta^{18}O$-δD and *d*-excess (*d*) signatures.

4. Discussion

The isotopic analysis of surface water (SW) and groundwater (GW) within the study area provides profound insights into regional hydrological dynamics. This study reveals the intricate interconnections between precipitation patterns, evaporative processes, and groundwater contributions, as evidenced by distinct isotopic signatures (δD and $\delta^{18}O$) and derived *d*-excess for GW and SW sources.

4.1 Surface water and groundwater dynamics

Surface water δD and $\delta^{18}O$ signatures show substantial heterogeneity, indicative of multiple influencing factors including meteoric water input, upstream inputs, evaporation and its associated isotopic fractionation. Riverine δD and $\delta^{18}O$ signatures range widely, indicating a mix of recent meteoric input and upstream discharge from dambo storage. Alignment of specific surface water clusters relative to the GMWL and local *d*-excess line underscore the role of fresh meteoric water input in sustaining riverine flows. Lake water samples exhibit pronounced isotopic enrichment and forms SW end-member cluster, depicting intense evaporative fractionation due to prolonged residence times and elevated surface area-to-volume ratios. Compared to surface water, groundwater δD and $\delta^{18}O$ signatures show less variability, yet still reflective of complex hydrological interactions when compared to GMWL and a local *d*-excess line. The majority of groundwater samples showed evidence of g direct recharge dominated by local meteoric water with minimal isotopic modification. Groundwater sub-samples, particularly from near- lake and dambo-wetland sites show localized influence of evaporation and mixing with multiple source water inputs. The former could be through secondary evaporation of surface runoff prior to recharging groundwater or within aquifer system post recharge. This underscores the multi-faceted nature of groundwater and surface water dynamics and influence of their hydraulic interactions with proximal SW bodies like lakes, rivers and reservoirs in the study area.

4.2 Seasonal variability of surface water

Analysis of surface water lines (SWLs) for wet and dry seasons exhibits progressive fractionation from wet to a maximum in dry season primarily due to evaporation (Figure. 6b). This is supported by a considerable shift in slope of the modelled SWLs (6.4±0.2 (SWL_{wet}) to

5.7±0.2 (SWL_{dry})) compared to GMWL slope of 8 (Figure 6b). The isotopic depletion observed in wet season suggest dominant source contribution from fresh meteoric water but exposed to limited evaporation; whereas the dry season isotopic enrichment indicate intense evaporation and mixing with enriched input sources. The disparity of high isotopic enriched surface water observed in wet season is attributed to high retention of enrichment in wet season lake water samples (Figure 6b), and from localised river sites in close proximity with dambo and/or wetland environment. The disparity in high isotopic depletion in surface water observed in dry season is ascribed to convergence of highland-plateau and rift-margin river systems in rift valley escarpment zone, whereby fresh headwaters from the latter river system rejuvenates the mature stage of the former river system before draining into the Lake Malawi. This could also be influenced by hydraulic mixing with depleted groundwater.

4.3 Spatial variability

Remarkable spatial variations were observed in groundwater and surface water isotopes across the study area. Comparisons between different catchments revealed influence of localized hydrological and geological factors on groundwater and surface water isotopic signatures. The groundwater and surface water isotopes in eastern part of the basin are relatively enriched compared to the western part, reflect a spatial gradient in meteoric water input signal which relates to the Lake Malawi basin's hydrologic flow regime (Table 13; Figure 5a/b). The difference in groundwater isotopic signatures at catchment-scale provide critical insights into the influence of aquifer characteristics and local hydrological processes, compounded by secondary evaporation and multiple moisture source contributions. The mean $\delta^{18}O$-δD and derived *d*-excess for groundwater showed strong influence of non-evaporated meteoric water input in

western part (WRA 7) compared to the eastern part (WRA16) which borders the Lake Malawi shoreline.

4.5 Policy implications

The findings of this study have the following significant implications for water resource management policy :

- Water resource management: Understanding variability in δD and $\delta^{18}O$ signatures can inform predictive modelling of water resource quality and availability, crucial for managing drinking water supplies and irrigation.
- Conservation strategies: Identifying areas susceptible to high evaporative losses can guide implementation of conservation measures, such as wetland restoration to buffer against excessive evaporation.
- Infrastructure development: Insights into groundwater recharge and surface water dynamics can inform location and design of water-related infrastructure, improving resilience to hydrological changes.
- Climate adaptation: Knowledge of seasonal and spatial variability help in developing strategies for adaptation to climate-induced changes in water resource availability.
- Policymakers should integrate isotopic analysis into regular monitoring frameworks to ensure sustainable water usage and proactive management of water resources in the face of climatic and anthropogenic changes.

5. Conclusion

This study developed for the first time, a sub basin-scale surface water (SW) and groundwater (GW) isotopic baseline for WRA 7 and WRA 16, and a comprehensive assessment of drivers influencing meteoric water attenuation in this under-represented middle section of the Lake Malawi basin. The study found spatial and seasonal variability of groundwater and surface water δD and $\delta^{18}O$ signatures and derived *d*-excess across the study are. The key outcomes of this study include the following:

- There are considerable differences in groundwater and surface water isotopic signatures which underscore influence of diverse input sources and processes on these water sources, such as meteoric water inputs, evaporation, and water mixing;
- Groundwater and surface water are largely replenished by fresh meteoric water inputs, but with minimal evaporation effect;
- There are a strong-seasonal enrichment gradients of surface water isotopes from wet to dry seasons, with seasonal SWL slopes depicting progressive evaporative enrichment from wet to dry seasons.
- Deuterium excess signal of surface water derived from meteoric water input indicates influence of mixed and contrasting sources of precipitation-air moistures, primarily oceanic source, with contribution from recycled air moisture at both local and continental scales.

Overall, the study provides a transformative baseline isotopic data for current and future isotope-based studies at local and regional scales that underpins water resource monitoring and management.

CRediT authorship contribution statement

Limbikani Chitsundi Banda: Conceptualisation, methodology, validation, formal analysis, investigation, data curation, resources, writing—original draft preparation, writing—review and editing, project administration, funding acquisition**. Robert Michael Kalin:** Methodology, formal analysis, resources, writing—review and editing, project administration, funding acquisition**. Vernon Phoenix:** Resources, project administration, funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data Availability Statement

The research data provided in this study will be made available on reasonable request from the corresponding author.

7.5 Research Article 5: Supplementary Materials

Table SM 1. Descriptive statistics of surface water $\delta^{18}O$-δD and *d*-excess signatures

Variable	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
δD ‰ VSMOW	106	-27.7	1.37	14.1	-46.7	-30.6	14.7	61.4
$\delta^{18}O$ ‰ VSMOW	106	-4.4	0.221	2.27	-7.3	-5.00	2.5	9.80
d-excess ‰	106	7.6	0.538	5.53	-11.4	9.90	16.7	28.1

Variable	Source Type	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
δD ‰ VSMOW	Lake	8	10.0	1.38	3.90	5.0	10.0	14.7	9.7
	Reservoir	8	-29.3	3.31	9.36	-45.0	-27.1	-19.3	25.7
	River	90	-30.9	0.98	9.33	-46.7	-31.7	8.9	55.6
$\delta^{18}O$ ‰ VSMOW	Lake	8	1.6	0.16	0.46	0.9	1.7	2.1	1.2
	Reservoir	8	-5.1	0.42	1.18	-7.0	-4.9	-3.8	3.2
	River	90	-4.9	0.17	1.57	-7.3	-5.2	2.5	9.8
d-excess ‰	Lake	8	-2.6	0.70	1.97	-6.4	-2.0	-0.9	5.5
	Reservoir	8	11.4	0.35	0.99	10.3	11.0	13.0	2.7
	River	90	8.2	0.52	4.97	-11.4	9.9	16.7	28.1

Table 10. Seasonal variability of surface water $\delta^{18}O$-δD and *d*-excess (*d*) signatures.

Isotopic Tracer	Season	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
δD ‰ VSMOW	Dry	52	– 24.2	1.77	12.8	– 42.0	– 26.9	9.50	51.5
	Wet	54	– 31.0	1.98	14.6	– 46.7	– 35.4	14.7	61.4
$\delta^{18}O$ ‰ VSMOW	Dry	52	– 3.8	0.30	2.16	– 6.50	– 4.40	2.50	9.0
	Wet	54	– 5.0	0.30	2.23	– 7.30	– 5.80	2.10	9.4
d-excess ‰	Dry	52	5.9	0.83	6.01	– 11.4	6.90	14.1	25.5
	Wet	54	9.2	0.62	4.52	– 6.40	10.7	16.7	23.1

7.6 Research Article 6: Main Paper

Groundwater and surface water resource conceptualisation using δD and $\delta^{18}O$ tracers in Songwe /Lufira River, North Rukuru River and Karonga lakeshore catchments: A transboundary Lake Malawi sub-basin.

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Abstract: This groundbreaking study establishes a baseline for δD and $\delta^{18}O$ isotopes of surface water (SW) and groundwater (GW) at a sub-basin scale in the underrepresented northernmost section of the Lake Malawi basin. It sheds light on the dynamics of meteoric water attenuation and hydrological processes in the area. Our research reveals that the influx of meteoric water primarily comes from oceanic and recycled air moisture, characterized by a *d*-excess offset of +13.3 ‰ from the Global Meteoric Water Line (GMWL). Our findings indicate that both GW and SW mainly originate from recent meteoric water inputs, with δD and $\delta^{18}O$ signatures closely aligning with the GMWL and exhibiting *d*-excess values around +10 ‰. Notably, SW sources demonstrate high levels of meteoric water attenuation, particularly in lake water, which shows significant evaporative enrichment tied to prolonged residence times. The analysis also uncovers considerable variability in δD and $\delta^{18}O$ signatures, highlighting the diverse influences of local precipitation, evaporation, and GW mixing. River water reflects a mixture of recent precipitation

and upstream contributions, while lake sites exhibit substantial isotopic enrichment due to evaporation. GW signatures, though less variable, closely follow local precipitation trend, showing seasonal pattern with depleted heavy isotopes during the wet season and enriched heavy isotopes coupled with reduced deuterium excess in the dry season. Spatial isotopic variability indicates differences between the Songwe/Lufira River, North Rukuru River and Karonga lakeshore catchments, shaped by local hydrological and geological factors. Our study suggests significant interactions between GW and SW, evidenced by consistent isotopic signals and contributions of spring discharges to river flows. These findings highlight complexity of the hydrological system in the Lake Malawi sub-basin and emphasize the need for integrated water resource management strategies that consider the interactions SW and GW systems, local precipitation patterns, and evaporation processes. This research enhances our understanding of the Lake Malawi basin's hydrological cycle and sets the foundation for adaptive management strategies aimed at ensuring sustainability of water resources in the Lake Malawi basin.

Key words: stable isotopes; *d*-excess; water resource management, seasonal dynamics, groundwater-surface water interactions

1. Introduction

Globally, the unsustainable extraction of groundwater is leading to a decrement in aquifer volumes, an issue particularly pressing in Malawi, where groundwater caters to the daily needs of approximately 65% of the population. The dependency on groundwater not only poses formidable challenges in water resource management but also necessitates an urgent and nuanced understanding of the correlation between groundwater extraction and replenishment (Jasechko et al., 2024; Jasechko et al., 2021). The deepening disparity between extraction rates and the

natural recharge of aquifers underscores a critical need for enhanced scientific investigations. These studies should elucidate the complex dynamics between surface water and groundwater to inform sustainable water resource allocation and management practices effectively.

Notwithstanding the imperative need, current scientific research concerning groundwater recharge processes, the provenance of surface water, and their spatiotemporal interactions remain distressingly inadequate (Banda et al., 2024). This deficiency severely impedes the formulation of effective water resource management strategies, which are increasingly vital amid the adverse impacts of climate change (Kalin et al., 2022). Furthermore, the evolving unpredictability in precipitation patterns and surface water trends presents significant challenges for water resource planning, particularly affecting large-scale irrigated agriculture and the reliability of rural gravity-fed water systems in Malawi (Kalin et al., 2022). These compounding challenges underline the necessity for a comprehensive understanding of the hydrological cycle, capable of guiding sustainable water resource management practices. To address these issues, we build upon previous targeted catchment and basin-wide investigations (Banda et al., 2019a, 2020c, 2021, 2024; Dwight et al., 2018; Hinton et al., 2024; Kambuku et al., 2018; Missi & Atekwana, 2020; Monjerezi, 2012a, 2012b; Monjerezi & Ngongondo, 2012; Nkhoma et al., 2021; Rivett et al., 2018, 2020). These previous studies laid foundational groundwork for enhancing scientific understanding and data concerning various critical water resource areas within Malawi.

The primary goal of this study is to contribute to a rigorous and expansive body of scientific knowledge that will facilitate a refined conceptualization of water resources, thereby aiding the development of water policy and the effective implementation of Integrated Water Resources Management (IWRM). In pursuit of this goal, the study is structured around several key objectives: (i) To establish a comprehensive baseline for $\delta^{18}O$-δD isotopic signatures in both

groundwater and surface water, expected to serve as a pivotal benchmark for tracking future changes due to increased land-use development and climatic variations. (ii) To examine variability of $\delta^{18}O$-δD isotopic signals across diverse catchments to identify the source and process controls influencing this variability.

2. Study Area Description

The study area covers the Songwe River/Lufira River, North Rukuru River, and Karonga Lakeshore catchments), marked by diverse physiographic zones in the East African Rift System. Collectively these catchments form a Lake Malawi sub-Basin that spans ca. 7,763 km^2 (MoAIWD., 2014). This is a transboundary water resource in terms of both surface water and aquifers and is shared among Malawi, Tanzania, Mozambique, and Zambia (Fraser et al., 2020; Kalin et al., 2022).

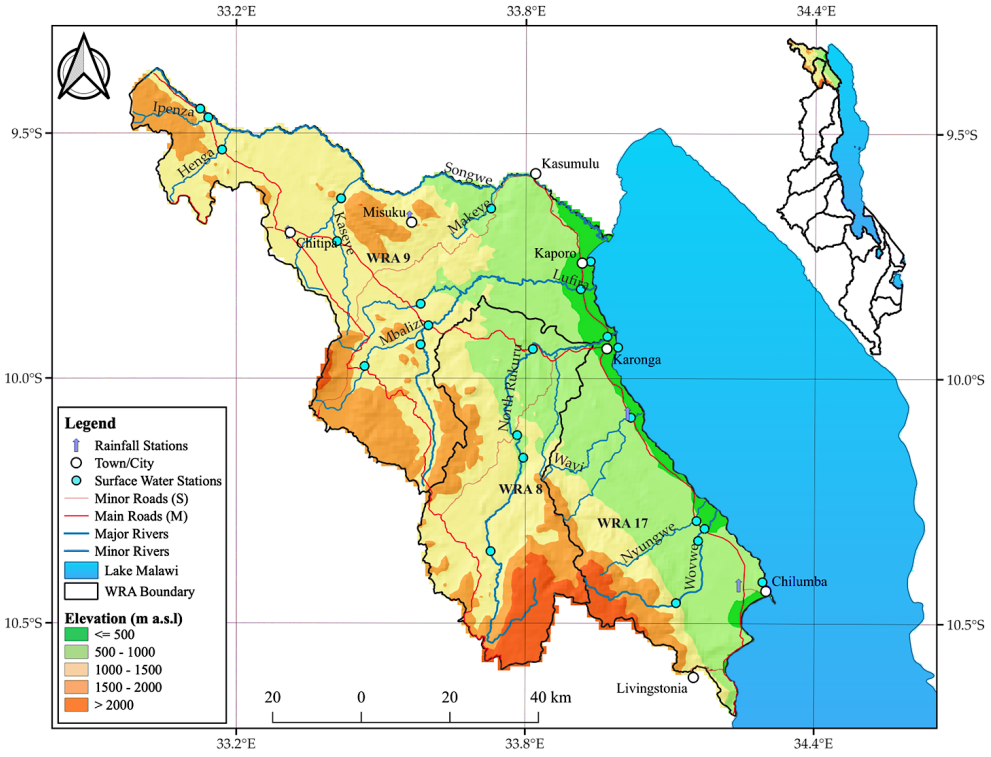

Figure 1. Study area extent showing topographic spread (SRTM elevation data: USGS), water resource areas (WRAs), major rivers and surface water sampling points.

2.1 Drainage and geographic influence

The Lake Malawi sub-basin encompass significant perennial rivers, including the Songwe, North Rukuru, and Lufira, which primarily drain the basin into Lake Malawi. Other rivers, such as the Chambo and Kasisi, are largely seasonal and mostly flow during rainy periods (MoAIWD., 2014; Kalin et al., 2022). The WRA 8 is mainly drained by North Rukuru River, which originates from the Nyika Plateau at an elevation of ca. 2,400 m asl. This WRA, covering ca. 2,088 km², experiences a sharp elevation decline from 1,400 to 100 meters, transitioning from dense forests and populated areas to expansive valleys (Kalin et al., 2022). The river plunges 500 meters toward the lakeshore at an elevation between 450 and 500 m. This steep descent tends to lead to seasonal flash floods, influenced by t varied topography and climatic conditions. To the south, WRA 9 drains an area of ca. 3,730 km² and is primarily covers the Karonga district. This WRA 9 consist of highlands in the west and lowlands in the east. Notable conservation zones include the Mafinga Hills and Misisi Forest Reserves (MoAIWD., 2014; Kalin et al., 2022). The hydrology in the WRA 9 is largely defined by the Songwe River, which receives contributions from several tributaries, including the Makeye, Kaseye, and Lufira Rivers. Bordering Lake Malawi western shoreline is the WRA 17, also called the Karonga Lakeshore catchment which covers ca. 1,945 km (Kalin et al., 2022). Water predominantly flows from western highlands eastward through rivers such as the Wovwe, Wayi, and Nyungwe. In the Misuku Hills, river flow generally takes a northwest direction, consistent with the regional geological structure, forming a network-like drainage pattern. However, this pattern is occasionally disrupted by rivers such as the Kanga and North Rukuru, which cross these typical paths and may reflect underlying structural controls like faults or joints. Rivers such as the Lufira and Chambo typically follow

deeply incised, meandering courses consistent with drainage patterns established prior to significant geological uplift and erosion events in the area.

2.2 Geology and hydrogeology

The Lake Malawi basin has a renown complex hydrogeological structure, consisting of a diverse alignment of hydrostratigraphic units that significantly influence groundwater dynamics and resource management within the basin. In this part of the Lake Malawi basin, these hydrostratigraphic units are delineated into three primary aquifer groups: Group 1: consolidated sedimentary rock aquifer; Group 2: unconsolidated sedimentary units overlying weathered basement aquifer; and Group 3: weathered basement units overlying fractured basement (Figure X). Aquifer Group 1 primarily consists of sandstone and shale, forming a sturdy framework critical for groundwater storage. These aquifers are predominantly situated in the northern part of the basin, though they are not widespread. Aquifer Group 2 consists of colluvial and alluvial deposits and is mainly found in the western sections of the basin. The loose configuration of these sedimentary layers enhances their porosity and permeability, thereby facilitating efficient groundwater accumulation and flow. Remarkably, this type of aquifer can yield water at rates of up to 20 litres per second, highlighting their substantial hydrogeological impact. Aquifer Group 3 mainly consist of charnockitic gneiss and hornblende-biotite-gneiss, predominantly found along the eastern regions near rift scarp zones. The weathered nature of these units, along with the underlying fractured basement, supports groundwater movement through interconnected spaces, fissures, and joints. However, they typically have lower yields, reaching up to approximately 2 litres per second.

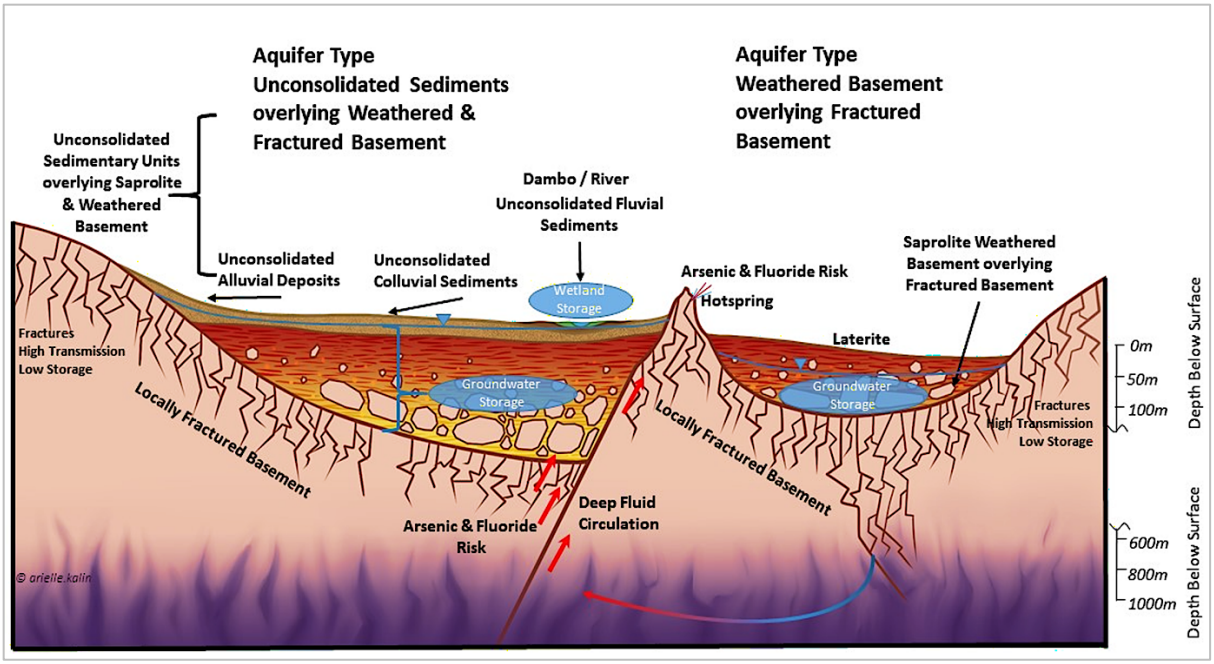

Figure 2. Idealised cross-section of the hydrostratigraphic aquifer units in the study area (after Kalin et al., 2022).

Spatial distribution of these aquifer types across the basin is notably uneven, with significant accumulations of unconsolidated fluvial, colluvial, and alluvial sediments along the Lake Malawi shoreline and adjacent rift valley plains. This spatial variability is crucial in determining the availability and sustainability of groundwater resources and reflects the intricate interplay between geological formations and hydrogeological processes within the basin. Generally, the aquifers' mineralogical composition substantially influences the geochemical characteristics of groundwater in the basin. Dominant minerals include plagioclase, pyroxenes, feldspars, amphiboles, and biotite, each introducing various chemical species into the groundwater, thus affecting its chemistry. For instance, the decomposition of calcic plagioclase minerals releases calcium and sodium, while the dissolution of mafic minerals tends to release magnesium, iron, and other ions into the groundwater system. These elements, along with fluoride ions, have critical implications for groundwater quality.

2.3 Climate

The Lake Malawi sub-basin experiences a tropical-continental climate influenced by various elements including altitude, geographic relief, and the presence of Lake Malawi. According to the Köppen-Geiger classification system, the climate of the basin is designated as Aw, or Savannah, characterized by distinct rainy and dry seasons (Peel et al., 2007). The rainy season spans from November to April, while the dry season occupies the months of May through October. During the dry months, the prevailing southeastern winds affect the region, whereas the rainy season is shaped by northeastern winds, the Intertropical Convergence Zone (ITCZ), the Congo Air Boundary (CAB), and Tropical Cyclones, which serve as the main sources of precipitation (Ngongondo et al., 2011; Vincent et al., 2014). Peak rainfall typically occurs in January, and overall, rainfall is heaviest between December and March. The eastern regions of the basin, particularly near the Lake Malawi shoreline, receive most rainfall in March (Nicholson, 1998; Nicholson et al., 2014). Factors such as the basin's topography and Lake Malawi itself play critical roles in determining the spatial distribution of rainfall across the region (Vincent et al., 2014; Sene et al., 2016; DCCM, accessed in January 2023).

3. Methodology

3.1 Water sample collection

Water samples were collected from surface water (rivers and lakes) and groundwater (springs, protected dug-wells, and boreholes equipped with hand pumps) during the dry and wet seasons. Surface water sites were selected and sampled first, followed by adjacent groundwater to to allow examination of their interactions. Each water sample was filled in a 50-ml high-

density polyethylene (HDPE) bottle that had been thoroughly pre-cleaned. The water sampling bottles rinsed three time with water sample and filled to capacity to avoid any air space, thus mitigating the risk of isotopic fractionation. To preserve the integrity of stable isotopes in the samples, each water sampling bottle was sealed with paraffin film and reinforced with waterproof tape. This procedure minimized risks associated with leakage, evaporative losses, and alterations via chemical or biological reactions. The water samples were consistently stored at 4°C and shielded from direct sunlight until the time of analysis. As a preparatory step, the bottles were repeatedly rinsed with water from the sampling site to ensure conditions reflective of native environments. For rivers, the strategy involved sampling directly from the central flow channel to accurately represent the water body. In smaller rivers, a simple grab sampling approach was adequate, whereas larger rivers required structured sampling at designated intervals across the breadth of the river, commonly facilitated by the use of bridges. Spatially, river samples typically spanned upstream, midstream, and downstream sections to effectively track isotopic inputs and outputs. Lake samples were extracted approximately 1 km from shorelines, particularly from estuarine zones using a depth-sampling device. Groundwater samples were taken from actively used community boreholes; these were sufficiently purged to avoid contamination with stagnant water. If boreholes were not in regular use, they were purged for at least five minutes to ensure a fresh sample reflective of the aquifer conditions. Whenever borehole construction data was accessible, the purging guidelines recommended an output of three times the borehole's volume before sample collection (Diamond., 2022). Springs were sampled precisely at their main discharge points, deliberately avoiding stagnant adjacent pools that are prone to isotopic change due to evaporative and atmospheric factors.

3.2 Water sample analysis

3.2.1 Field analysis

Onsite measurements were conducted to accurately record water quality parameters such as temperature, electrical conductivity (EC), total dissolved solids (TDS), and pH. These measurements were undertaken using a precisely calibrated portable multi-meter (Model: HI-98194, Hanna Instruments, Woonsocket, RI, USA). Due to the susceptibility of these parameters to environmental alterations during transport from collection sites to the laboratory, immediate onsite measurement was essential for maintaining data integrity. For each parameter, the multi-meter readings were allowed to stabilize for a period ranging between 2 and 5 minutes before data was captured, ensuring consistency in the results obtained. When measuring in flowing surface water, the multi-meter's probe was submerged to a minimum depth of 100 mm, avoiding static water bodies to prevent skewed data. For spring water, measurements occurred directly at the primary discharge points. Groundwater samples from boreholes and dug wells were collected into a 250 ml beaker after which immediate onsite measurements were performed. These procedures provided preliminary insights into the onsite conditions and served as a reference to identify any potential alterations in water quality during sample transit and storage.

3.2.2 Laboratory analysis

The isotopic composition of the samples was determined using a Picarro 2140i CRDS Isotopic Water Analyser (Model: L2140-i, Picarro Inc., Santa Clara, CA, USA). This analysis boasted a precision of ± 0.2 ppm for oxygen-18 and ± 2.0 ppm for deuterium. The isotopic analyses were facilitated by the IAEA at the Isotope Hydrology Laboratory in Vienna, Austria, acknowledging the institution’s global recognition in isotopic studies. The sample preparation

for isotope analysis followed a structured protocol involving the filtration of a 1 ml sample through a 0.45 μm filter into a 2 ml glass vial. The sample prepped vials were loaded into an autosampler on the IWA, which was pre-conditioned by running deionized water for 60 minutes to equilibrate the concentration peaks within a range of 19,000 to 21,000 ppm. To ensure rigorous quality assurance and control, each batch of ten samples processed included prescribed calibration and control standards. The analysis ran in a high-precision mode entailing three autoruns, with dry synthetic air as the carrier gas and injections set at six-minute intervals to minimize interferences. Standards used included enriched and depleted standards as reference points, and the first three injections were discarded to prevent memory effects in the data. The remaining data underwent residual memory correction and normalization against established isotopic scales, Vienna Standard Mean Ocean Water (VSMOW), and Standard Light Antarctic Precipitation (SLAP). The output data, representing isotopic variations, were expressed as delta (δ) values which quantifies these isotopic variations in parts per thousand (‰). This notation denotes deviations in isotopic compositions relative to the standards, with positive δ values indicating isotopic enrichment and negative values indicating depletion. These methodologies adhere to International Standard Procedures (IAEA., 2009), ensuring the reliability and global standardization of the research outcomes.

Deuterium excess (*d*-excess or *d*), defined by the equation $d = \delta D - 8\delta^{18}O$ ‰VSMOW (Dansgaard, 1964), is another reliable tracer that is primarily employed to reflect meteorological conditions at the moisture source (Gat et al., 2000; Merlivat & Jouzel, 1979; Rozanski et al., 1993). A *d*-excess near 10 ‰ typically suggests ocean-derived moisture, whereas higher values are indicative of secondary moisture recycling processes, potentially linked to variations in the atmospheric humidity of the source region (IAEA., 2005). Conversely, *d*-excess values less than

+10‰ are associated with the influence of secondary processes such as raindrop evaporation and evaporation from terrestrial water bodies, which reduce the *d*-excess (Froehlich et al., 2002; Rozanski et al., 1993).

4. Results

4.1 Stable isotope characteristics of surface water sources

Stable isotopic signatures of surface water samples (n = 48) demonstrated a broad spectrum of δD values, ranging from –45.3 to +28.9‰, with an average of –21.5‰, while $\delta^{18}O$ signatures ranged from –6.9 to +5.1‰ with a mean of –3.6‰ (Table 1). The surface water *d*-excess values varied from –11.9‰ to +15.9‰, averaging +7.3‰. River water samples recorded δD values from –45.3 to –11.7‰, with a mean of –26.8‰, and $\delta^{18}O$ values ranging from –6.9 to +1.5‰, averaging –4.5‰ (Table 1). For lake water samples, δD values ranged from +7.5 to +28‰, with an average of +15.6‰, and $\delta^{18}O$ values ranged from +1.3 to +5.1‰, averaging +2.6‰. The higher positive δD-$\delta^{18}O$ values observed in lake water samples relative to river water samples indicate strong evaporation and high retention effect of the lake. Mean *d*-excess values for lake and river water samples provide strong evidence of distinct influences of evaporation and meteoric water input signal on these surface water sources.

Most surface water samples from river sites (cluster A) aligned with the local *d*-excess line (Banda et al., 2024) and Global Meteoric Water line (Craig, 1961), suggesting strong contributions from meteoric water input, but with minimal evaporation effects (Figure 2a). A subset of surface water samples (cluster B) deviated from the meteoric water lines, instead plotting along a modelled surface water line (SWL) defined as $\delta D = (5.98 \pm 0.13)\ \delta^{18}O + (0.03 \pm 0.56)$. The isotopic deviation suggests enrichment due to evaporative fractionation, with lake

samples forming an end-member cluster C (Figure 2b). The SWL is influenced by progressive evaporative fractionation and water mixing from different inputs.

Table 1. Descriptive summary of δ^{18}O-δD and *d*-excess signatures in surface water sources

Isotopic Tracer	Source Type	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
δ^{18}O ‰	SW	48	–3.6	0.4	2.7	–6.9	–4.3	5.1	12.0
δD ‰	SW	48	–21.5	2.3	16.2	–45.3	–25.2	28.9	74.2
d-excess ‰	SW	48	7.3	0.9	5.9	–11.9	9.4	15.9	27.8
Isotopic Tracer	Source Type	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
δ^{18}O ‰	Lake	6	2.6	0.6	1.5	1.3	2.1	5.1	3.8
	River	42	–4.5	0.2	1.2	–6.9	–4.6	–1.5	5.4
δD ‰	Lake	6	15.6	3.2	7.8	7.5	14.8	28.9	21.4
	River	42	–26.8	1.2	7.9	–45.3	–27.6	–11.7	33.6
d-excess ‰	Lake	6	–5.3	1.8	4.4	–11.9	–3.6	–1.4	10.5
	River	42	9.1	0.5	3.3	0.10	9.9	15.9	15.8

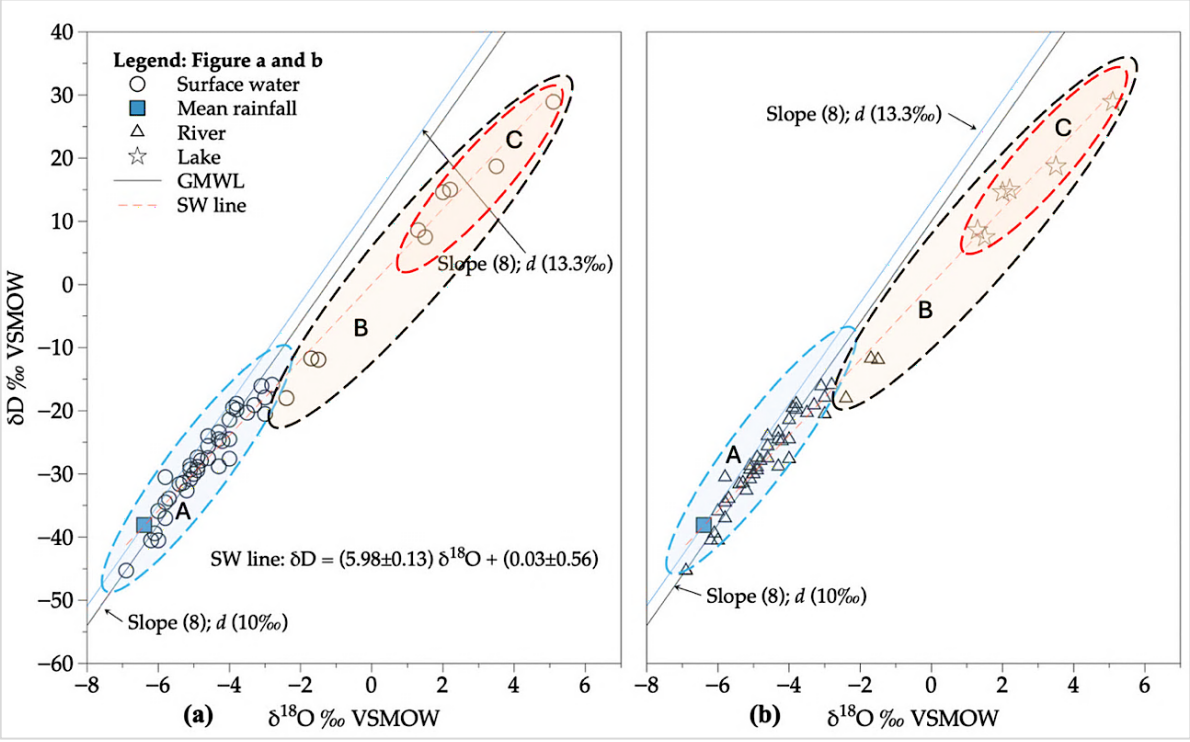

Figure 3. Bi-variate plots of δ^{18}O-δD signatures in river and lake water

4.2 Stable isotopic characteristics of groundwater sources

The isotopic analysis of groundwater samples (n = 103) exhibit a wide range of δD values, from –40.3 to –15.8‰, with an average of –30.9‰ (Table 2); whereas $\delta^{18}O$ signatures range from –6.9 to –2.9‰, with a mean of –5.3‰. Groundwater *d*-excess values varied from +1.3‰ to +19.3‰, averaging +11.1‰. The groundwater samples largely cluster along the meteoric water lines, implying that it is primarily recharged by recent meteoric water input (Figure 4). A dual subset of groundwater samples plotted below and above from the meteoric water lines. The groundwater samples plotting below indicate influence of evaporative fractionation occurring either during runoff before groundwater infiltration or through shallow groundwater evaporation within the aquifer (REF). It could also mean mixing of newer meteoric water with older groundwater that has undergone intense evaporation or water-rock interaction, resulting in an enriched composite along the groundwater flow path (REF). The groundwater samples plotting above the meteoric water lines suggest excess deuterium higher than 10‰ of the GMWL, associated with meteoric water input influenced by localised moisture recycling effect (Yurtsever et al., 1980; Banda et al., 2024).

Table 2. Descriptive summary of $\delta^{18}O$-δD and *d*-excess signatures in groundwater sources

Tracer	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range	IQR
δD ‰	103	–30.9	0.6	6.3	–40.3	–33.0	–15.8	24.5	10.1
$\delta^{18}O$ ‰	103	–5.3	0.1	0.8	–6.9	–5.4	–2.9	4.0	1.1
d-excess ‰	103	11.1	0.2	2.5	1.3	10.9	19.3	18.0	1.8

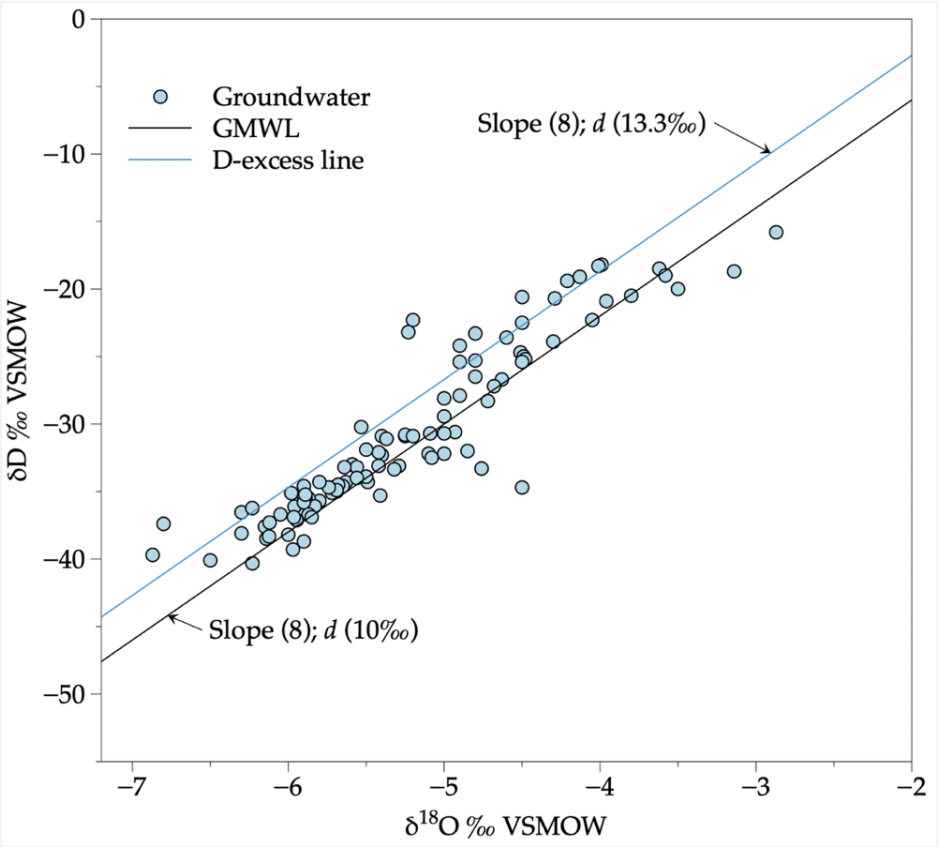

Figure 4. Bi-variate plots of $\delta^{18}O$-δD signatures in GW samples across the Lake Malawi sub-basin.

4.3 Co-variability of groundwater isotopes in different aquifer groups

Analysis of stable isotope data for samples from aquifer Groups 1, 2, and 3 suggest influence of geological characteristics on isotopic profiles of groundwater (Table 3). Aquifer G1, characterized by consolidated sedimentary rocks, exhibits a notably consistent isotopic signature with δD‰ mean value of –37.0‰, and standard deviation of +2.5‰. The narrower ranges of +5.8‰ for δD‰ and +0.7‰ for $\delta^{18}O$ observed in groundwater samples from G1 are a proxy indicator of a more controlled and homogeneous hydrogeological aquifer formation, likely less affected by surface interactions and rapid infiltration, typical of more consolidated aquifers.

Table 3. Descriptive summary of $\delta^{18}O$-δD and *d*-excess signatures in groundwater sources across different aquifer groups.

Variable	Aquifer Group	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range	IQR
δD ‰	Group 1	4	–37.0	1.23	2.45	–40.1	–36.9	–34.3	5.8	4.7
	Group 2	67	–30.2	0.77	6.30	–40.3	–32.0	–15.8	24.5	9.9
	Group 3	32	–31.4	1.10	6.24	–39.7	–33.3	–18.2	21.5	9.0
$\delta^{18}O$ ‰	Group 1	4	–6.1	0.18	0.36	–6.5	–6.1	–5.6	0.9	0.7
	Group 2	67	–5.2	0.10	0.79	–6.8	–5.2	–2.9	3.9	1.2
	Group 3	32	–5.3	0.14	0.79	–6.9	–5.6	–3.1	3.7	1.0
d-excess ‰	Group 1	4	11.5	0.25	0.50	10.7	11.6	11.9	1.2	0.9
	Group 2	67	11.0	0.31	2.51	1.3	10.7	18.6	17.3	2.1
	Group 3	32	11.3	0.45	2.53	4.8	11.0	19.3	14.5	8.0

Group 1	Consolidated Sedimentary Rock
Group 2	Unconsolidated Sediments overlying Weather Basement
Group 3	Weathered Basement overlying Fractured Basement

Groundwater samples from G2 and G3, associated with unconsolidated sediment, weathered and fractured basement formations, exhibit greater isotopic variability, particularly G2, indicative of dynamic and heterogeneous aquifer environment (Table 3). This could be attributed aquifer interactions modern meteoric water and older groundwater water inputs, coupled with influence of evaporation fractionation, more pronounced in unconsolidated sedimentary aquifers.

4.4 Spatial distribution of groundwater and surface water isotopes

4.4.1 Surface water sources

The $\delta^{18}O$ and δD signatures of surface water samples exhibit notable variability across WRAs 8, 9, and 17 (Figure 5a). The $\delta^{18}O$ values show significant differences, with WRA 8 displaying a mean of –5.5‰ (SD = 0.9‰), WRA 9 at –4.3‰ (SD = 1.2‰), and WRA 17

demonstrating the highest variability with a mean of –2.0‰ (SD = 3.9‰). A similar pattern is observed in the δD values: WRA 8 has a mean of –33.8‰,–25.4 for WRA 9 ‰, and –11.8‰, for WRA 17, with WRA 17 exhibiting the highest standard deviation at 23.1‰. The *d*-excess values also vary among the WRAs, with WRA 8 averaging +10.0‰ (SD = 2.2‰), WRA 9 averaging +8.6‰ (SD = 3.5‰), and WRA 17 recording the lowest mean of +4.3‰, but with the highest standard deviation of 8.4‰. When examining the mean $\delta^{18}O$ and δD signatures of surface water samples from these three catchments, along with the slopes of the surface water

Table 4. Descriptive summary of $\delta^{18}O$-δD and *d*-excess signatures for surface water sources across different catchments and topographic landscapes.

Isotopic tracer	WRA	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
$\delta^{18}O$ ‰	8	4	–5.5	0.4	0.9	–6.0	–5.9	–4.2	1.8
	9	28	–4.3	0.2	1.2	–6.9	–4.3	–1.5	5.4
	17	16	–2.0	1.0	3.9	–6.2	–3.7	–5.1	11.3
δD ‰	8	4	–33.8	3.3	6.6	–40.5	–34.9	–24.8	15.7
	9	28	–25.4	1.5	7.7	–45.3	–26.5	–11.7	33.6
	17	16	–11.8	5.8	23.1	-40.5	–21.6	28.90	69.4
d-excess ‰	8	4	10.0	1.1	2.2	7.5	10.3	12.1	4.6
	9	28	8.6	0.7	3.5	0.10	9.9	12.1	12.0
	17	16	4.3	2.1	8.4	–11.9	7.40	15.9	27.8
$\delta^{18}O$ ‰	Lowland	30	–3.1	0.6	3.1	–6.2	–4.2	5.1	11.3
	Upland	18	–4.4	0.4	1.5	–6.9	–4.6	–1.5	5.4
δD ‰	Lowland	30	–18.2	3.4	18.4	–40.5	–24.3	28.9	69.4
	Upland	18	–27.2	2.2	9.5	–45.3	–28.2	–11.7	33.6
d-excess ‰	Lowland	30	7.0	1.3	6.9	–11.9	10.0	15.9	27.8
	Upland	18	7.9	0.9	3.6	0.1	9.2	11.9	11.8

regression lines, it is evident that WRA 8 is comparatively depleted, while WRA 17 is notably enriched (Table 4; Figure 5a). The variations in the slopes of the regression lines indicate an isotopic fractionation trend towards enrichment as surface water moves toward the lake. The lake water samples serve as an end-member along the surface water regression line, with the enrichment observed in WRA 17 primarily influenced by this cluster of lake water samples.

A distinct spatial trend is evident as surface water flows from upland to lowland areas within these catchments (Figure 5b). Surface water Cluster A demonstrates that the $\delta^{18}O$-δD signatures of samples collected from upland sites are relatively more depleted. In contrast, Surface Water Cluster B exhibits isotopic enrichment in samples from lowland sites, particularly those associated with lake water, which comprise the end-member Cluster C (Figure 5b). The regression slopes for surface water from upland (6.12 ± 0.37) and lowland (5.88 ± 0.13) sites are both lower than that of the Global Meteoric Water Line (GMWL, 8), suggesting that surface water from both upland and lowland regions has undergone some degree of evaporative fractionation.

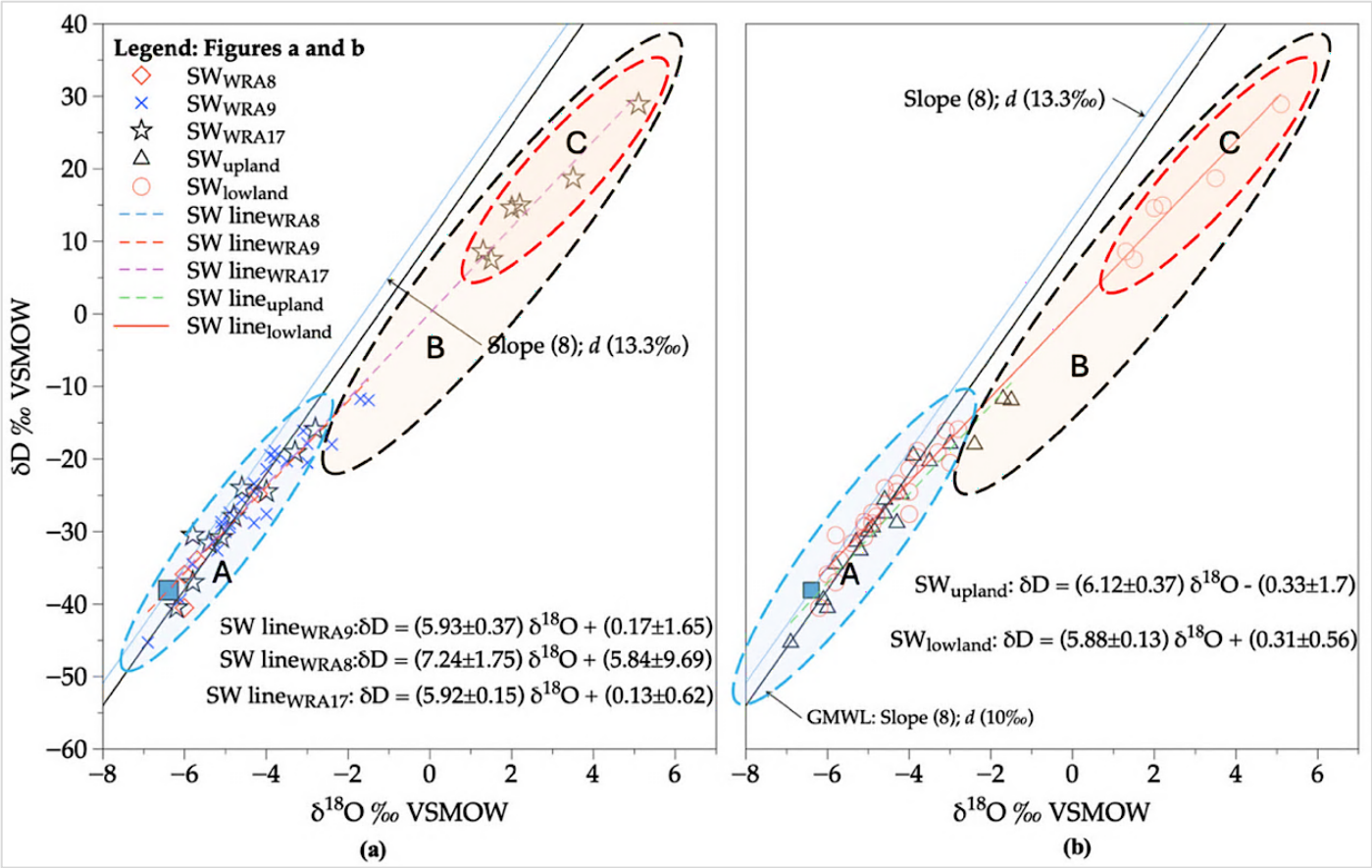

Figure 5. Spatial variability of $\delta^{18}O$-δD signatures in surface water sources across different catchments and topographic landscapes.

4.4.2 Groundwater sources

The distribution of groundwater $\delta^{18}O$-δD signatures across Water Resource Areas (WRAs) 8, 9, and 17 exhibits subtle variations. WRA 8 recorded a mean δD value of –34.9‰, with a standard deviation of +3.5‰, indicating a relatively narrow range around the mean that suggests a uniform recharge source. In contrast, WRA 9 showed a higher mean δD of –30.8‰ along with a wider range of +22.1‰. Notably, WRA 17 displayed the greatest variability, with a mean δD of –28.3‰ and a standard deviation of +5.8‰. The *d*-excess values among the WRAs showed less variability, suggesting that groundwater recharge is primarily influenced by similar

Table 5. Descriptive summary of $\delta^{18}O$-δD and *d*-excess signatures for groundwater sources across different catchments.

Isotope Tracer	WRA	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range	IQR
δD ‰	8	14	–34.9	0.9	3.5	–40.1	–35.2	–28.3	11.8	6.0
	9	70	–30.8	0.8	6.5	–40.3	–33.2	–18.2	22.1	10.6
	17	19	–28.3	1.3	5.8	–38.2	–29.4	–15.8	22.4	8.3
$\delta^{18}O$ ‰	8	14	–5.7	0.2	0.6	–6.9	–5.8	–4.7	2.2	1.0
	9	70	–5.3	0.1	0.8	–6.8	–5.5	–3.1	3.7	1.1
	17	19	–4.9	0.2	0.9	–6.3	–4.9	–2.9	3.4	1.1
d-excess ‰	8	14	10.6	0.6	2.4	4.8	10.8	15.3	10.5	2.4
	9	70	11.3	0.3	2.6	1.3	10.9	19.3	18.0	1.8
	17	19	10.9	0.4	1.9	7.2	10.9	13.9	6.7	2.5

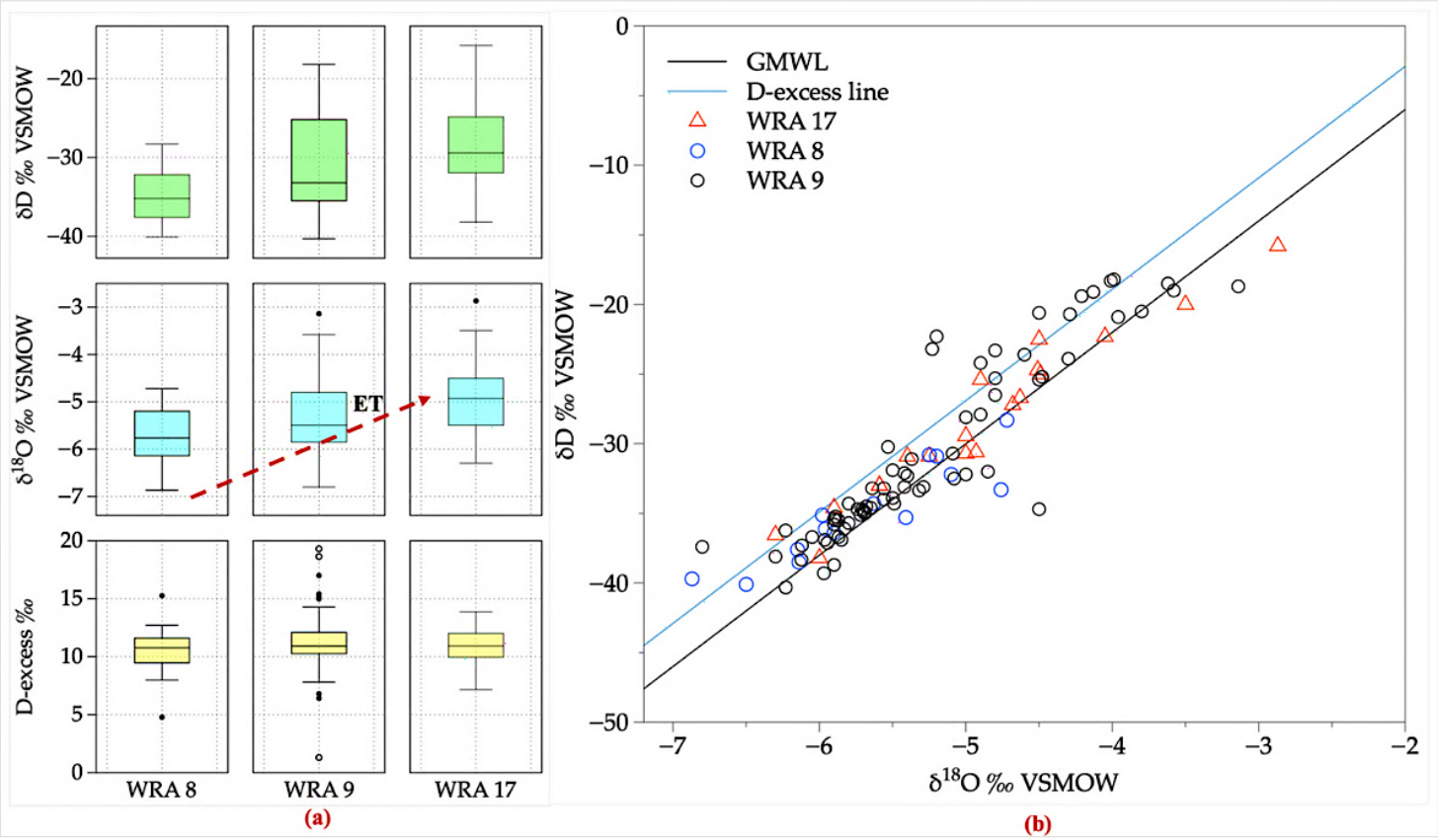

Figure 6. Bi-variate plot of $\delta^{18}O$-δD and *d*-excess signatures in groundwater sources across different catchments.

meteorological inputs across these areas. The WRA 8 recorded a mean *d*-excess of +10.6‰ (SE:±0.6), with a standard deviation of +2.4‰. The WRA 9 recorded a mean of +11.3‰ (SE:±0.3) and a standard deviation of +2.6‰, while WRA 17 recorded a mean *d*-excess of +10.9‰ (SE: ±0.4), with a lower standard deviation of +1.9‰ (Table 5).

4.5 Seasonal changes in surface water isotopes

The isotopic signatures of $\delta^{18}O$ and δD in surface water from the Lake Malawi sub-basin exhibit significant seasonal variability, which is crucial for understanding the underlying hydrological processes. During the dry season, $\delta^{18}O$ values ranged from –5.7 to +5.1‰, with an average of –3.1‰ and a median of –3.8‰. In this season, δD values varied between –33.9 and +28.9‰, yielding a mean of –17.8‰ and a median of –20.4‰. In contrast, the wet season displayed markedly different isotopic characteristics, with $\delta^{18}O$ values ranging from –6.9 to +3.5‰, an average of –4.2‰, and a median of –5.0‰. During this period, δD values spanned –45.3 to +18.7‰, resulting in a mean of –25.3‰ and a median of –29.1‰. This data indicates that both δD and $\delta^{18}O$ values are lower (more negative) during the wet season, suggesting that surface water during this time is relatively more depleted of heavy isotopes. Conversely, the dry season is characterized by surface water that is enriched with these isotopes.

The *d*-excess values of the surface water also showed distinct seasonal trends. In the dry season, *d*-excess ranged from +11.9 to +12.8, with a mean of +6.6 and a median of +9.1. During the wet season, *d*-excess exhibited a wider range of –9.3 to +15.9, with a mean of +8.1 and a median of +9.6. The wet season's mean *d*-excess value of +8.1‰ reflects a significant influx of fresh meteoric water, highlighting its critical role in the hydrology of the Lake Malawi basin. The dry season's mean *d*-excess of +6.6‰ suggests relative isotopic enrichment, likely due to

evaporative fractionation associated with strong evaporation during this time of year. Increased standard deviations and broader ranges in *d*-excess observed during the dry season indicate greater intra-seasonal variability in surface water isotopic signatures. This variability may be attributed to the influx of multiple sources into the surface water system and its interaction with groundwater.

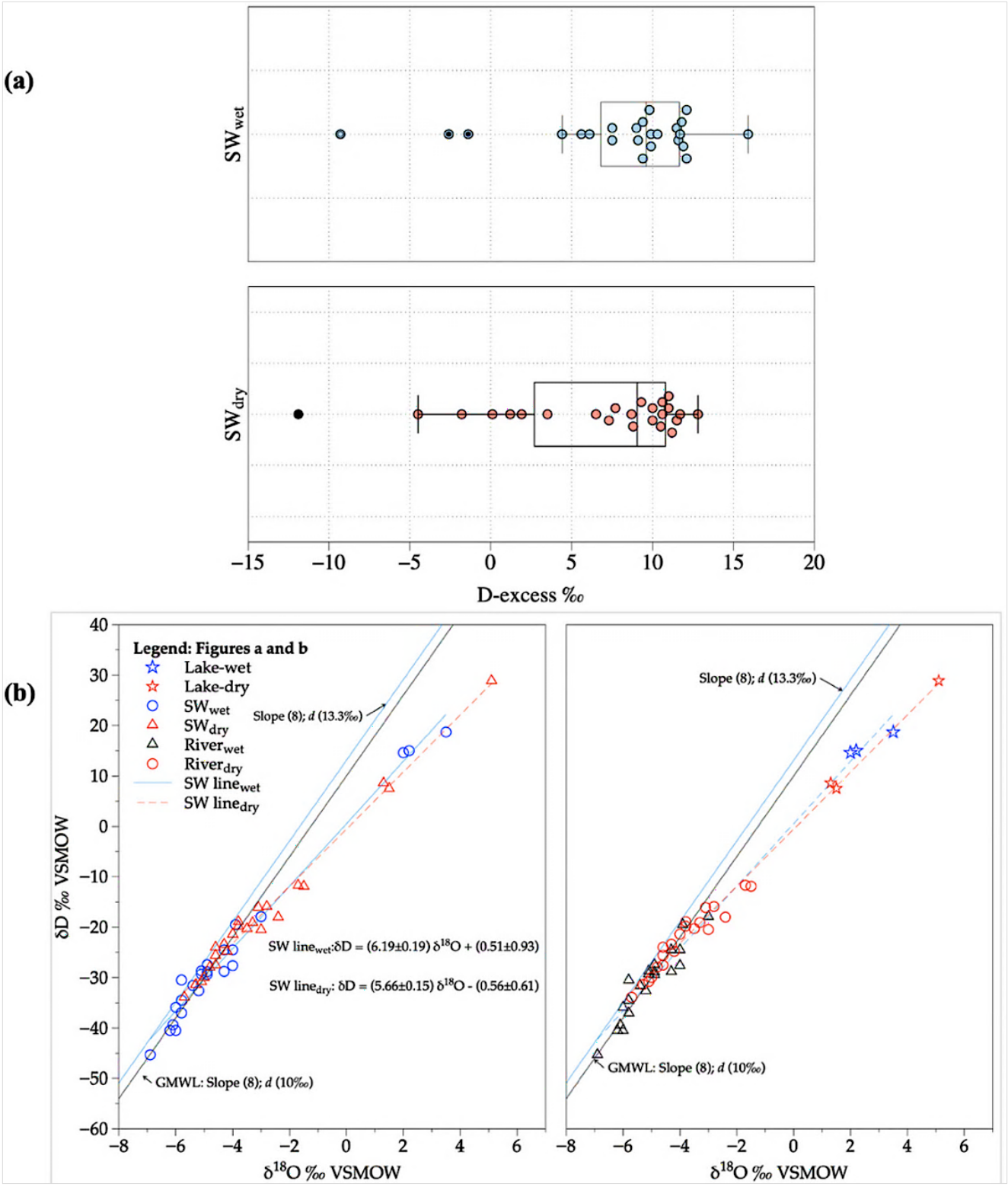

Figure 7. Seasonal variability of $\delta^{18}O$-δD and *d*-excess (d) signatures in different surface water sources.

Table 11. Descriptive summary of $\delta^{18}O$-δD and *d*-excess signatures in surface water across different seasons.

Isotope Tracer	Season	N	Mean	SE Mean	Std Dev	Min	Median	Max	Range
$\delta^{18}O$	dry	24	–3.1	0.6	2.5	–5.7	–3.8	5.1	10.8
	wet	24	–4.2	0.6	2.8	–6.9	–5.0	3.5	10.4
δD	dry	24	–17.8	2.9	14.4	–33.9	–20.4	28.9	62.8
	wet	24	–25.3	3.5	17.2	–45.3	–29.1	18.7	64.0
d-excess	dry	24	6.6	1.3	6.2	–11.9	9.05	12.8	24.7
	wet	24	8.1	1.1	5.6	–9.3	9.60	15.9	25.2

4.6 Precipitation, surface water and groundwater dynamics

The local mean *d*-excess line offset (d = +13.3 ‰) suggests that precipitation in the Lake Malawi basin is sourced from a combination of oceanic moisture and recycled atmospheric water (Banda et al., 2024) (Figure 8b). Precipitation is a crucial component of the hydrological cycle within the study area, as evidenced by the majority of groundwater and surface water samples aligning with the meteoric water lines (Figure 8b). This observation is further supported by the mean *d*-excess for groundwater (d = +11.1 ‰) and river water (d = +9.1 ‰), which closely match the Global Meteoric Water Line (GMWL) (d = +10 ‰. However, the meteoric water input signal appears significantly attenuated in lake water, likely due to extended exposure to evaporation, which significantly reduced the *d*-excess (Mean; SE: –5.3 (±1.8) ‰ (Table 5). These findings highlight that precipitation primarily contributes to the recharge of both groundwater and surface water sources.

The clustering of groundwater and surface water data points in a common region along the meteoric water lines indicates a potential interaction between these two sources. This

observation is consistent with prior research that identified interactions between groundwater and surface water in this section of the basin (Kelly et al., 2020). Such interactions may occur through channel leakage, a process where surface water replenishes groundwater, particularly in the lower reaches of the basin. Also, surface water abstracted for irrigated agriculture could facilitate recharge of shallow groundwater aquifers as it is diverted into large-scale irrigation systems which largely supports rural livelihoods. Groundwater also interacts with surface water through localised spring discharges that contribute to riverine flow systems within the basin.

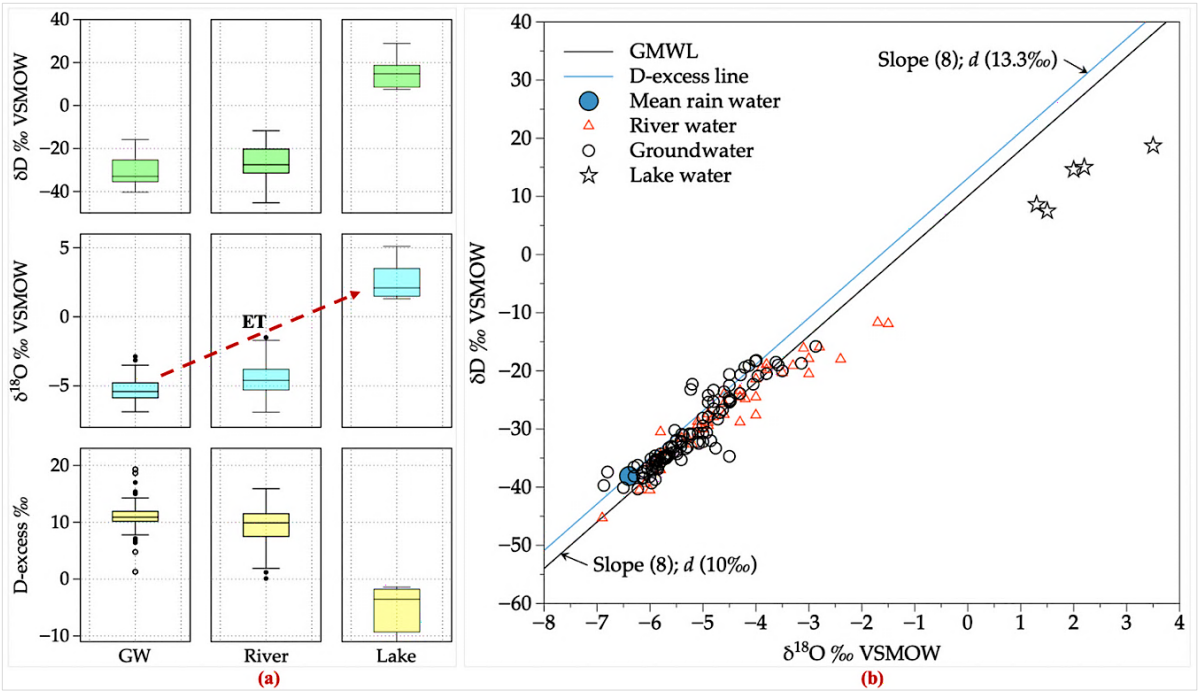

Figure 8. Comparison of $\delta^{18}O$-δD and *d*-excess (d) signatures in rivers, lakes and groundwater sources.

5. Discussion

The isotopic signatures of surface water and groundwater provide valuable insights into the hydrological processes occurring within the basin. Data from surface water isotopes

demonstrate a strong influence from local precipitation, evident in the close alignment of the majority of samples with both local and global meteoric water lines. This alignment suggests that evaporative effects on these samples are minimal. However, a subset of samples deviates along a unique surface water line (SWL), indicating the effects of evaporative fractionation, particularly at lake sites where significant isotopic enrichment has occurred. This enrichment can be attributed to prolonged evaporation, which corresponds with the elevated δD and $\delta^{18}O$ values observed in lake water. The considerable variability in isotopic signatures among surface water samples highlights the spatial heterogeneity of precipitation patterns and their contributions to surface water bodies. In contrast, the isotopic data for groundwater reveal distinct differences among tracer groups, with WRA 17 exhibiting the highest variability in δD values. This variability points to diverse sources or processes influencing the groundwater, such as differing recharge conditions or the mixing of waters from various origins. The increased mean $\delta^{18}O$ and d-excess values observed in WRA 9 suggest potential differences in the isotopic composition of the recharge water or post-recharge processes that affect these specific samples. Despite the variability in δD and $\delta^{18}O$, the relatively consistent d-excess values across tracer groups indicate that the overall characteristics of moisture sources remain similar. These findings highlight the complexity of groundwater systems and underscore the necessity for further investigation to clarify the factors driving isotopic variability. Understanding these processes is essential for effective water resource management and for predicting the impacts of climatic and environmental changes on water availability. Additionally, the significant spatial variability in the isotopic composition among surface water and groundwater samples reflects the various hydrological processes and sources that influence these water bodies. The pronounced variation in $\delta^{18}O$ and δD values, particularly within WRA 17, indicates that multiple sources or processes

are at play. This could result from variable recharge conditions, different mixing regimes, or distinct evaporation rates affecting different tracer groups. The elevated mean $\delta^{18}O$ and δD values found in WRA 9 imply significant differences either in the composition of the recharge water or in the post-recharge processes impacting these samples.

The distinction between lowland and upland water samples further emphasizes how topography affects isotopic signatures. Upland samples, characterized by more negative $\delta^{18}O$ and δD signatures, suggest different moisture sources or less evaporative enrichment than those found in lowland areas. The higher d-excess values in upland samples might indicate variations in evaporation processes or sources of moisture, potentially reflecting a more substantial influence from precipitation at higher altitudes or differing climatic conditions. Moreover, the notable variability in δD and $\delta^{18}O$ values among groundwater tracer groups highlights the intricate nature of subsurface hydrological dynamics. The most pronounced variability in WRA 17 implies a complex interplay of factors affecting groundwater, including differing recharge scenarios and the mixing of diverse water sources. Despite the differences in δD and $\delta^{18}O$, the consistent d-excess values across tracer groups suggest that overarching characteristics of moisture sources remain stable.

Seasonal variability in $\delta^{18}O$-δD signatures of surface water in the Lake Malawi sub-basin offers critical insights into local hydrological processes and moisture source influences. The more negative $\delta^{18}O$ and δD values observed during the wet season point to a stronger contribution from fresh meteoric water, characterized by lower enrichment in heavy isotopes. This trend aligns with the increased precipitation and reduced evaporation typical of the wet season. In contrast, the enriched heavy isotopes seen in the dry season suggest substantial evaporative fractionation, likely driven by higher temperatures and reduced precipitation,

resulting in elevated evaporation rates. The differences in *d*-excess values between seasons further clarify these dynamics; the elevated mean d-excess during the wet season indicates a dominant influence from fresh meteoric water, while the lower mean *d*-excess in the dry season reflects the effects of evaporative enrichment. Additionally, the greater variability in *d*-excess values throughout the dry season suggests that multiple sources, including evaporated water and potentially groundwater inputs, contribute to the surface water system at this time.

Understanding these isotopic variations is crucial for predicting the impacts of climatic and environmental changes on water availability. The significant disparities in isotopic signatures across surface and groundwater samples reveal the diversity of hydrological processes and sources affecting these water bodies. This complexity necessitates further research to better elucidate the factors driving isotopic variability. By aligning these findings with established theories and concepts in isotope hydrology, we can enhance our understanding of the underlying hydrological processes at play. This knowledge is vital for formulating effective strategies for sustainable water resource management amid changing climatic conditions.

6. Conclusion

This study is the first to develop a sub-basin-scale baseline for surface water (SW) and groundwater (GW) isotopes, as well as a comprehensive assessment of the factors influencing meteoric water attenuation in the underrepresented northernmost section of the Lake Malawi basin. The study successfully examined the meteoric water input and how it interacts with GW and GW sources, while considering spatial and seasonal dynamics across this sub-basin. The key findings of this study include the following:

- Influx of the meteoric water into the Lake Malawi basin originates from oceanic and recycled air moisture sources, characterized by a *d*-excess offset of +13.3 ‰ from the

GMWL. This input of meteoric water is largely modern and primarily influenced by unique meteorological factors, along with geospatial variability and the amount effect; however, the elevation effect remains unclear and warrants further investigation.

- The GW and SW sources are primarily replenished by recent meteoric water input, as indicated by the majority of GW and SW samples, particularly for rivers, aligning along the meteoric water lines. This is supported by mean *d*-excess values of +9.1‰ for rivers and +11.1‰ for GW which are consistent with +10 ‰ for GMWL, highlighting the essential role of meteoric water interactions in the water cycle of this Lake Malawi sub-basin.

- The meteoric water input attenuation responses are high in GW sources compared to SW sources, predominantly in lake water which exhibited intense evaporative enrichment signals (Mean; SE: $\delta^{18}O$ = +2.6 (±0.6) ‰; δD = +15.6 (±3.2) ‰; *d*-excess = –5.3 (±1.8) ‰) linked to prolonged residence time.

- Clustering of the majority of $\delta^{18}O$ and δD signatures of GW and river water (Mean; SE $\delta^{18}O_{SW}$ = –4.5 (±0.2) ‰; $\delta^{18}O_{GW}$ = –5.3 (±0.1) ‰) consistently reinforces evidence of their interactions. This is further substantiated by localized contributions of spring discharges to river flows, as well as surface water abstraction for extensive irrigated agriculture within the sub-basin.

CRediT authorship contribution statement

Limbikani Chitsundi Banda: Conceptualisation, methodology, validation, formal analysis, investigation, data curation, resources, writing—original draft preparation, writing—review and editing, project administration, funding acquisition**. Robert Michael Kalin:** Methodology,

formal analysis, resources, writing—review and editing, project administration, funding acquisition**. Vernon Phoenix:** Resources, project administration, funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data Availability Statement

The research data provided in this study will be made available on reasonable request from the corresponding author.

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7.8 Postface

This chapter explored the hydrological intricacies of three distinct sub-basins within the Lake Malawi basin, located in the African Great Rift Valley. Through focused sub-basin surveys employing stable isotopic and hydrochemical tracers, the chapter clarified complex interactions between meteoric water inputs, surface water, and groundwater within this transboundary water resource system.

Initially, the Chapter focussed on the hydrological dynamics of Sub-basin I, encompassing the Bua River, Dwangwa River, and Nkhotakota Lakeshore catchments. The findings indicate that the stable isotopic compositions of groundwater and surface water exhibit both seasonal and spatial variations. Notably, the influx of meteoric water is markedly higher during the wet season, decreasing significantly in the dry season. Subsequent investigations in Sub-basin II, which includes the South Rukuru/North Rumphi River and Nkhata Bay lakeshore catchments, as well as Sub-basin III, comprising the Songwe/Lufira River and Karonga Lakeshore catchments, showed significant stable isotopic variability in both groundwater and surface water. This variability is attributed to diverse contributions from meteoric water inputs, evaporation, and potential mixing of multiple water sources. In river waters, δD (Deuterium) and $\delta^{18}O$ (Oxygen-18) signatures highlighted a convergence of recent precipitation and inputs from upstream depleted sources. Conversely, lakes and reservoirs predominantly showed signs of evaporative fractionation, resulting in relatively enriched stable isotopic signatures.

Moreover, this chapter highlights the potential impacts of various hydrological and geological factors. Unlike surface water, groundwater stable isotopic signatures exhibited limited variability. Most groundwater samples aligned closely with the meteoric water lines, indicating primary recharge inputs predominantly from contemporary precipitation. However, in proximity

to lakes and in dambo areas, significant attenuation of the meteoric water isotopic signal was observed, with some samples plotting below the meteoric water lines, suggesting isotopic enrichment.

The findings presented in this chapter underscore the inherent complexity of the hydrology within the Lake Malawi basin. They emphasize the imperative for comprehensive monitoring of water resources to inform sustainable water management strategies. Serving as a critical foundational benchmark, this chapter supports the ongoing research and practical application of isotope hydrology for effective water resources management in Malawi and the broader regional context. Overall, it advocates for the integration of rigorous scientific research into effective policymaking and resource conservation frameworks.

CHAPTER 8: DISCUSSION OF KEY THESIS FINDINGS AND THEIR IMPLICATIONS

8.1 Introduction

The initiation of this research stemmed from an understanding of the complex interactions within the water cycle, emphasizing the need for a thorough understanding of its components: precipitation, groundwater, and surface water. The study was particularly motivated by serious concerns regarding the quality and accessibility of water in Malawi, especially in rural areas. The worsening quality of groundwater and surface water, combined with the visible impacts of climate change, have aggravated these issues. Moreover, the widespread mismanagement of water resources has caused considerable concern among stakeholders. This problem is worsened by a significant lack of data and a basic understanding of water dynamics, leading to ineffective policy decisions. This noticeable lack of detailed research on these matters led to the formulation of the key focus areas of this thesis, thereby shaping its goals. The outcome of this research has produced a valuable collection of data and insights, which are essential for the wise management of water resources in Malawi and surrounding areas. Aimed at offering a comprehensive view and developing a detailed conceptual framework for the Lake Malawi basin, this thesis examines the systems of precipitation, groundwater, and surface water. It carefully analyses how these systems are interrelated and the resulting implications for sustainable water resource management. By exploring four critical research questions, this thesis not only achieves but expands upon its defined goals. Furthermore, it offers specific policy recommendations and establishes a basis for future research initiatives. The subsequent discussions will provide more details on these findings and

recommendations, contributing deeper insights into the sustainable management of water resources.

8.2 Stable Isotopic Baseline for Precipitation

The establishment of the Local Meteoric Water Line (LMWL) for Malawi marks a significant advancement in understanding regional hydrological cycles. By defining the LMWL as $\delta^2H = 8.0\ (\pm 0.3)\ \delta^{18}O + 13.0\ (\pm 2.0)$, this research not only deepens our comprehension of isotopic distribution in precipitation but also emphasizes the influence of local meteorological factors, such as evaporation and transpiration, on isotopic signatures. This baseline is vital for interpreting hydrological processes in Malawi and lays the groundwork for continued scientific exploration of water resource dynamics amidst changing climatic conditions. The alignment of local precipitation with the Global Meteoric Water Line (GMWL) underscores a robust global climatic influence while also highlighting significant local vapor recycling. These findings are crucial for developing localized climate models and improving the accuracy of existing ones. An analysis of deuterium excess reveals a localized atmospheric moisture recycling process that may be key to predicting future hydrological responses to regional climate changes. Observed spatial and intra-seasonal variability in isotopic values across Malawi reveals the complexity of the hydrological network and its vulnerability to diverse climatic systems, such as the Inter Tropical Convergence Zone (ITCZ). This variability indicates that regional water management strategies should be adaptable and tailored to local conditions, considering the detailed isotopic mapping provided by this study.

The establishment of the Malawi Network of Isotopes in Precipitation (MNIP) represents a major and exemplary methodological contribution that sets the stage for long-term water

resource monitoring. By enabling systematic data collection, the MNIP supports not only hydrological research but also plays a crucial role in integrated water resource management (IWRM). This infrastructure allows for a detailed understanding of the dynamic interactions between precipitation patterns and water availability. The results from this study provide strategic insights essential for policymakers involved in water resource planning and management. Armed with a detailed isotopic framework, strategies can be formulated to manage not only the quantity and quality of water resources but also their distribution in response to growing demographic pressures and climatic variability. Policies aimed at enhancing water sustainability should incorporate these isotopic insights to build resilience against hydrological extremes such as droughts and floods.

The contribution of this research to the global database on isotopes in precipitation (GNIP) has wider implications for addressing regional and global environmental challenges. By filling critical data gaps, this study aids in the refinement of regional and global hydrological and climatic models, thus enhancing the prediction and management of the impacts of global climate change. Moreover, the establishment of a stable isotopic baseline for precipitation through this research offers an invaluable tool for understanding and managing hydrological processes in Malawi. The practical applications of these findings extend beyond theoretical analysis to provide actionable solutions for sustainable water management and climate adaptation strategies. Enhanced understanding of these isotopic patterns is expected to benefit not only the scientific community but also help local communities in making informed decisions regarding water use, conservation, and management.

In summary, the foundational stable isotopic baseline established in Chapter 4 provides a comprehensive understanding of the meteoric water characteristics of Malawi's water cycle.

It underscores the vital role of isotopic characterization in revealing local moisture dynamics and the influence of regional climatic factors. The findings demonstrate that while global models offer valuable context, local nuances play a crucial role in managing water resources sustainably. Recognizing the interplay between climate change, population growth, and land development is essential for implementing informed, strategic interventions tailored to Malawi's unique geographical and climatic conditions.

8.3 Groundwater Resource Conceptualisation

The thesis findings that modern precipitation primarily drives groundwater recharge is crucial. This finding highlights the dynamic nature of the region's water cycle, heavily influenced by current climatic conditions. With the changing global climate altering precipitation patterns, the sustainability of groundwater recharge is at risk. There could be a decrease in recharge rates or a shift in recharge zones, posing threats to water availability in the Lake Malawi Basin. To confront these challenges, it is imperative to develop adaptive management strategies that can accommodate varying climatic conditions, securing water resources for future generations. The dominance of Ca-Mg-HCO_3 facies in the groundwater emphasizes the significance of silicate weathering processes, which are essential for maintaining natural water quality in the area. The chemical composition of groundwater is critical, impacting its fitness for human consumption and suitability for agriculture. A deeper grasp of these geochemical processes is necessary for foreseeing changes that might result from increased human activity and climate shifts. These changes could impact mineral dissolution rates, hence altering the groundwater chemistry. The observed spatial and seasonal variations in groundwater composition present complex challenges for effective management. These variations necessitate tailored management approaches for

different areas within the basin. Establishing seasonal monitoring and developing adaptable management practices will improve groundwater management efficiency, ensuring consistent water quality and availability throughout the year. The findings from this research stress the need for comprehensive policies that address the interconnectedness of surface and groundwater. The adoption of Integrated Water Resources Management (IWRM) principles could lead to more sustainable water resource practices, promoting collaboration across various sectors and disciplines. These policies should focus on achieving Sustainable Development Goal 6 (SDG 6), which aims at ensuring availability and sustainable management of water and sanitation for all. This thesis underscores the current knowledge on the groundwater systems in the Lake Malawi Basin, advocating for a stronger and more sustainable hydrological future. Through careful analysis, this research could greatly influence both local and wider policy frameworks, potentially driving significant advancements towards sustainable water resource management in the region.

8.4 Surface Water Resource Conceptualisation

In Chapter 6, the novel integration of isotopic and hydrochemical tracers has transformed our understanding of surface water dynamics within the Lake Malawi Basin. It revealed how stable isotopes, specifically $\delta^{2}H$ and $\delta^{18}O$, alongside hydrochemical parameters, effectively trace water sources and flow paths. This comprehensive approach not only refined the conceptual model of the basin's hydrology but also identifies key processes such as evaporation, precipitation, and groundwater interactions that shape water composition and distribution. Significant seasonal variations in isotopic compositions showcase the interplay between climatic factors and hydrological processes. During the wet season, isotopic levels are depleted,

suggesting prominent direct precipitation with minimal influence from evaporation. In contrast, the dry season shows enriched isotopic values, indicating enhanced evaporative effects and diminished precipitation contributions. Such seasonality is crucial for managing water resources, especially in strategizing for use and conservation during periods of scarcity. Isotopic co-variability and hydrochemical facies have unravelled distinct water pathways and origins within the basin, highlighting a complex hydrological network. For example, the merging of rivers from highland-plateaus with those from rift margins critically influences the chemical and isotopic makeup of inflows into the lake. This understanding is key to predicting basin responses to environmental shifts and managing transboundary waters effectively.

The study also notes a pronounced evaporative signature in lake waters, significant for managing the lake's ecological balance and water quality. High evaporation rates not only concentrate chemicals but also alter the isotopic composition of lake waters, potentially affecting aquatic life and water usability. Addressing these impacts necessitates strategies that mitigate both climatic effects and human-induced factors enhancing evaporation. Considering the transboundary nature of the Lake Malawi Basin, these findings are pivotal for international water cooperation. Isotopic and hydrochemical baselines can facilitate equitable water sharing and conflict resolution. Knowledge of the natural variability and factors driving water dynamics enables riparian states to craft informed, mutually advantageous water management policies. The complexity and observed variability in the Lake Malawi Basin point to the need for further research, especially in refining isotopic techniques and applying them to future global climate scenarios. Continuous monitoring and advanced modelling are vital for predicting hydrological responses and guiding sustainable water management amid increasing uncertainty and change. Policy recommendations from this study underscore the necessity of integrated water resource

management (IWRM) that encompasses both surface and groundwater systems. Policies should also bolster climate resilience through infrastructural adaptations and community involvement in water conservation. Moreover, enhancing regional cooperation to address transboundary water challenges is essential for the sustainable development of the region. This discussion underlines the vital role of integrated isotopic and hydrochemical studies in comprehending and managing complex lake basins like Lake Malawi. The insights from such studies are indispensable, paving the way for strategies that balance ecological necessities with human demands, ensuring the sustainability of water resources.

8.5 Groundwater and Surface Water Dynamics

The findings obtained from the three Lake Malawi sub-basin studies provide new and unique insight into the isotopic-hydrochemical dynamics of surface and groundwater within the Lake Malawi basin, contributing valuable new data towards a holistic understanding of its hydrological processes. Each study, albeit focusing on different aspects of hydrology, synthesized the impact of meteoric inputs and evaporation on isotopic compositions, crucial for informing sustainable water management in the region.

Lake Malawi sub-basin I, covering the Bua River, Dwangwa River and Nkhotakota lakeshore catchments, elucidates the pathways of meteoric water fingerprints into the Lake Malawi basin's hydrological cycle and its substantive influence during different seasonal conditions. This study employed dual stable isotopes (δD and $\delta^{18}O$) and local deuterium excess line, alongside the Global Meteoric Water Line for an elaborate analysis. A significant revelation from this study is strong stable isotopic signal of meteoric water in the wet season which becomes attenuated in the dry season due to increased evaporation and reduced inflow. Moreover, the study notes specifically higher attenuation in riverine flows compared to groundwater, pointing

towards more direct meteoric recharge in the groundwater systems. The consistent stable isotopic enrichment in lake waters despite fluctuating meteoric inputs is another critical insight, suggesting a buffer effect in lake basins against immediate stable isotopic alterations from seasonal changes.

Lake Malawi sub-basin II, covering South Rukuru River, North Rumphi River and Nkhata Bay lakeshore catchments, examined spatial and seasonal variability in stable isotopic profiles, providing a robust comparative analysis between different water bodies under varying hydrological conditions. The study underscored influence of local precipitation, evaporation, and groundwater interactions. What sets this study apart is its primary focus on stable isotopic discrepancies among different water catchments, providing new insights that underline the non-uniform influence of climate and geographical attributes across the basin. The application of stable isotopic tracers in a more segmented manner (rivers, lakes, reservoirs differently) supplemented a detailed understanding of source-specific stable isotopic behaviour, especially noting evaporative fractionation in lake sites being relatively more pronounced.

Lake Malawi sub-basin III, covering Songwe River, Lufira River and Karonga lakeshore catchments, emphasized on establishing a baseline for stable isotopic signatures of groundwater and surface water while clarifying stable isotopic variability across temporal and spatial scales thoroughly. The alignment of groundwater stable isotopic signatures with the Global Meteoric Water Line across all sampled sites strengthened the argument for direct meteoric recharge inputs mentioned in sub-basins I and II but also alludes to some degree of localized evaporative enrichment not extensively covered in the previous studies. Furthermore, it deepens the discussion on local precipitation and upstream contributions dynamics, particularly in river waters.

Overall, the three Lake Malawi sub-basin studies collectively helped clarify the complex relationships among meteoric inputs, evaporation, and catchment-specific factors influencing stable isotopic compositions in the Lake Malawi sub-basin. There is a consistent acknowledgment across all three sub-basin studies of significant seasonal and spatial inhomogeneity in stable isotopic signals, driven by both climatic conditions and inherent hydrogeological characteristics of the basin. The observed stability and limited spread in groundwater stable isotopic signatures reaffirms groundwater's resilience to immediate seasonal shifts observed in surface waters, highlighting its reliability as a reliably stable water source. However, the comparative isotopic stability in lake waters across different studies suggests a nuanced understanding of lake systems which might be leveraging both buffer capacities against rapid changes and a mix of water sources including deeper, older groundwater inputs.

8.6 Integrated Water Resource Management and Water Policy

Chapters 4 through 7 present a detailed examination of the hydrological and hydrogeological processes within the Lake Malawi basin. They delve into stable isotopic and hydrochemical analyses alongside groundwater and surface water dynamics, contributing significantly to the framework of Integrated Water Resources Management (IWRM). The research is contextualized within the framework of the Water Resources Act, Malawi's water policy, and the Malawi 2063 Development Agenda, underscoring the urgency of adopting proactive strategies to manage water resources sustainably in response to climate change, population growth, and socio-economic development. The establishment of a stable isotopic baseline in Chapter 4 is crucial for enhancing our comprehension of the hydrological cycle in

Malawi. The study emphasizes the complex interdependencies within water resource systems and underscores the necessity for IWRM-based methodologies. The findings particularly shed light on the subtleties of hydrological processes in the Lake Malawi basin, supporting the formulation of targeted initiatives that align with national water management goals. These objectives include ensuring the sustainable use and protection of water resources, encapsulated in the vision of "Water and Sanitation for All, always." Stable isotopic and hydrochemical characterizations provide insights capable of informing data-driven and adaptable resource management practices that take local climatic conditions into account. Effective water resource stewardship, a key element of the Water Resources Act, depends on the availability of precise and comprehensive data akin to what has been presented in the thesis. Moreover, the advocacy for more water resources monitoring stations indicates a need to broaden data gathering efforts, which are vital for grasping evolving trends and shifts in water availability as environmental and anthropogenic pressures increase.

This research aligns with the objectives of the Malawi 2063 Development Agenda, aiming for climate resilience and sustainable resource management. Chapter 5 discusses the growing dependency on groundwater in the face of demands that surpass natural replenishment rates. This presents a pressing need for integrated water management strategies that address groundwater recharge dynamics and the unique characteristics of aquifer systems. Reporting the presence of nitrates in the groundwater serves as a critical reminder of human impacts on water quality, pointing to a need for proactive water resources monitoring and tackling contamination issues. Furthermore, harmonizing groundwater management practices with Sustainable

Development Goal 6 (SDG 6) brings out the vital intersection between sustainability and human development. The 2063 Development Agenda prioritizes the health of natural resources and recognizes the centrality of groundwater management for achieving food security and sustainable livelihoods. In Chapter 6, the integration of stable isotopic and hydrochemical tracers offers important insights into the connectivity between surface water and groundwater systems. Understanding these connections is fundamental for effective water management, as it informs stakeholders about the primary forces driving hydrological processes such as groundwater baseflows and evaporation. These insights are pivotal for shaping policies that promote sustainable water use in the Lake Malawi basin and beyond, highlighting the interactions between highland-plateau rivers and rift margin headwaters within the IWRM context.

As Malawi strives to enhance its water security through the 2063 Development Agenda, translating these research findings into practical applications becomes critical for policymakers and environmental managers. The need for an integrated approach is a recurring theme across the thesis, essential for fostering collaboration aimed at sustaining water resources. By fostering engagement among stakeholders, including local communities, government entities, and NGOs, the principles of IWRM can be foundational in meeting the complex challenges of water resource management. These chapters not only offer new and unique insights that can profoundly inform Malawian water policy and legislation but also emphasize the importance of innovative, integrated, and participatory approaches for safeguarding water resources for current and future generations. This comprehensive view enables Malawi to address its hydrological challenges

effectively while building resilience and adaptive capacity within its communities. Ultimately, the chapters serve as a call to action for sustainable water management in Malawi.

8.7 Summary

This thesis enhances the understanding of water resource management in Malawi by conducting detailed isotopic and hydrochemical analyses within the Lake Malawi basin. It establishes a stable isotopic baseline for precipitation, showing how climatic variations affect water availability and quality. This thesis reveals the complex interactions between surface water and groundwater, which are key to developing adaptive management strategies in response to climate change and growing population needs. The research supports the necessity of Integrated Water Resource Management (IWRM) in Malawi for sustainable water use and conservation, recommending policies that are adaptable, data-driven, and inclusive of various stakeholders like local communities, government agencies, and international entities. It suggests further expansion of isotopic hydrology research for monitoring environmental changes and stresses the importance of transboundary cooperation for regional water management. Overall, the thesis advocates for the use of isotopic and hydrochemical tools to improve water management practices in Malawi, integrating scientific research with practical policy applications to achieve sustainable water management and contribute towards global sustainability goals.

CHAPTER 9: CONCLUSIONS AND RECOMMENDATIONS

9.1 Introduction

This section provides a summary of the overall conclusions and recommendations of the thesis. Given that the thesis consists of a series of research articles, it is important to acknowledge that specific conclusions and recommendations have been addressed in individual articles themselves. Hence, this section outlines summary of conclusions and recommendations that encapsulate both the critical insights from the individual articles and the thesis as a whole.

9.2 Restatement of Research Aim and Objectives

The research aimed to examine meteoric water inputs and their interactions with surface water and groundwater systems to enhance transformative understanding of hydrological processes in the Lake Malawi basin. The stated research aim was achieved by addressing a set of research questions with a set of corresponding objectives through an innovative multi-method approach that integrated stable isotopic and hydrogeochemical tracers (Figure 20). This approach yielded a distinctive and new body of transformative research data and information, offering pioneering stable isotopic and hydrochemical insights into the basin's hydrological dynamics. The first research question (RQ 1) examined how water isotope tracing could deepen our understanding of local precipitation, which is crucial for integrated water resource management. In response, the thesis established a national-scale isotopic baseline for precipitation, developed a local meteoric water line, and identified the moisture sources affecting local precipitation through

the use of the deuterium excess tracer. The second question (RQ 2) delved into how an isotopic and hydrogeochemical multi-tracer approach could enhance the conceptualization of groundwater resources to support sustainability. This required establishing a basin-scale isotopic and hydrogeochemical baseline for the groundwater system using deuterium (δ^2H), oxygen-18 ($\delta^{18}O$), and major ionic tracers. It also involved identifying groundwater recharge sources and geochemical reactions that control the chemistry and evolution of groundwater along its flow path. The third question (RQ 3) investigated how an isotopic and hydrochemical mixed-proxy approach could facilitate the conceptualization of surface water resources to support integrated water resources management. This part of the thesis set up a basin-scale isotopic and hydrochemical baseline for the surface water system using deuterium (δ^2H), oxygen-18 ($\delta^{18}O$), and major ionic tracers. It explored the inputs and mechanisms controlling surface water hydrochemistry and the attenuation of isotopic signals in water inputs. The fourth question (RQ 4): clarified occurrence of groundwater and surface water interactions dynamics in the Lake Malawi basin. Investigated seasonal and spatial distribution of isotopic and hydrochemical signatures in the Lake Malawi basin at a sub-basin scale. The thesis developed a transformative basin-scale conceptual understanding of water resources in the Lake Malawi basin, informed by critical outcomes detailed in Chapters 4, 5, 6 and 7. The thesis findings are expected to significantly enhance the monitoring of water resources and provide informed guidance to water policy initiatives, which are vital for implementing integrated water resources management (IWRM) and achieving Sustainable Development Goal (SDG) 6.

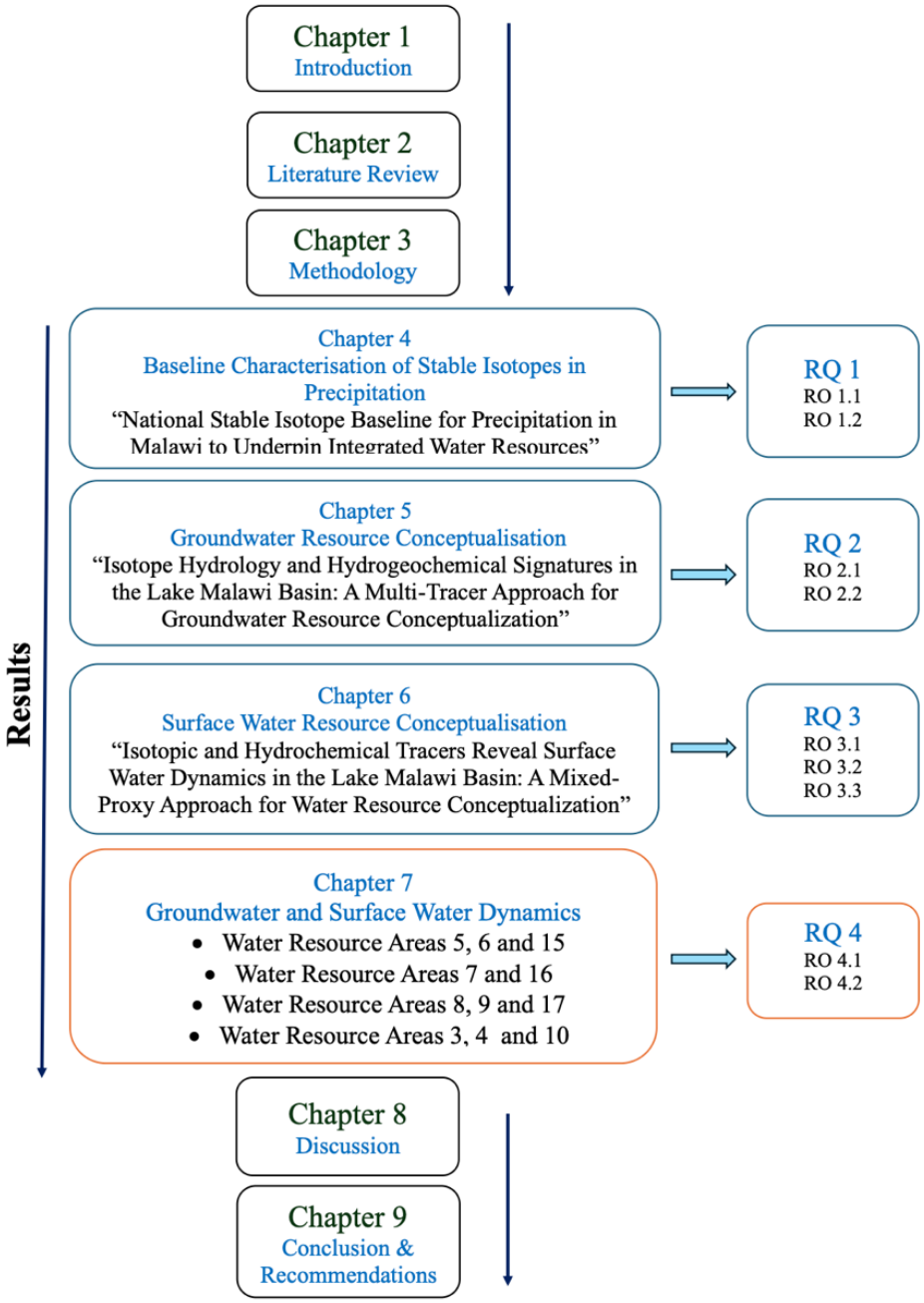

Figure 6. Summary of thesis structure flow chart

9.3 Conclusions

Chapter 4 addresses research question 1: "How can the application of isotope hydrology contribute to an enhanced understanding of precipitation to support IWRM?" This chapter

establishes a baseline characterization of stable isotopes in precipitation and presents the first-ever LMWL for Malawi, thus meeting research objective 1.1. By embedding the local isotopic data within regional and global contexts, the chapter sets the stage for comprehensive analysis. As part of its findings, Chapter 4 highlights that oceans and continents are crucial sources of atmospheric moisture for precipitation in the Lake Malawi basin, fulfilling Research Objective 1.2. The chapter demonstrates that tropical storms and trade winds from the Indian Ocean are significant oceanic contributors to local precipitation. Additionally, there are considerable continental contributions through the recirculation and re-precipitation of air moisture, primarily driven by large-scale evaporation from the African Great Lakes and the seasonal shifts of the ITCZ in Central Africa, which captures warmer air masses.

Chapter 5 explored a vital aspect of the hydrological cycle in the Lake Malawi basin: the dynamics of groundwater resources. This chapter addressed Research Question 2 by examining how isotope hydrology enhances our understanding of groundwater, especially in terms of recharge processes and geochemical evolution. Highlighting groundwater's crucial role in water security, the chapter aligned with the Malawian Water Policy and the objectives of Sustainable Development Goal (SDG) 6. It investigated the processes that control groundwater recharge and its chemical transformation. This chapter achieved the first isotopic and hydrogeochemical baseline characterization of the Lake Malawi basin's groundwater, meeting Research Objective 2.1. It unveiled significant spatial and seasonal variations in groundwater chemistry, offering an in-depth analysis of the factors shaping these characteristics. By linking isotopic data from meteoric water (discussed in Chapter 4) with the hydrochemical facies identified here, the study provided valuable insights into groundwater recharge dynamics. Notably, it found that groundwater recharge mainly originates from non-evaporated, modern precipitation derived from oceanic air moisture. The study also noted that isotopic signals from local precipitation,

influenced by recycled air moisture, are generally obscured or absent in recharged groundwater, thus fulfilling Research Objective 2.2. This implies that precipitation from recycled air moisture contributes minimally to groundwater recharge, or that further detailed research supported by extensive local data might be necessary. The chapter asserted that the isotopic composition of recharging waters is significantly affected by the origin of air moisture, as well as local interactions between groundwater and surface water, particularly in lakeshore floodplains and dambo areas. This interaction underscores the complex relationship between groundwater and surface water systems, stressing the importance of understanding their interconnectivity for effective water management. Using modelled hydrogeochemical data, the chapter pinpointed mineral-water interactions as the primary drivers of groundwater evolution. The dominant geochemical processes shaping the basin's groundwater chemistry were identified as silicate dissolution reactions coupled with the potential precipitation of calcite and high-Mg dolomitic carbonates, influenced by ion exchange processes. The spatial and seasonal variations in groundwater chemical composition reflect a multifaceted relationship between meteoric water inputs, evaporative effects, recharge mechanisms, and hydrological mixing processes. The chapter also highlighted the widespread presence of nitrate across the lake basin, indicating significant anthropogenic impacts on groundwater quality. This concerning finding emphasizes the critical need for advanced modelling efforts to forecast nitrate trends in groundwater, thereby offering essential support for achieving SDG 6 objectives and ensuring the sustainable management of Malawi’s water resources in the future.

Chapter 6 delves into the concluding element of the hydrological cycle in the Lake Malawi basin: surface water dynamics. It specifically addresses Research Question 3: "How does the application of isotope hydrology advance our understanding of the surface water system in the Lake Malawi basin?" This chapter elucidates the intricate dynamics governing the

hydrological processes in the Lake Malawi basin and underscores the vital contributions of isotope hydrology to a deeper comprehension of these dynamics. In achieving Research Objective (RO) 3.1, the chapter establishes a stable isotopic and hydrochemical baseline for surface waters within the Lake Malawi basin. It also addresses RO 3.2 by examining the sources contributing to the surface water and analysing how the isotopic signals from these inputs are attenuated. Noteworthy findings point to the significant role of wet season precipitation, which predominantly derives from oceanic moisture from the Indian Ocean and continental moisture sources. Moreover, the chapter accentuates the substantial input from groundwater baseflow and spring discharges to the surface water systems. These inputs are crucial for an integrated water resources management (IWRM) perspective, since groundwater baseflow sustains streamflow during dry periods, serving as a buffer against hydrological variability. Building on the discussions in Chapter 5 about the interactions between groundwater and surface water, there is a demonstrated need for integrated management strategies that consider both water resources to ensure sustainability and resilience against climate-driven stressors. This chapter further clarifies the complexities that govern the evolution of surface water in the basin by illustrating how isotopic signals from meteoric waters transform as they travel along the flow paths from headwaters to discharge zones. The interaction between highland-plateau and rift margin river systems particularly calls for further focused research and management practices that recognize their interconnectedness. Key factors that influence surface water chemistry are identified as water-rock mineral interactions, evaporation, and precipitation, with groundwater baseflow playing a considerable role. Variations in d-excess values, such as +9.7‰ for rivers and +9.9‰ for reservoirs during the wet seasons, indicate the influence of regional moisture sources. Conversely, reduced values in the dry season point towards the impact of lighter precipitation and increased evaporation rates. By integrating the insights from Chapters 4, 5, and 6, this

chapter enhances the conceptual framework of hydrology within the Lake Malawi basin, thereby fulfilling RO 3.3.

Chapter 7 revealed critical evidence of interactions among meteoric, surface, and groundwater systems. It delineated dynamic hydrological exchanges within Lake Malawi basin. The chapter findings demonstrate significant seasonal and spatial variations in water composition, predominantly influenced by variable contributions from precipitation, evaporation, and the amalgamation of different water sources. This research accentuates the critical influence of these dynamics on the isotopic profiles of diverse hydrological contexts—rivers, lakes, and reservoirs—each manifesting distinctive responses to hydrological and geologic factors. Particularly, the presence of evaporative fractionation in lakes and reservoirs, along with groundwater isotopic alignments with meteoric water lines, highlights the fundamental role of natural processes in sculpting the region's water resources. These insights not only enhance our comprehension of the hydrological mechanisms in the Lake Malawi basin but also underscore the broader implications for regional water management and conservation initiatives.

9.4 Recommendations

Chapter 4 effectively established a national-scale isotopic baseline for precipitation and developed a local meteoric water line using stable isotopes of deuterium and oxygen-18. The investigation into the characteristics of local meteoric water identified several areas requiring further in-depth study, which are as follows:

- *Enhancing understanding of the isotopic input signal of local precipitation to increase its reliability for natural hydrological tracing studies.* To improve the application of stable

isotopes as natural tracers in research, it is essential to advance our understanding of the isotopic signals in the precipitation of Malawi. This effort requires regular monitoring of these signals at intervals that are strategically timed and as close to the target study area as possible. Such monitoring would facilitate the identification of probable isotopic influences during periods or in regions where direct data might be unavailable, thus enhancing the predictions for storm-related studies and boosting the effectiveness of rapid response systems. The classification method of air masses used in this study has exhibited promising outcomes. Future studies should aim to separate the deuterium excess tracer from both continental and oceanic air masses, to better understand their distinct implications. Furthermore, to establish the statistical correlations between isotopic signals and the underlying atmospheric processes, it is imperative to work closely with meteorologists or climatologists. Adopting this collaborative approach will provide a more thorough comprehension of isotopic patterns and their significance in the management of water resources.

- *Resolving uncertainties regarding isotopic effects influencing local precipitation such as altitude effect.* There is a pressing need to expand and upgrade the Malawi Network of Isotopes in Precipitation (MNIP) to broaden its spatial coverage. This expansion should include establishing new sampling sites in remote and underrepresented areas such as the Mchinji, Mulanje, Mangochi, and Zomba districts. Furthermore, significant upgrades are essential for the Malawi Isotope Hydrology Laboratory to maintain its continuous and dependable operation. These enhancements should enable the analysis of a wider array of carbon and nitrogen-related isotopes. It is crucial to commit to the ongoing and long-term collection of isotopic data at MNIP stations. Such an initiative is fundamental for enhancing the accuracy of the Local Meteoric Water Line (LMWL), which in turn boosts

its relevance in isotopic characterization at both regional and global levels.

- *Cultivating and fostering collaboration with local and international agencies*. The Water Resources Department (WRD) should collaborate with both local and international agencies to leverage existing data, historical records, and expert knowledge. Such collaboration could enhance the MNIP dataset and provide valuable insights into national and regional isotopic hydrology frameworks.

Chapter 5 established a current baseline for understanding the isotope hydrology and hydrogeochemistry of groundwater in the Lake Malawi basin. This baseline is essential for monitoring future changes in the region's water resources. The following recommendations from Chapter 5 are critical for monitoring these future changes:

- *Tracing of nitrate enrichment for predictive modelling using a mixed-method approach that integrates to isotopic ($\delta^{15}N-NO_3$; $\delta^{18}O-NO_3$) and hydrochemical (major ions; DIN; DON; NH_4, NO_3; NO_2) tracers. This is reactive to widespread presence of measured nitrate revealed in Chapter 5.* Developing a comprehensive model to examine groundwater contamination from nitrogen inputs is crucial. This importance is heightened by the escalating use of fertilizers, pit latrines, and septic systems, which are proliferating due to rapid population growth. A detailed analysis of nitrate pollution will enhance our understanding of the risks associated with these sanitation systems and the extensive use of fertilizers. Such understanding is vital for taking measures to safeguard our drinking water sources and contributes to achieving the objectives of Sustainable Development Goal (SDG) 6.

- *Future isotope hydrology studies should include cultivating and fostering collaboration with local and international agencies $\delta^{15}N-\delta^{18}O$ (NO_3), $\delta^{13}C$ (dissolved and mineral phases), and $\delta^{34}S-\delta^{18}O$ (SO_4).* The observed stable isotopic co-variability in groundwater within the Lake Malawi basin warrants further investigation. To ascertain if these isotopic patterns are linked to morphological, climatological, or historical recharge conditions, a comprehensive sampling network is essential. Ideally, this investigation should encompass measurements of isotopes such as ^{2}H, ^{3}H, ^{18}C, ^{13}C, ^{14}C, and dissolved noble gases. These measurements will aid in determining the age of the groundwater and provide additional insights into its recharge processes.

- *Cultivating and fostering collaboration with local and international agencies.* The Water Resources Department (WRD) should collaborate with both local and international agencies to leverage existing data, historical records, and expert knowledge. Such collaboration could enhance the MNIP.

- Recognizing the distinct characteristics of various groundwater types is crucial for informed land-use planning. Groundwater recharge zones that are particularly sensitive may necessitate more stringent regulations to maintain water quality and promote sustainable usage.

- Policy measures must highlight the importance of ongoing monitoring of both the quality and quantity of groundwater. It is essential to enforce regulations that govern land-use activities near recharge zones and areas where groundwater is protected, utilizing hydrochemical and isotopic tracers for effective management.

Chapter 6 presents a developed isotopic and hydrochemical baseline characterization of

the hydrology in the Lake Malawi basin. Drawing from an extensive study on isotopic baselines and the hydrochemical analysis of surface water in the Lake Malawi region, we recommend the following policy implications for effective water resource management and to promote sustainable development:

- Quantification of seasonally-variant groundwater baseflow inputs to streamflow using isotopic tracers, critical for sustaining riverine flows, especially during periods of surface water deficit. Chapter 6 has provided stable isotopic evidence for the potential contribution of groundwater baseflow to streamflow. This expands upon earlier research in sub-basin V of the study area, where this contribution was quantitatively assessed. Consequently, further studies should concentrate on the remaining sub-basins (1 to 3).

- Tracing of leakage from reservoirs and lake water infiltration to aquifer systems. Chapter 6 demonstrates that reservoirs and lakes effectively retain enriched stable isotopic signals, making these isotopes reliable tracers for identifying leakage from reservoirs and the infiltration of lake water into nearby aquifers. Therefore, the use of these application considering the intricacies revealed by this research, we propose the following strategic recommendations to steer future water resource management and policy development in the Lake Malawi basin:

- Integrated Water Resource Management (IWRM): Formulate and implement an IWRM strategy that acknowledges the interconnectivity of surface water, groundwater, and meteorological influences. This strategy should engage stakeholders at local, national, and transboundary levels to promote inclusive and comprehensive water resource governance.

- Enhanced Monitoring and Data Collection: Establish an extensive hydrological monitoring framework employing advanced technologies, such as remote sensing and

automated isotopic sampling devices, to continuously observe changes throughout the basin. This infrastructure should be supported by periodic field investigations and robust data-sharing mechanisms among riparian nations.

- Climate Resilience Enhancement: Incorporate climate adaptation measures into water management policies to improve the basin's capacity to withstand climate variability. Initiatives could include breeding drought-resistant crop varieties, developing rainwater harvesting schemes, and constructing flood management systems.

- Capacity Building and Education: Bolster local capacities through specialized training programs focused on sustainable water management practices, isotopic analysis methods, and climate change mitigation. Additionally, public awareness campaigns are crucial in fostering water conservation and safeguarding water quality.

- Policy and Research Integration: Strengthen the connection between ongoing research endeavours and policymaking activities. Regular updates to water management strategies should be encouraged, reflecting the latest scientific insights and technological innovations.

- Transboundary Water Cooperation: Enhance collaboration among the nations sharing the Lake Malawi basin to ensure a unified approach to sustainable water management. This should include collaborative efforts in research, monitoring, and emergency management.

Adhering to these recommendations will enable stakeholders to effectively address current challenges and anticipate future concerns in the Lake Malawi basin, thus ensuring the long-term sustainability and resilience of this essential water resource for future generations.

9.3.1 General Thesis Recommendations

- Malawi should formally join the Global Network of Isotopes in Precipitation (GNIP) to effectively contribute to the global network. This involves adding the current MNIP dataset to the IAEA's GNIP database. Joining the Global Network of Isotopes in Precipitation (GNIP) would greatly enhance Malawi's management of water resources by integrating data from the Malawi Network of Isotopes in Precipitation (MNIP) into the International Atomic Energy Agency's (IAEA) database. This integration would not only boost Malawi's contributions to global hydrological research but also improve the precision of climate models. Additionally, it would foster international collaboration and broaden access to support from global sources. This initiative would also provide policymakers with improved data, thereby supporting well-informed decisions for sustainable water management practices.

- Malawi needs to become a member of the Global Water Analysis Network (GloWAL), which empowers countries to independently generate chemical, biological, and isotopic data. Joining the Global Water Analysis Network (GloWAL) would significantly enhance Malawi's ability to independently produce critical water data, offering numerous advantages. Firstly, it would upgrade the national laboratory facilities, improving the country's technical capacity to conduct chemical, biological, and isotopic analyses. Additionally, membership would foster global collaboration, allowing Malawi to engage in knowledge and technology exchanges with more advanced laboratories worldwide. This would not only strengthen local capacity to produce accurate, reliable, and timely water data but also build local expertise essential for effective water management.

Furthermore, such collaboration could advance Malawi's efforts toward achieving Sustainable Development Goal 6, which focuses on ensuring access to clean water and sanitation for all. Lastly, joining GloWAL would support strategic water management initiatives, such as the Water Action Agenda, facilitating sustainable water resource governance. Overall, becoming a member of GloWAL would be crucial in lifting Malawi's water management standards to meet both national requirements and global benchmarks.

- Malawi should champion participation in the IAEA Water Availability Enhancement Project. This important project assists UN Member States in enhancing long-term freshwater access through the use of scientific, thorough evaluations of their national water resources. Malawi's involvement in the IAEA Water Availability Enhancement (IWAVE) project brings significant benefits as it supports UN Member States in enhancing freshwater access through detailed assessments and advanced management strategies. By participating, Malawi will be able to improve water data management by boosting its capabilities in producing, managing, and analysing water resource data, which facilitates informed decision-making. The adoption of cutting-edge techniques will enable efficient and sustainable water management. Additionally, the initiative will build local capacity by training personnel in modern water management practices, thus promoting self-reliance. It will also ensure long-term sustainability through the promotion of the sustainable use of water resources to satisfy future needs. Moreover, the project fosters international collaboration, providing access to global expertise and technologies, and facilitating cooperation with other nations on shared water resource challenges. Ultimately, engaging in this project will position Malawi to enhance its water security and sustainability, which are essential for its development and environmental stewardship.

9.5 Future of Isotope Hydrology in Malawi

Future research in isotope hydrology within Malawi should aim to expand monitoring networks in order to develop comprehensive datasets. This expansion will enable detailed isotopic analyses and facilitate tracking hydrological dynamics over time. It is essential to encourage cross-disciplinary collaborations between hydrologists, chemists, ecologists, and social scientists. Such cooperative efforts will drive a holistic understanding of water resource issues and catalyse innovative, socially engaged solutions. There is a critical need to prioritize research on the impacts of climate change on hydrological processes, especially in vulnerable regions like Malawi. This research should focus on evaluating changes in precipitation patterns, evaporation rates, and the impacts of land use on water resources. Employing isotopic tracers to investigate land management practices will help gauge their effects on water quality and availability, which in turn will inform sustainable agricultural initiatives and land-use planning. Involving local communities in data collection and research processes through citizen science initiatives can significantly enhance local capacities in water resource management. This ensures that developed policies are culturally appropriate and broadly supported. Moreover, broadening the scope of isotopic research to include transboundary aquifers and river basins will support regional collaboration among Southern African countries. This is crucial for addressing collective water resource challenges and advancing regional sustainability efforts. In a regional and global context, such efforts are aligned with the objectives of the GloWAL Network, IWAVE, GNIP, and GNIR. The GloWAL Network enhances inter-laboratory collaboration and knowledge exchange, essential for creating robust datasets and building capacity. IWAVE aims to improve in-country capabilities for generating and managing water resource data, crucial for understanding the impacts of climate change and land management. GNIP and GNIR focus on

the importance of isotopic data in comprehending global water cycles and regional hydrology, underscoring the need for expanded monitoring and regional cooperation. This thesis substantially progresses the knowledge of isotope hydrology in Malawi, emphasizing its significance in sustainable water management. By blending isotopic research with policy development, community engagement, and regional collaborations, this work provides an optimistic vision for Malawi and its neighbours as they confront challenges posed by water scarcity, climate change, and socioeconomic pressures. Ongoing work in isotope hydrology will continue to shape sustainable practices and policies, securing resilient water resources for future generations.

9.6 Summary

The thesis systematically addressed three research questions (RQ) through a novel multi-method approach, integrating stable isotopic and hydrogeochemical tracers. RQ 1 explored local precipitation using water isotope tracing to establish a national-scale isotopic baseline, develop a local meteoric water line, and identify the moisture sources impacting regional precipitation. This foundational work is vital for integrated water resource management within the basin. RQ 2 focused on groundwater, utilizing an isotopic and hydrogeochemical multi-tracer strategy to establish a basin-scale conceptual understanding. This included setting baselines and identifying the sources and geochemical reactions that influence groundwater's chemical properties and its evolutionary path. RQ 3 examined surface water resources through a mixed-proxy approach of isotopic and hydrochemical analysis. This study established a basin-scale baseline and investigated the factors influencing surface water hydrochemistry and the dispersal of isotopic signals in water inputs. The combined exploration of these elements led to an enhanced conceptual understanding of the Lake Malawi basin's water resources, detailed in Chapters 4

through 7. This comprehensive understanding aids in addressing the pressing issues of water quality and availability, particularly in rural areas of Malawi, affected by environmental degradation and climate change. By thoroughly examining the roles and interactions of precipitation, groundwater, and surface water, and by developing a substantial repository of data, this thesis contributes decisively to the body of knowledge required for informed decision-making in water resource management in Malawi and potentially other similar regions. In conclusion, this thesis not only achieved its foundational aims and objectives but also paved the way for future research directions. It offers targeted policy recommendations that are hoped to inspire and inform future strategies and interventions aimed at sustaining the hydrological resources of the Lake Malawi basin.

10: APPENDICES

10.1 Supplementary Research Articles

Supplementary Research Article 1

water

IMPACT FACTOR 3.0

CITESCORE 5.8

Article

Water–Isotope Capacity Building and Demonstration in a Developing World Context: Isotopic Baseline and Conceptualization of a Lake Malawi Catchment

Limbikani C. Banda, Michael O. Rivett, Robert M. Kalin, Anold S.K. Zavison, Peaches Phiri, Laura Kelly, Geoffrey Chavula, Charles C. Kapachika, Macpherson Nkhata, Sydney Kamtukule et al.

Special Issue

Application of Isotopic Data to Water Resource Management

Edited by

Dr. Bradley K. Esser, Dr. Christopher T. Green and Dr. Ate Visser

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water

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Article

Water–Isotope Capacity Building and Demonstration in a Developing World Context: Isotopic Baseline and Conceptualization of a Lake Malawi Catchment

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Abstract: Developing countries such as Malawi require improved access to isotope tracer tools to better characterize and manage water resources threatened by land development, deforestation and climate change. This is the first published study to use an isotope facility developed in Malawi for this purpose, instead of relying upon sample analyses from abroad. Results from this new facility are used to evaluate an important Lake Malawi catchment in the Rift Valley. This work successfully established a stable-isotope baseline, hydrochemical signatures, and system conceptualization against which future policy change and management strategies may be measured. Precipitation isotopic composition was consistent with the Global Meteoric Water Line, but varied, confirming different precipitation systems nationally. Groundwater largely followed a Local Meteoric Water Line, with limited isotopic variation indicating predominant areal groundwater recharge, but with dry-season evaporative enrichment of groundwater near Lake Malawi. Surface-water isotopes widely varied with local precipitation, suggesting the latter accounted for wet-season river flows, but upstream dambo (complex wetlands occupying a shallow, seasonal waterlogged depression) helped sustain dry-season flows. Isotope capacity reinforced water-resource conceptualization and provenance in a hydrologically complex, but not atypical, Rift Valley system, exhibiting a noted complexity of groundwater–surface-water interactions. The latter, critical to integrated water resource management, requires more focused study, to which an expanded array of isotopes will contribute to tracking Sustainable Development Goal 6 targets. This study and future catchment studies should help underpin Malawian water-resource policy implementation on several identified fronts.

Keywords: isotope tracers; stable isotopes; groundwater; SDG 6 (sustainable development goal 6); integrated water resource management (IWRM); conceptual model; Malawi

1. Introduction

Water-isotope tracing is a powerful tool for conceptualizing hydrological–hydrogeological systems [1–3], including the characterization of hydrological conditions, flow-system evolution, groundwater–surface-water exchange, groundwater recharge and water-source provenance [4–7]. The repertoire of isotope tracers continues to grow, offering increasing insight and versatility [8–11]. As such, isotopes increasingly underpin integrated water resources management (IWRM) [12–14]. Their potential to help strategically address Millennium, and now Sustainable Development, Goals (M/SDGs) in the developing world, remains not fully realized.

Several issues conspire to create this shortfall. Access to in-house isotope analytical facilities within developing countries may be non-existent or limited, a noted issue for Africa [15]. Although there has still been significant isotopic characterization of African water resources [16], much of those isotope data have been secured through sample export and analysis and interpretation abroad [17,18]. This is especially true for developing countries where data can be very sparse [16] and in-house isotope capacity (both analysis and interpretative) fails to develop. The development of developing country water resources is often undertaken in isolation, rarely seeking to understand surface-water–groundwater relationships. African rural resource development has focused almost exclusively on groundwater, typically hand-pumped boreholes for communities [19,20], with little perceived need for isotopes, understanding of the sustainability of the water resource at large, and system linkages.

Significant rationale exists for the uptake of isotopic tools in developing countries, and is considered for Malawi here. Groundwater development in recent decades, although significant, has not been that strategic; water points in Malawi, mostly groundwater-related rural community supplies, now approach 100,000 [21]. Surface-water resources are also prominent. Lake Malawi is African's third largest lake and contains reservoir dams on its lake tributaries, serving, for example, its capital Lilongwe, and a pipeline from the lake's sole outlet, the Shire River, serving its second city, Blantyre. Large irrigation schemes are also planned, for instance the Shire River Irrigation Project to divert ~5% (20–50 m^3/s) of the Shire River flow into 130 km of feeder canals [22]. Large lakes such as Malawi and Chilwa are internationally significant environments and of national socio-economic significance; their drainage basins and underlying aquifers, providing (dry season) baseflows, demand integrated understanding. Groundwater recharge, essential to assessing sustainable aquifer yields, is often poorly constrained [23]. Climate conditions and sources of rainfall are also complex; Malawi's Rift Valley location, with significant topographic variation, causes marked within-country contrasts. Significant land use changes, e.g., urbanization, agricultural intensification and deforestation, may influence the recharge–runoff balance and pose pollution risks. Last, but not least, climate change vulnerability is considered high [24,25], with a predicted increased severity of droughts in Southern, and floods in Northern, Malawi [26]. An arsenal of isotopic tools may contribute to understanding of these issues.

These issues provided impetus for the recent development of a national isotope facility in Malawi, and the first baseline catchment study arising from that newly developed capacity presented herein. The Government of Malawi, with funding from the International Atomic Energy Agency (IAEA) established an Isotope Hydrology Laboratory in Malawi's Ministry of Agriculture Irrigation and Water development (MoAIWD) Central Water Laboratory in Lilongwe in 2018. The IAEA also helped finance establishment of the Malawi Network of Isotopes in Precipitation (MNIP), together with foundational water resource isotope–hydrochemical surveys and capacity building supported by the Climate Justice Fund-Water Futures Programme (CJF)—a wide-ranging research initiative led by the University of Strathclyde and funded by the Scottish Government to support the Government of Malawi in meeting SDG 6. This study is the first of an initial suite of isotopic baseline hydrochemical studies aiming to improve the conceptualization and understanding of Malawi's water resources, and demonstrate the practical value of the investments in resource management.

This study focused on a catchment of the Lake Malawi Basin with contrasting geographies arising from a location at the southern extremity of the East African Rift System. The objectives of this work were to (i) establish an isotopic baseline–hydrochemical understanding against which future change

arising from land use development and climate change may be measured; (ii) develop an integrated conceptual model of the system water resource that may underpin future IWRM; and (iii) identify areas of influence of Malawian policy implementation expected from this and its companion suite of studies on other catchments.

This study is the first to demonstrate the significance of an in-house, national isotope capacity in Malawi, a developing country ranking 170 out of 188 in the 2015 Human Development Index [27]. The study concludes that stable isotopes reinforce the process-based conceptualization of a varied water-resources, and helps confirm and provide insight into the diversity of groundwater–surface-water interaction processes. As such, the developing world vitally requires increased access to such tools.

2. Materials and Methods

2.1. Study Area Setting

2.1.1. Water Resources

The study area surrounds Lilongwe City and covers the Linthipe River Catchment and South West Lake Malawi River Catchment (including most of Water Resource Areas (WRAs) 3 and 4) (Figure 1). The Linthipe River is one of the major riverine inflows to Lake Malawi, Africa's second largest lake by volume and third by area, and an integral part of the international Zambezi River Basin System. The catchment contains several major storage reservoirs; the Kamuzu Dam I (of storage capacity 4.5 million m^3) and adjacent Kamuzu Dam II (18.5 million m^3) on the Lilongwe River, and the Bwanje Valley dam (5.6 million m^3) on the Namikokwe River. The Kamuzu dams supply the capital Lilongwe. The Bwanje Valley dam primarily serves the Bwanje Irrigation Scheme, with some water supply and hydro-power generation.

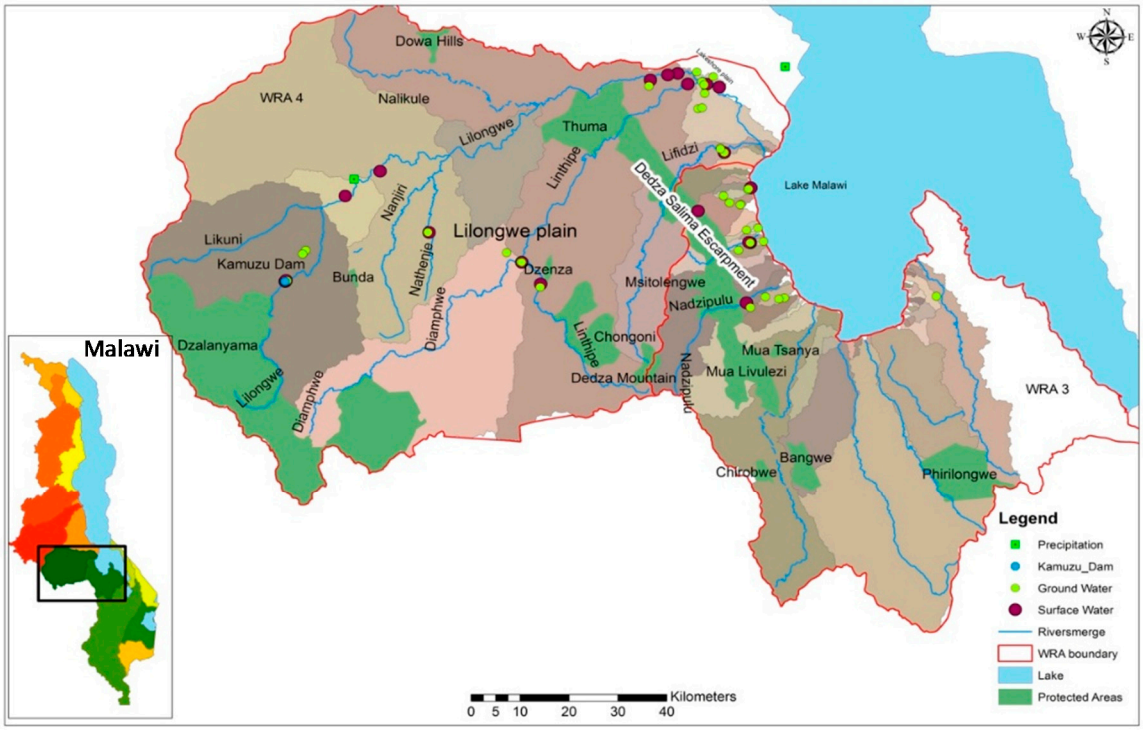

Figure 1. Study area showing surface water bodies, water resource area (WRA) catchments, river sub-catchments (variously coloured zones) and survey water-sampling points.

Water is used for domestic consumption, irrigated agriculture, industrial production, recreation and tourism, fisheries production and sustenance of biodiversity. Lake Malawi is pivotal to national

socio-economic development. Agriculture remains the major water use, followed by domestic use, municipal water supply and industry. Water resource distribution is highly variable, both seasonally and geographically. Around 90% of runoff in major rivers, flowing into Lake Malawi, occurs between December and June [28]. Major water management challenges stem from population growth at c. 3% and developmental pressures. Most rural communities are involved in intensive small holder farming, with attendant deforestation that poses a significant risk of increased runoff, reduction in groundwater recharge, and accelerated erosion, resulting in sedimentation of surface water bodies and a reduction in water-supply reservoir capacities. IWRM policy instruments are vitally required to sustainably manage water resources and maintain water supplies to both rural and urban communities alike, with existing plans to boost water supply (e.g., increased Kamuzu dam I capacity and Salima District supply pipeline from Lake Malawi), alongside irrigation (Bwanje) and hydro-power generation schemes.

2.1.2. Hydrological–Hydrogeological Setting

The study area sub-divides into four contrasting physiographic zones: the highlands, including the Dzalanyama Range, Dowa Hills and Dedza Mountain reaching elevations up to 2400 masl; the plateau area dominated by the Kasungu-Lilongwe Plain, a vast area of 6000 km^2 varying between 1000 and 1800 masl; the Rift Valley escarpment, varying in altitude between 600–800 masl; and the Rift Valley lakeshore plains. Surface water drainage across these zones is illustrated in Figure 2a. Flows in many rivers draining into Lake Malawi, including the Lilongwe, Diamphwe and Linthipe, are influenced by remote upland plateau occurrence of extensive 'dambo' grass-covered swampy valley(s) in the Chichewa language [29] (some illustrative areas of dambo occurrence are shown in Figure 2a).

Details of the geological setting detail are found within three articles covering various parts of the study area [29–31]. The area is mostly underlain by Precambrian 'Basement' Complex rocks comprising gneisses, schists and metamorphosed igneous intrusions. The Precambrian basement intrusives, typical of granular felsic intrusive igneous rock formation (Granite), occurs in the south west Dzalanyama Range. The coarse-grained intrusive igneous rocks (Syenite) occur within the Kasungu-Lilongwe Plain and parts of the Dedza District. The Quaternary alluvium, colluvium and lacustrine deposits occur along lakeshore areas of Lake Malawi within the Rift Valley plain. Most of the alluvial deposits arise from the erosion of rock material from the Rift Valley escarpment slopes [31,32]. The catchment area is characterized by Basement Complex aquifers, fracture zones in the escarpment zone, and alluvial aquifers (Figure 2b) in the rift valley floor. Basement aquifers occur in weathered or fractured zones of Cambrian Basement Complex rocks with generally low yielding boreholes, up to 2 L/s, that dominate the western and central areas. In the east, alluvial aquifers predominantly occur as Quaternary alluvial deposits and may be high yielding, up to around 20 L/s [33]. They predominantly comprise mixed clays, silts, sands and gravels. Borehole yields in the escarpment zone may be as high as 12 L/s [32,34]. Details of the above are considered further in our system conceptualization.

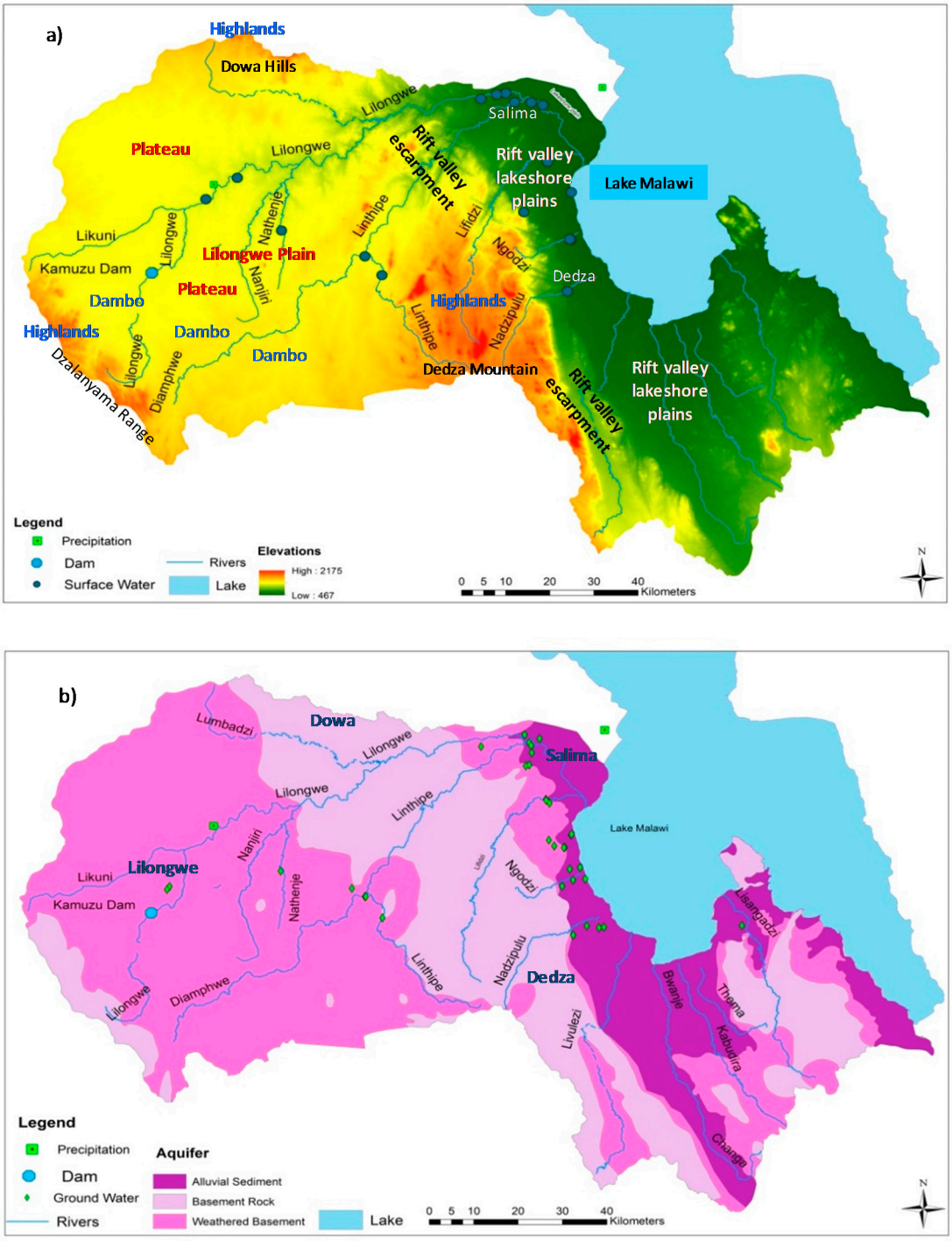

Figure 2. Study area: (**a**) Topography and key physiography; (**b**) Aquifer types.

2.1.3. Climate

The Lake Malawi Basin experiences a tropical–continental climate with two distinct seasons: a wet season from November to April, and a dry season from May to October [35]. The dry season is characterized by south-easterly trade winds (the Mwera) and the wet season by weaker north-easterly winds (the Mpoto). The Inter Tropical Convergence Zone (ITCZ), the Zaire Air Boundary (ZAB), and tropical cyclones are the three large-scale (synoptic) systems that bring rainfall to the basin [35]. According to the revised Köppen-Geiger system, which is based on a large global dataset of long-term monthly precipitation and temperature station time series, Malawi's climate may be classified as Aw

or Savannah. The defining criteria for this type of climate is Not (Af) & Pdry < 100 − MAP/25, where Af is rainforest, MAP is mean annual precipitation, and Pdry is precipitation of the driest month [36]. Based on 2000–2018 precipitation data gathered from Malawi's Department of Climate Change and Meteorological Services (DCCMS), annual rainfall in the catchment area exhibits a mean of 956 mm and a range of 482–2128 mm.

Temperatures are also influenced by the diverse topography, typically decreasing with increasing altitude. Mean maximum and minimum temperatures are 30.3 and 10.3 °C, respectively. Maxima occur in October/November and minima in June/July. Malawi is vulnerable to climate change influence, arguably already occurring on the basis of increased drought and flood event frequencies [24,25].

2.2. Water Sampling and Analysis

Water sampling was undertaken as three sets of isotopes and hydrochemical surveys aimed at capturing seasonal variability. A total of 221 samples were collected from 69 sampling points between March 2014 and June 2018, with a breakdown of sample type provided in Table 1. The first survey was conducted from March 2014 to August 2015 (82 samples), the second from June to December 2017 (43 samples) and the third from June to August 2018 (96 samples). Each covered a wide range of water types, aiming to provide representative catchment coverage. The precipitation samples from the MNIP were collected using dip-in samplers designed to prevent evaporation (and eliminate the need for paraffin oil) [37]. Our local precipitation data was augmented by precipitation isotopic data from the surrounding Global Network of Isotope in Precipitation (GNIP) stations in Mozambique at Gorongosa (eight samples) and Chitengo (four samples) and Zambia at Ndola (154 samples) to better characterize local meteoric conditions [38]. Our Local Meteoric Water Line (LMWL) was calculated based on errors-in-variables (EIV) regression [39] and is referred to as EIV-LMWL. Groundwater samples were collected from community supply boreholes fitted with (Afridev) hand pumps that were in regular use for supply and hence well purged. Lake Malawi isotope samples were collected remote from estuaries 1 km from the shoreline via boat and bespoke depth sampler.

Table 1. Summary of isotopic and hydrochemical sampling undertaken (2014–2018).

Source Type	No. of Sampling Points	No. of Isotope Samples	No. of Hydrochemical Samples
Surface water	22	50	23
Groundwater	43	73	38
Precipitation	4	37	-
Total	69	160	61

Water samples for stable isotope analysis were collected using dedicated amber bottles for analysis of deuterium and oxygen-18 ratios using an automated Picarro Isotopic Water Analyser (IWA) at the MoAIWD IHL, incorporating a water laser spectroscopy-based approach. Samples were stored at 4 °C and away from sunlight during transportation and holding at the laboratory. Analysis involved daily calibration of heavy and light standards encompassing the anticipated range of isotopic composition in samples, alongside use of a daily control mid-range standard intermediate between heavy and light standards. The IWA was prepared by running two vials of deionised water and the quality of measurement was checked by inspecting concentration peaks with an acceptable range of 19,000–21,000 ppm. The precision (2σ) of isotope analysis was ±0.2 ppm for Oxygen-18 and ±2.0 ppm for Deuterium. The isotopic analysis was conducted in line with International Standard Procedures [40] and quantification and validation of results was accomplished via dedicated LIMS software.

Electrical Conductivity (EC), Total Dissolved Solids (TDS) and pH were measured on site using a portable multi-meter (Model: HI-98194) for a representative subset of samples (61) also subjected to hydrochemical analysis. Hydrochemical samples were collected in a distilled water rinsed pair of acidified and non-acidified polyethylene bottles. Samples were stored at 4 °C during transportation and at the MoAIWD Laboratory, and analyzed there for major ions, iron and fluoride. The samples

were filtered through 0.45 µm Whatman filters prior to laboratory analysis. The anions (F^-, Cl^-, NO_3^-, SO_4^{2-}) and cations (Fe^{2+}, Na^+, K^+, Mg^{2+}, Ca^{2+}) were measured using ion chromatography (Ion Analyzer—Model: IA-300) Carbonate and bicarbonate concentrations were measured using titrimetric methods with hydrochloric acid. All field sampling and measurements, and laboratory analyses, were conducted in line with International Standard Procedures [41], and accuracy of analysis results was validated by calculating ion-balance, with adherence to an acceptable error of 5%. The detailed list of surface water, groundwater and precipitation (within study area) stations is presented in Supplementary Materials (SM)—Tables SM2a, SM2b and SM2c, respectively.

2.3. Baseflow Index Estimation

To support system conceptualization, baseflow index (BFI) estimation was undertaken. Baseflow represents the proportion of river flow derived from groundwater from aquifers and other stored sources. Other stored sources may include slow-moving interflow (as opposed to rapid interflow), connected lake or wetland systems, and temporary storage in the banks of the river channel. Although it is generally accepted that baseflow is mainly derived from groundwater, it is important to acknowledge, in the absence of detailed site investigations, that these other sources may also contribute, depending on the catchment characteristics, although typically to a lesser extent [42]. Baseflow is commonly expressed as the BFI, defined as the ratio of baseflow volume to the total river flow volume. For the current scope (non-exhaustive), we simply draw upon BFI mean data from our parallel CJF programme activity to quantify BFI trends across Malawi using hydrometric (river discharge) data obtained from the Surface Water Division of the Department of Water Resources in the MoAIWD.

The river data archive spans from 1953 to 2010, but with data recording gaps, and differences in monitoring periods between gauges. BFI estimates were hence made of annual (1 November to 31 October), wet season (1 November to 30 April) and dry season (1 May to 31 October) arithmetic means (averages) for the entirety of the data available for each gauge. This approach provided good spatial coverage of the study area, encompassing nine rivers, but there is still a need to examine specific time-period data in future work.

Baseflow separation was used to analyze the river data and determine BFI for 14 river gauging stations over the time periods indicated: Nadzipokwe River 3E1 (1953–2010) and 3E2 (1957–2003), Namikokwe River 3E2 (1957–2003) and 3E5 (1957–2010), Livulezi River 3E3 (1956–2008), Nadzipulu River 3F3 (1957–2004), Linthipe River 4B1 (1953–2009), 4B3 (1957–2008) and 4B9 (1974–2010), Diamphwe River 4B4 (1957–2010), Lilongwe River 4C2 (1957–2010), 4D4 (1953–2009) and 4D24 (1991–2005), Nanjiri River 4C11 (1985–2010) and Lingadzi River 4E2 (1959–2005). Due to the sporadic nature of the river data, this study followed the approach set out in a recent study by Kelly et al. (2019) [28] which specifically demonstrated how to work with sporadic river data to quantify temporal variations in BFI. The approach utilized the BFI programme, an MS Excel® based tool developed by the Department of Geosciences in the University of Oslo [43]. The programme performs baseflow separation on daily river flow and separates the river flow into its 'surface runoff' component and its 'baseflow' component, which, in turn, allows for determination of the BFI. The BFI was calculated as the ratio of the baseflow volume to the total flow volume using the smoothed minima technique developed by the Institute of Hydrology (1980) [44], as described in Kelly et al. (2019) [28].

3. Results

3.1. Baseflow Index Results

Spatial distribution of BFI estimates confirms that baseflow is an important contributor to all river flows (Figure 3). Dry season baseflows are typically much higher than wet season baseflows, which are more comparable to the annual average. Overall, averages and standard deviations of the presented BFI data are: annual 0.52 + 0.14 (27%), wet season 0.47 + 0.13 (28%) and dry season 0.86 + 0.067 (8%). The marked increase, and decreased variation, in the dry season BFI is ascribed to the greatly

reduced run-off. Towards the mid to late dry season there is little, if any, precipitation, with river flows becoming low (to very low) and tending to a BFI of unity—flows becoming totally dependent on groundwater baseflow. Where groundwater levels fall below riverbed, rivers may become influent and possibly cease to flow downstream. We do not examine low-flow data specifically, however, Sefe (1988) [45], who examined low-flow or no-flow conditions in the Linthipe catchment indicates of the five gauges considered in our study (covering central and northern areas), found that only the Linthipe 4B1 gauge regularly exhibited a no-flow condition.

Most annual and wet season BFI estimates, at around 0.5–0.6, indicate a consistent baseflow contribution to river flows. Gradual release from water storage sources such as dambo can account for the elevated BFI in upper reaches of the plateau. Low BFI values for the annual and wet season are prominent in two gauges close to Lilongwe City, and reasonably ascribed to increased runoff from urbanization there and the intensification of agriculture in surrounding areas. BFI trends observed along specific rivers demonstrate that Lilongwe baseflows decline downstream in the annual and wet season, but increase during the dry season (Figure 3). The river likely has influent reaches across the Lilongwe Plain. The Linthipe River baseflow declines between the plateau and just downstream of the escarpment, but a subsequent significant increase occurs towards the center of the Salima lakeshore plain (Figure 3). These data suggest river losses to groundwater at entry to the lakeshore plain, followed by a baseflow increase upon approaching the Lake Malawi foreshore.

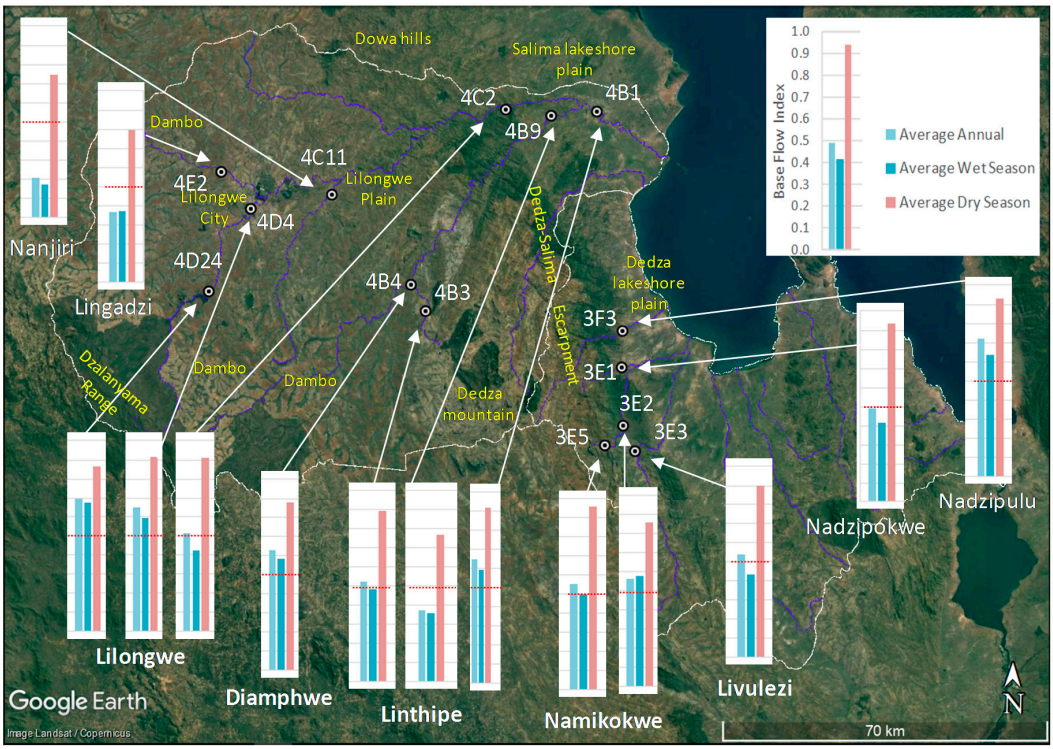

Figure 3. Average annual, wet-season and dry-season baseflow index (BFI) estimates from river flow gauging station records (all graphs are scaled per legend).

3.2. Hydrochemical Results

The descriptive summary for the hydrochemical analysis results of surface water and groundwater is presented in the Supplementary Material (SM)—Tables SM1a and SM1b, respectively, while full data sets for the hydrochemical analysis results of groundwater and surface water are presented in the Supplementary Material (SM)—Tables SM3a and SM3b, respectively. Surface waters are slightly alkaline (pH: 7.0–8.3) and fresh, with water hardness varying from very soft to hard (Figure 4a). TDS is generally low, ranging from 42 to 349 mg/L, with a mean of 145 mg/L. Dominant anions are bicarbonate

and chloride, and cations, calcium and sodium. Groundwater summary data reveal similar ions dominate, but at higher concentrations (Figure 4b). The pH range was fair, from 5.3 to 8.3 and of mean 6.91. Most groundwater points were slightly acidic, with TDS varying from low to moderate at 132–1474 mg/L, and of mean 541 mg/L and median 505 mg/L. These compare favorably with WHO guidance, with drinking water being recognized to be of good palatability at <600 mg/L TDS, but becoming increasingly unpalatable (and brackish) at >1000 mg/L TDS.

Groundwater may be classified into four main groups based on the Piper plot, with dominant occurrence of the Ca-Mg-HCO3 water type (Figure 5a). Cation exchange processes are evidenced by a mixing line in the cation ternary with the addition of sodium into the groundwater replacing calcium. The Durov plot (Figure 5b) supports the dissolution of evaporite minerals, simple mixing, and ion exchange as the possible controls. The majority of groundwater samples are in Fields 1 and 2, characteristic of fresh recharging waters rich in Ca-HCO3, followed by Field 5, groundwater exhibiting simple mixing or dissolution processes. The remaining populated fields contain few samples, inferring less important controls. These include Field 8, with three samples evidencing groundwater associated with reverse ion exchange of Na-Cl water type, and just a single sample in both Field 3 groundwater—rich in Na-HCO3, resulting from the ion exchange process, and Field 9—end-point waters with dominant occurrence of Na-Cl water.

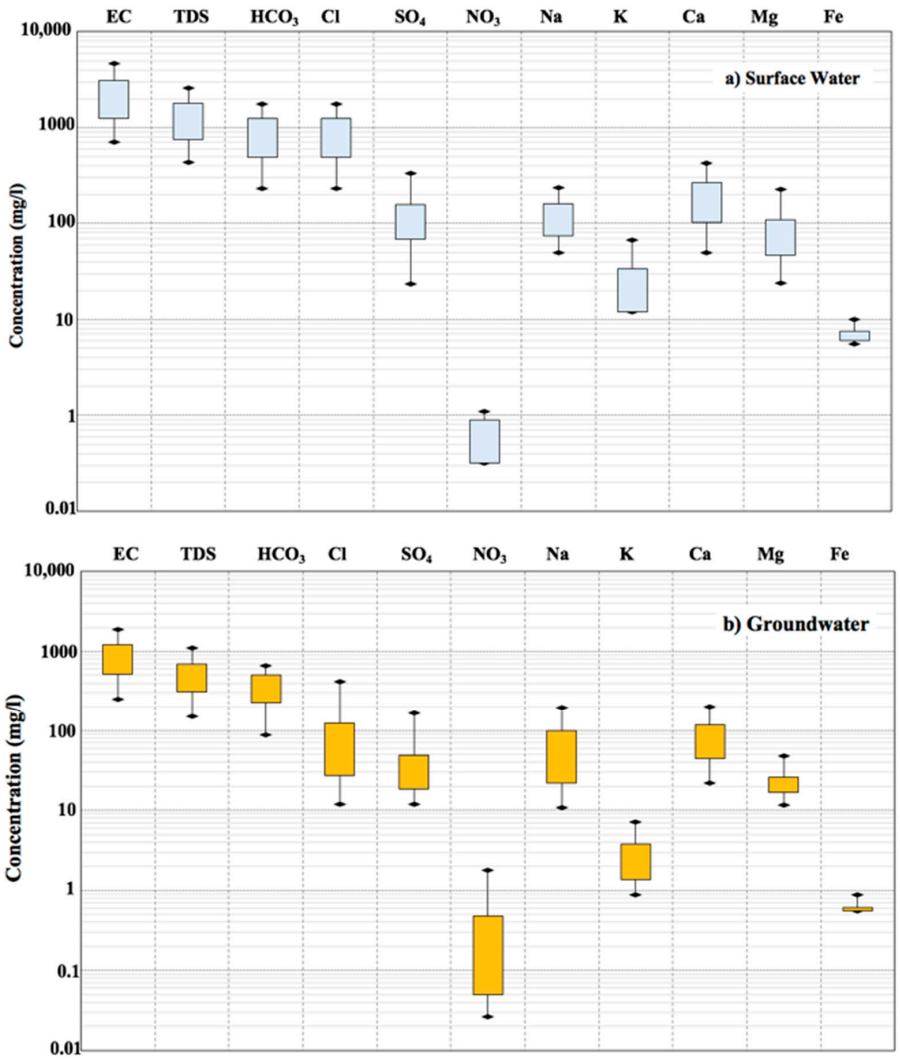

Figure 4. Observed electrical conductivity (EC), total dissolved solids (TDS) and major ions in: (**a**) Surface water; (**b**) Groundwater.

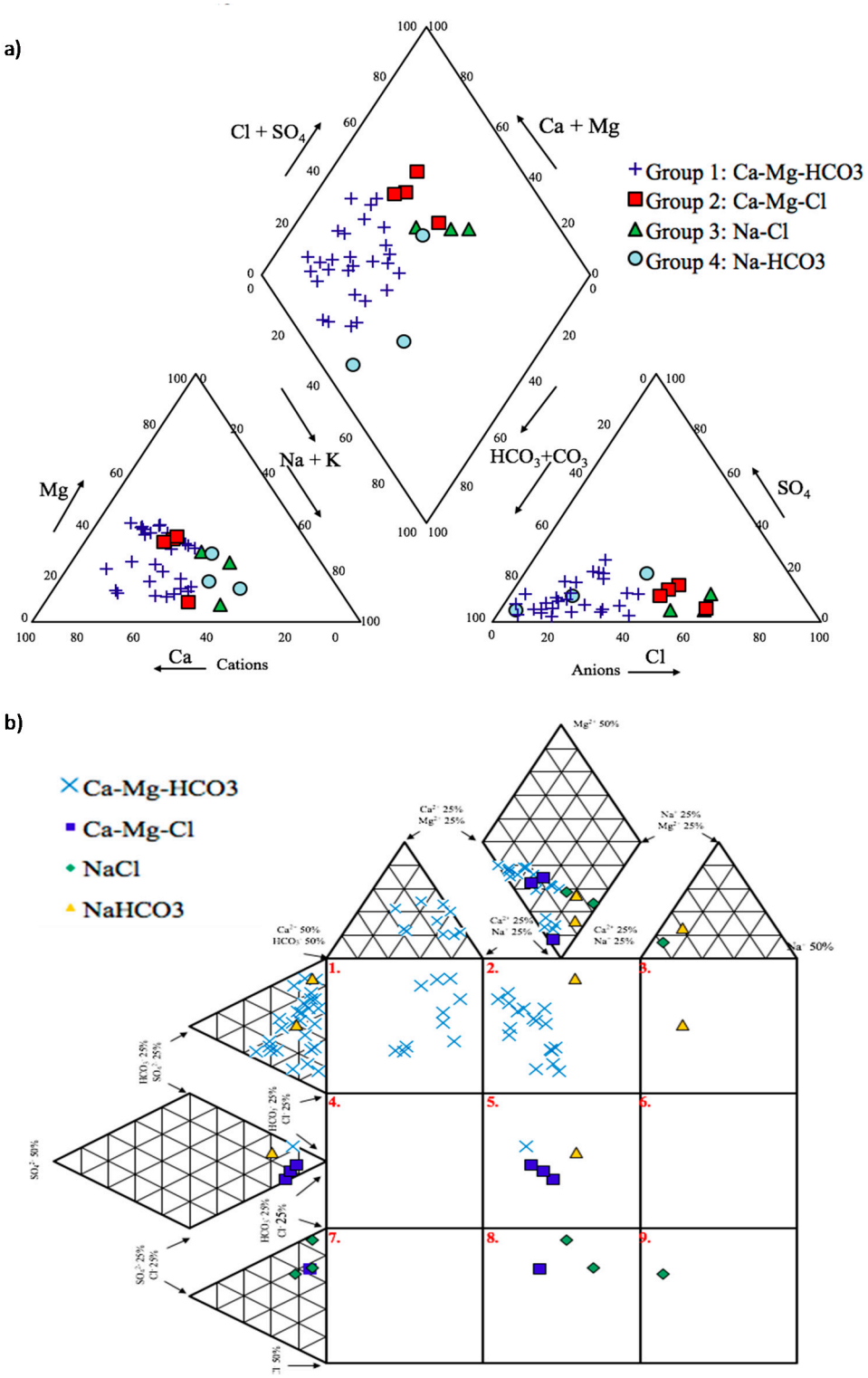

Figure 5. Observed groundwater data: (**a**) Piper trilinear plot; (**b**) Expanded Durov diagram (using hydroCHEM 2.0 software).

All upland, highland–plateau area sites are predominantly Ca-Mg-HCO3 water type (Figure 6) and accord with the quality expected of fresh recharging waters. All sites are near river systems and, hence, where discharge occurs, baseflow is probably of this water type. The predominant Ca-Mg-HCO3 water type remains evident in the lowlands, low escarpment to lakeshore plain area at 12 sites, however, hydrochemistry displayed is heterogeneous. The remaining eight sites contain other water types

enriched in calcium or sodium, four of the sites being those closest to the Lake Malawi shoreline. The reverse is shown for the most northern assemblage of lakeshore plain sites (just south of the Lilongwe River in Salima) that exhibit enriched calcium or sodium water types towards the inland side rather than the shoreline. This observation may be ascribed to river infiltration and/or increased precipitation (compared to the upland plateau).

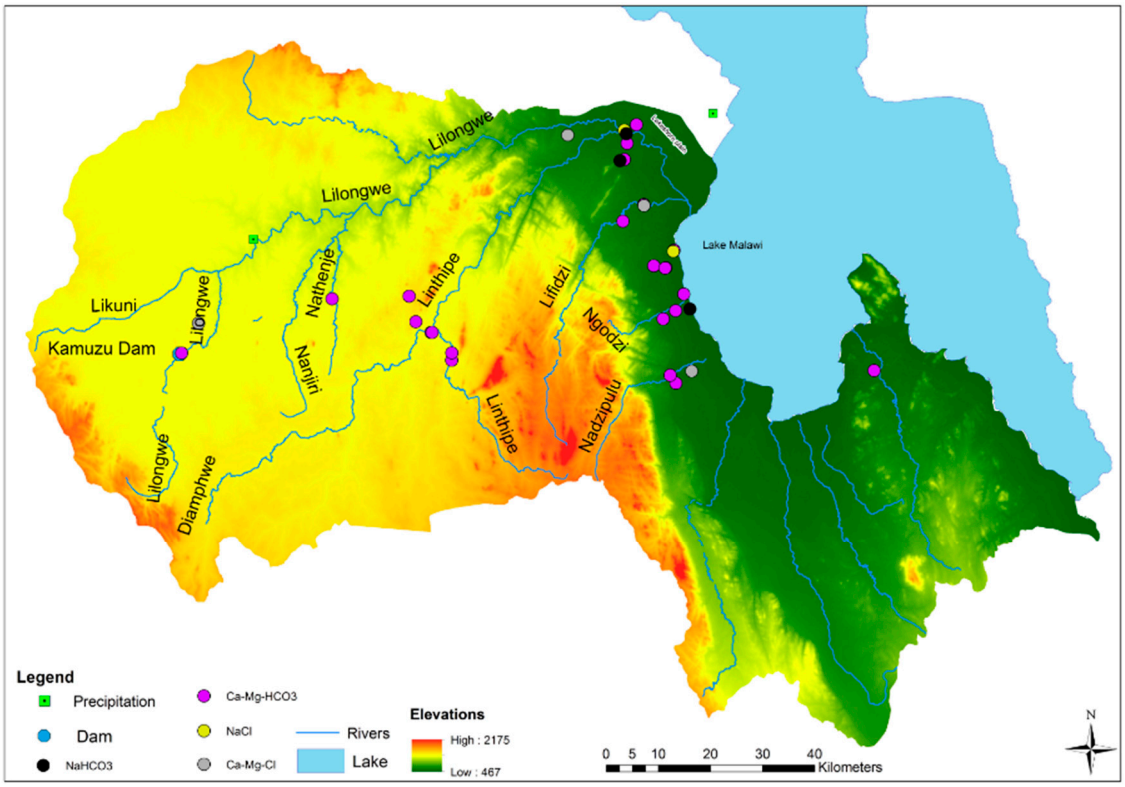

Figure 6. Groundwater types observed spatially in the study area.

Heterogeneity of water types in the flood plain implies a combination of processes, including river infiltration contributing lower TDS water to aquifers; enriched calcium or sodium in samples, indicative of older groundwater of a longer flowpath and increased mineral solution and/or the influence of lowland (phreatic) evaporation influences or wet-season infiltration of Lake Malawi water. Certainly, the lowland groundwater hydrochemical heterogeneity is indicative of more complex, multi-process controls compared to the homogeneity and inferred process uniformity in the probable recent recharge-dominated upland groundwater.

3.3. Stable Isotope Results

3.3.1. Precipitation

Precipitation δ^2H values (n = 203) ranged from −121.2‰ to 24.2‰, with a mean of −29.8‰, and $\delta^{18}O$ ranged from −17.5‰ to 3.0‰, with a mean of −5.2‰ (Table S1 in Supplementary Materials). Linear (EIV) regression defined the Local Meteoric Water Line (LMWL) as: $\delta^2H = 7.7\ (0.09)\ \delta^{18}O + 10\ (0.55)$, $R^2 = 0.99$ (Figure 7), which compares with the Global Meteoric Water Line (GMWL) defined by Craig (1961) [46] as $\delta^2H = 8\ \delta^{18}O + 10$. The local precipitation isotopic data has a mean intercept of 14.3‰, exhibiting excess deuterium ascribed to local vapor recycling, slightly above the GMWL intercept of 10‰. The wide variation evident in isotopic composition (range: 88.4 for δ^2H, 10.6 for $\delta^{18}O$) (and found in our wider Malawi studies) is ascribed to the aforementioned different rain-bearing

systems-influenced local precipitation, alongside the influence of geographic controls upon local rainfall variation.

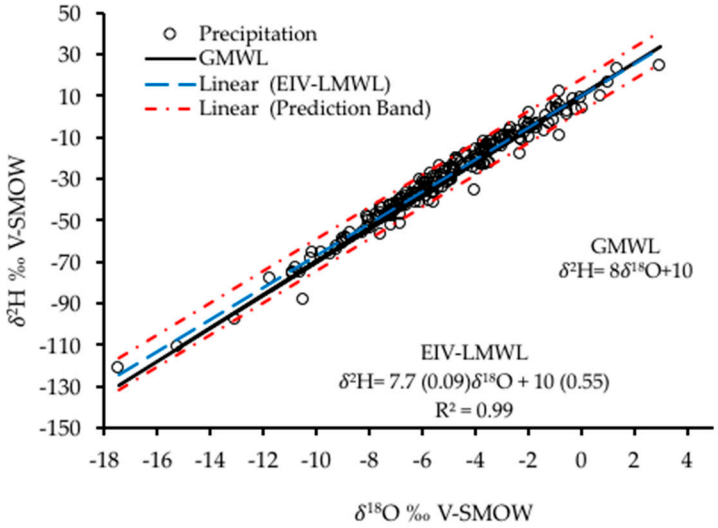

Figure 7. Plot of δ^2H and $\delta^{18}O$ for precipitation isotopic samples. LMWL represents the Local Meteoric Water Line for the Linthipe River and South West Lake Malawi Catchments calculated based on errors in variables (EIV).

3.3.2. Groundwater

Groundwater δ^2H (n = 73 samples (from n = 43 points)) ranged from −43.9‰ to −23.3‰ of mean −37.6‰, and $\delta^{18}O$ from between −6.7‰ and −4.2‰ of mean −5.9‰ (Table S2 in Supplementary Materials). Deuterium excess ranged from 0.94‰ to 13.0‰ of mean 9.6‰. Most groundwater samples plot within the prediction interval and along the meteoric water lines (Figure 8a) providing strong evidence of non-evaporated local precipitation recharge input to groundwater in those samples, arbitrarily assigned as 'Group G1' in Figure 8a. Some groundwater samples, though, assigned as 'Group G2', deviate from the meteoric water lines and follow a local evaporation line (LEL) defined by $\delta^2H = 5.3\ \delta^{18}O - 6.2$. Such deviation is ascribed to excess $\delta^{18}O$ arising from secondary evaporative enrichment and accounted for by groundwater subjected to evaporative fractionation, either during the runoff that preceded infiltration, or occurring within the groundwater body itself (probably from shallow groundwater phreatic evaporation), or possibly groundwater-containing infiltrated Lake Malawi water previously subject to evaporative enrichment. Data segregation to lowland versus upland groundwater (Figure 8b) confirms that the more enriched (although not all) of the Group G1 data correspond to 'lowland' groundwater points in the lakeshore districts of Salima and Dedza.

In sum, groundwater isotopic compositions largely follow the LMWL with modest variation (range: 21‰ δ^2H, 2.5‰ $\delta^{18}O$) suggesting a simple areal groundwater recharge, largely by local precipitation. Some isotopic shift below the LMWL, however, suggests significant evaporative enrichment of groundwater near Lake Malawi during the dry season (see later). The full datasets for the stable isotopes analysis results of groundwater are presented in the Supplementary Material (SM)—Table SM4a.

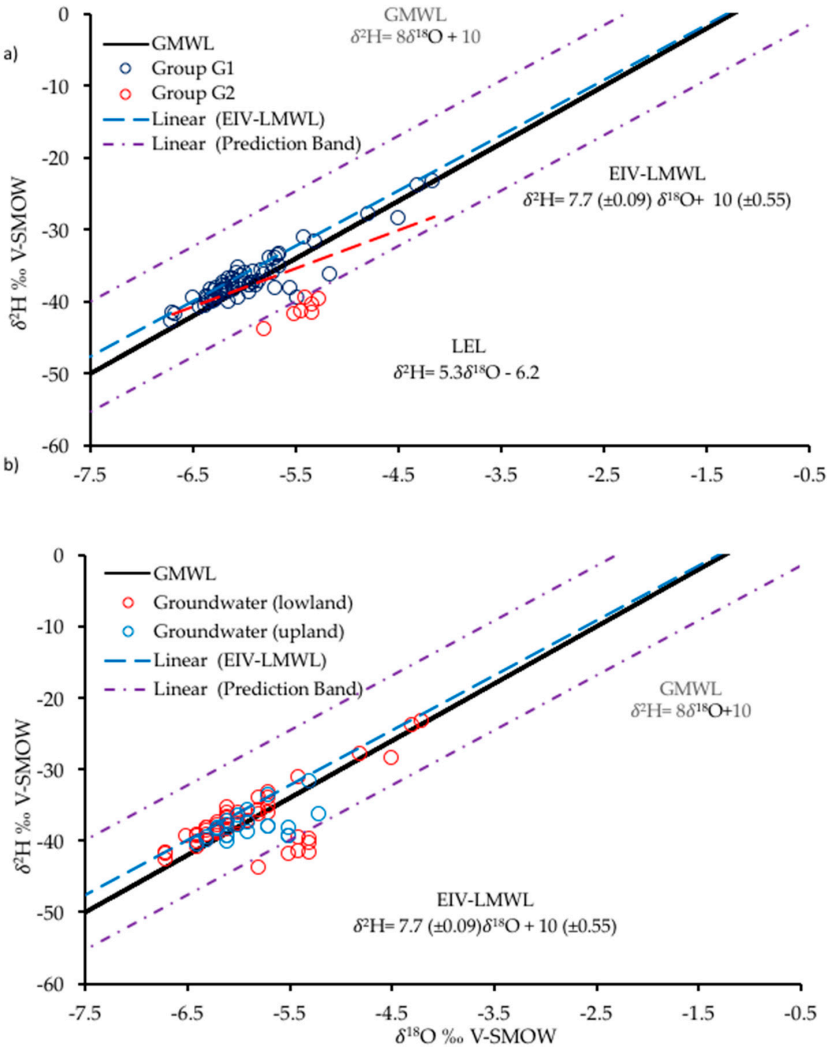

Figure 8. (**a**) Plot of δ^2H and $\delta^{18}O$ for groundwater samples; (**b**) Shown (zoomed in) with data segregated to upland and lowland sample sites.

3.3.3. Surface Water

Fifty surface-water isotope samples from 22 points (16 rivers, three reservoir (Kamuzu) dams, three from Lake Malawi) yielded wide-ranging δ^2H compositions from −44.3‰ to −20.1‰ of mean −15.3‰, and for $\delta^{18}O$, between −6.8‰ and 3.0‰ of mean −2.5‰ (Table S3 in Supplementary Materials). Most samples plot outside the prediction interval and below the meteoric water lines, along a Local Evaporation Line (LEL) defined by $\delta^2H = 6.3\ \delta^{18}O + 0.57$, comprising Lake Malawi (we note that additionally including lake data from the Gonfiantini et al. (1979) study [47] would have resulted in only a minor shift in our LEL intercept, from 0.57 to 0.54), the Kamuzu dam (dry season) and the river samples arbitrarily assigned to Group S2 (Figure 9a). Although, for the lower value data ($\delta^2H < c.$ −20‰, $\delta^{18}O < c.$ −3.5‰), most do follow the meteoric water lines, comprising the Kamuzu dam (wet season) and river samples assigned to Group S1. Samples from Group S2, Lake Malawi, during all seasons, and the upland Kamuzu dam in the dry-season, all exhibited isotopic evidence of evaporative enrichment, with Lake Malawi samples forming the high-evaporation end member. Samples from Group S1, the vast majority of river samples, and the Kamuzu dam in the wet season exhibited isotopic signatures consistent with local precipitation that followed the LMWL and infers that runoff (and rapid interflow) accounted for most riverine flows.

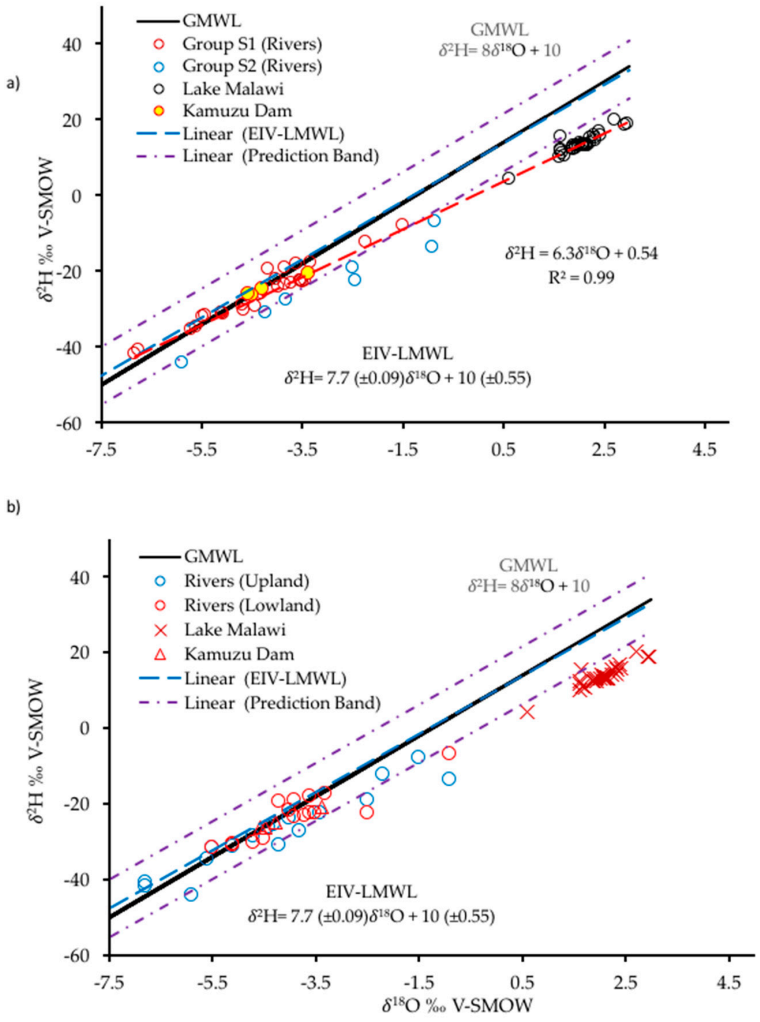

Figure 9. (**a**) Plot of δ^2H and $\delta^{18}O$ for surface water samples; (**b**) Shown with data segregated to upland and lowland sites.

Six river samples exhibited a degree of enrichment, intermediate between the bulk of river data and Lake Malawi samples. Segregating the data between upland and lowland sites reveals that the least evaporated signatures ($\delta^2H < c.\ -30‰$, $\delta^{18}O < c.\ -4.0‰$) are mainly upland sites and the more evaporated signatures (over the above range) are mainly lowland river sites (Figure 9b). For instance, of the six intermediate signature sites, four are upland. Although not conclusively shown, long residence times in dambo, vulnerable to evaporation influences may contribute to enhanced evaporative signatures in the upland river samples. Generally, though, the variation in surface water is consistent with that of precipitation, suggesting that recent local precipitation significantly contributes to river flows in the catchments.

In sum, isotopic compositions of surface water show a wide variation (range: 64‰ δ^2H, 9.8‰ $\delta^{18}O$) consistent with local precipitation spatial variation, and support the view that local precipitation contributes largely to river flows, particularly during the wet season. The full datasets for the stable isotopes analysis results of surface water are presented in the Supplementary Material (SM)—Table SM4b.

3.4. Groundwater–Hydrochemical and Isotopic Evidences Combined

The dominant Ca-Mg-HCO3 groundwater type is plotted along the LMWL length, thus supporting the young water occurrence from non-evaporated local precipitation recharge (Figure 10a). Relationships, however, are not clear. This water type also occurs as outliers removed from the LMWL.

Likewise, the other water types also occur both along the LMWL and as outliers. The latter is expected, as those water types may arise, in part, from evaporative processes. Examining the TDS of these samples is not conclusive either (Figure 10b). Whilst some outliers do correspond with the higher TDS anticipated from evaporation, higher TDS points also occur on the LMWL. TDS also varies across both the data outliers and data plotting along the LMWL. Whilst not easy to interpret, collectively the data suggest a heterogeneous mix of influential processes relating to groundwater sample flow-path history and/or evaporative influences. Notably though, the greatest complexity of the processes suggested by the variation in hydrochemical type and isotope signatures is most apparent near the lakeshore area, where much of the outlier data tend to occur. This signature complexity is consistent with the process complexity anticipated in the lakeshore plains near Lake Malawi, towards the termination and possible convergence of different groundwater flow paths and water histories.

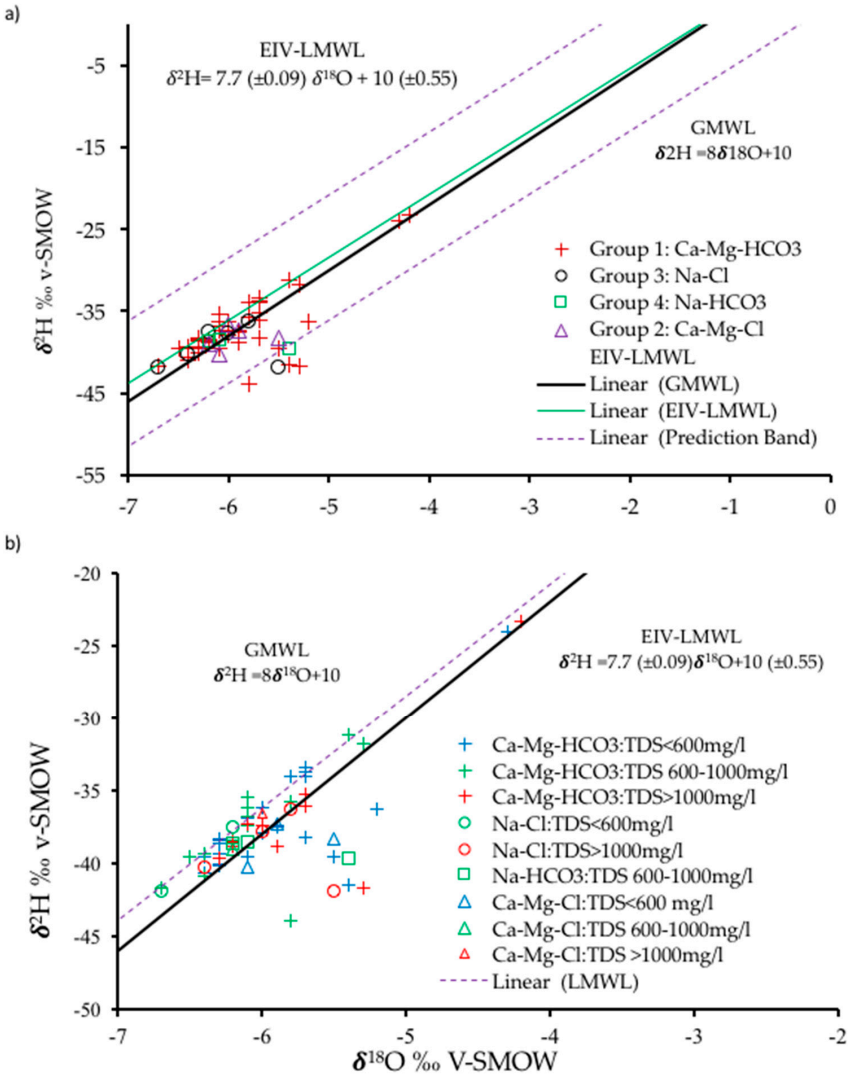

Figure 10. (**a**) Isotopic composition of groundwater types; (**b**) Isotopic composition of TDS-classified (blue lowest, red highest) groundwater types.

3.5. Dynamics: Seasonal Effects and Groundwater–Surface-Water Interactions

Seasonal variability in surface-water isotopic composition is observed, with samples plotting along the meteoric water lines during the wet season, but with a pronounced tendency to plot below lines during the dry season (Figure 11a). This supports the theory of isotopic enrichment due to increased evaporative effects occurring during the dry season. Lowland and upland river samples

both show dry season enrichment. These results are consistent with the probable influence of dambo, sustaining dry season flows and their extensive surface area, combined with prolonged water residence times causing them to be vulnerable to evaporation processes.

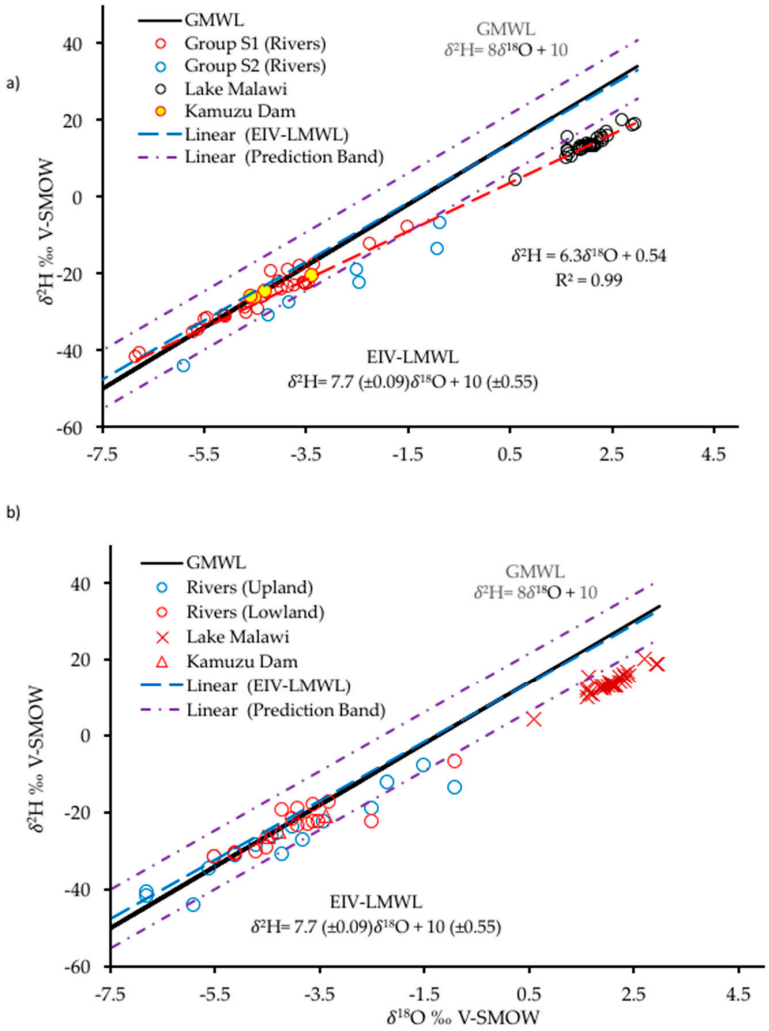

Figure 11. Seasonal variation in isotopic composition observed in: (**a**) Surface water, (**b**) Groundwater samples (dry season—red symbols; wet season—blue symbols).

Groundwater isotopic composition also varies between the dry and wet season (Figure 11b). Points cluster along the meteoric water lines during the wet season with minimal departure during the dry season, although samples both plot along and deviate from meteoric lines. Such seasonal responses in groundwater, regarded as slow moving and often unable to dynamically respond, suggest that parts of the groundwater system are moderately dynamic. The fact that the majority of samples do plot along the meteoric water lines suggests most groundwater samples comprise relatively recent, local recharge precipitation inputs. This is consistent, with most wells sampled generally being shallow, 30–50 m depth, and screened perhaps 0–20 m below water table. Observations would also be consistent with the low storage of the (uplands) fractured and weathered bedrock aquifers, which would lead to a high turnover of water. The latter would also occur in the shallow alluvial aquifers, where these are transmissive and permeable (sand/gravel rich). These observations are consistent with the 'young' hydrochemical Ca-Mg-HCO_3 water type widely encountered.

Groundwater points exhibiting enrichment of dry season samples (Figure 11b), displaying predominant occurrence in the lakeshore plains (Figure 8b), support the probable influence of evaporative processes on some areas of the lakeshore plain groundwater. The variation in hydrochemistry of these samples

(Figure 10) does suggest that a mix of processes are responsible, including phreatic evaporation, infiltration of evaporated influent river waters and residual, infiltrated, earlier wet-season Lake Malawi water, yet to be flushed from the aquifer system.

Most groundwater isotope signatures occur within a quite restricted portion of the surface-water signatures (compare shaded boxes in Figure 11a,b), suggesting the groundwater sampled did not contain large quantities of infiltrated river, or Lake Malawi, surface water. This accords with a groundwater baseflow-dominated exchange with the surface water system. That said, boreholes would probably need to be very close to an infiltrating river reach, or temporarily infiltrate Lake Malawi, to predominantly extract influent waters undiluted by resident groundwater.

3.6. System Conceptual Model

A conceptualization of the water resource system is illustrated in Figure 12 and expanded upon below. The model is generated from our survey findings above and knowledge gained from our detailed review of the hydrogeological [33] and geological (memoir) literature pertaining to the study area [29–31] variously referred to below. Whilst dated, this late 1960s to early 1980s archive of research remains valuable due to its limited updates since. The linking of isotopic lines of evidence to processes is conveniently summarized within the Figure 12 'isotopic signatures' labels. The key 'flow processes' and 'hydrochemistry' controls are also labeled. Conceptualization of the various physiographic zones is briefly expanded upon below.

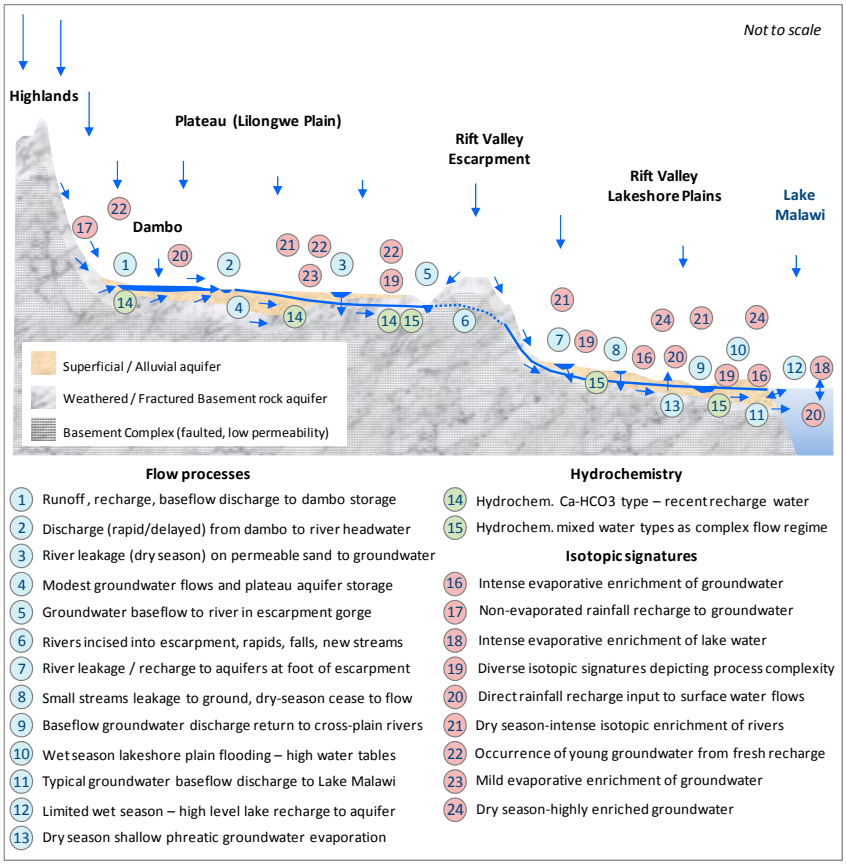

Figure 12. System conceptual model of water resource occurrence, process controls and isotopic signature features (acknowledging the contributions of flow understanding from Smith-Carington and Chilton, (1983) [33] (their Figure 3.18)).

3.7. Dambo

A Dambo comprises a system of poorly defined water channels in waterlogged sediments. Predominantly fine-grained sediments accumulate in the centre, with more sandy, permeable deposits at the head and periphery [29]. Groundwater is near the ground surface, draining into the dambo from the surrounding fractured basement aquifer units with supporting, often perennial, baseflow to the dambo from adjoining weathered basement and colluvium [31,33]. Geological control occurs, dambo and water courses aligning with faulted or jointed areas of structural weakness that may serve as preferential conduits of groundwater flow [29,30]. Rainfall on saturated dambo results in steeply rising river hydrograph limbs, forming anomalously broad peaks. These arise from delayed discharge of impeded, tortuous flows through and around the dambo low-permeability sediments and grasses. Dambo hence provide temporary reservoir storage, buffering precipitation inputs and delaying groundwater baseflow expression. Although end-of-wet-season flows may ultimately decline steeply, accelerated by high evaporative losses from the dambo surface, often, slow groundwater underflow and subsequent baseflow contributions persist, allowing dambo to sustain river flows overall, or for much of the dry season [33]. Our observed enhanced evaporative isotopic signatures in some upland river samples support the above conceptualization.

3.8. Plateau–Upland Area

Water courses traversing the plateau appear subject to geological control. The long, straight stretch of the Lilongwe River on the South Lilongwe Plain near the Likuni Mission area may be ascribed to the strike of the gneisses or strike joints [30]. Such occurrences may facilitate the groundwater discharge to baseflow, although flows from the underlying weathered basement to the plateau reaches are probably not significant [33]. Superficial deposits may be thick, up to 40–50 m on the Lilongwe Plain, with the accumulated sandy riverbed alluvium common to many major rivers that could support baseflows [29,30]. On some reaches, groundwater levels may be (seasonally) below the base of the river, which then become influent and recharge underlying groundwater [33]. Upland area isotope signatures generally support a non-evaporated rainfall recharge to groundwater and direct rainfall input to surface flows and young groundwater from recent recharge. A greater spatial and temporal density of sampling would be required to confirm the seasonal and/or spatial groundwater–surface-water relationships postulated, together with further hydrograph–river gauging works. Hydrochemical contrasts between mostly young waters appear to be limited, and hence less diagnostic.

3.9. Rift Valley Escarpment

Approaching the rift valley up-warped escarpment edge, weathered basement–superficial deposits are typically thin and groundwater underflows through the eastern plateau area are potentially limited. Most groundwater likely drains towards increasingly incised, deep gorge, main river channels and contributes to the baseflow. Rivers dissect the escarpment that falls stepwise to the rift valley floor due to "en echelon" faulting where gorges and rapids occur [33]. Main rivers are joined by many smaller rivers (e.g., the Ngodzi) having their headwaters in the escarpment (Figure 2a, recognizing smaller rivers are not shown). Although baseflow may occur from the fractured basement rock to the rivers and underflow into the alluvial deposits, these are likely modest, as groundwater storage and transmissivities are generally low (although not easily quantified due to (faulted) system discontinuity) [33]. Our survey does not characterize this zone, but it is reasonably surmised that hydrochemical–isotope signature ranges may begin to increase as they manifest gathering process complexities.

3.10. Lakeshore Plains

Very gentle gradients across the rift valley lakeshore plains lead to significant deposition of river sediment loads, with channels becoming tortuous and the plains vulnerable to wet season flooding. Dambo may also occur on the lakeshore plain [31]. Most main rivers leave the escarpment on a level

with the lakeshore plain, and may initially lose much of their flow into the alluvial sediments and weathered basement that is hydraulically contiguous close to their entry to the plains, especially where flowing over alluvial fan-permeable sediments that have debouched from the escarpment [33]. Streams there may often cut through the thin veneer of sediments into basement rock. Further downstream, groundwater baseflows to rivers may, however, subsequently return and increase across the plain. The Linthipe River BFI data (Figure 3) referred to earlier support this conceptualization. Larger rivers rising in the highland often continually flow, albeit at much reduced rates in the dry season, and most smaller streams exhibit ephemeral intermittent flow and cease to flow in the dry season [33]. For instance, Walters (1972) [31] observes that "many streams die away into the sandy alluvium before reaching the lake".

The Lilongwe-Linthipe system approaches perennial flow due to the extensive catchment upstream, but it should be noted that flows, on average, cease for around 25 days annually [31]. Similarly, Sefe's (1988) [45] aforementioned low-flow analysis of the Linthipe (gauge 4B1) confirms that no-flow conditions occur in the dry season around the Salima lakeshore plain. Intermittency is ascribed to the remote upland-dambo primary sources of flow to the river and the likelihood of groundwater levels being beneath river levels, especially in the permeable alluvial deposits, extensive around Salima, that build during flood events. Moreover, influent river conditions of good quality water, causing locally improved groundwater quality (lower TDS), were observed here by Smith-Carington and Chilton (1983) [33]. That river leakage, combined with increased precipitation (1400 mm pa in the lakeshore Linthipe estuary area compared to 800–1000 mm pa in the Lilongwe Plain), [48], were predicted by Smith-Carington and Chilton [33] to cause an increased groundwater recharge of fresh water and further counteract the typical progression of increased salinity by mineral solution in groundwater slowly migrating towards the lakeshore. The heterogeneous hydrochemical water type and TDS data in this area display such trends, as per our earlier discussion of Figure 6 (data points in the north east). These process complexities, adding to the evaporative enrichment of the shallower groundwater and the Lake Malawi interaction–flooding, are supported by the increased variation in hydrochemical type and isotope signatures apparent near the lakeshore area, where most outlier data tend to occur. The significant range in the processes contributing to isotope signature variations is apparent in Figure 12. It is an area deserving of more focused study.

3.11. Lake Malawi–Groundwater Interaction

Whist hydraulic gradients towards Lake Malawi in the low-relief lakeshore plains are minimal at 0.001–0.01, transmissivity estimates from pumping tests in the Salima district area of 100–300 m^2/d cause the estimated underflow in the alluvium and discharge to the lake to still be significant; discharge was calculated at around 0.13–0.38 $\times$ 10^6 m^3 annually per kilometer of shoreline (for a gradient of 0.0035) [33]. Some wet season flow reversal in the local vicinity of the lake shoreline is likely, as more rapidly responding lake levels can become 1–2 m higher than the groundwater, thereby driving temporary storage of invading lake water into the alluvial aquifer. However, such invaded water may later return to the lake upon the seasonal re-establishment of gradients towards Lake Malawi. Smith-Carington and Chilton (1983) [33] calculate storage of invading lake water equivalent to around 10% of the groundwater discharge-to-lake volume (calculated above), with the invasion estimated to reach just 500 m inland. Hence, although exerting a relatively small influence volumetrically, this may generate complexity in near-shoreline groundwater hydrochemical and isotopic signatures. The complexity of the isotope signatures in the lakeshore plain–Lake Malawi approach and the dry–wet season isotope contrasts observed are supportive of the above dynamic interactions, together with the large flood event and groundwater evaporative processes occurring. Again, more targeted high resolution spatial and temporal studies would be necessary to isolate details of individual processes and their interactions.

4. Discussion and Conclusions

4.1. Catchment Management Implications

This study has successfully used stable isotope tracers to establish an isotopic baseline–hydrochemical understanding for an important Lake Malawi catchment. The catchment includes its capital city Lilongwe, but also extensive rural–agricultural areas with representative coverage of the divers Rift Valley physiography. The study has reinforced the conceptualisation of water resource occurrence and provenance in what has proven to be a hydrological–hydrogeological complex scenario, but one that can reasonably be assumed to be representative of a Rift Valley catchment. This is the first published study to use an isotope facility developed in-house within Malawi, that has not relied upon the export of water samples for analysis or interpretation abroad. The study endorses that isotope tools may offer increased insight and/or confirmations, including about the nature and type of water resources available, not just in Malawi, but in any country. Making such tools more widely available to developing countries would allow a more robust delivery of SDG 6 and sustained future IWRM.

The complexities associated with groundwater–surface-water interactions and their diverse occurrence in the study area is a notable feature. These include: delayed, slow-release of water from dambo, that may critically sustain system flows in the dry season; the occurrence of influent and effluent river reaches in various parts of the plateau and lakeshore plains, some of which may exhibit seasonal reversals; and a complexity of processes occurring at the Lake Malawi–foreshore interface where, again, the seasonal reversal of groundwater and lake water flows may occur. Resolving the detail of these and other processes will require more focused, higher spatial/temporal resolution studies, to which isotope tools may be significant. It is especially important that an increased range of tracer isotope and chemical (e.g., CFCs) forensic tools become more available, building upon the stable isotope base achieved. In Malawi, these need to be underpinned by expansion of the fledgling isotope precipitation sampling station network, and continued monitoring, to generate LMWL for all 'Managed Catchments'. This is important, recognizing the wide variation evident in precipitation isotopic composition that is attributable to different rain-bearing systems nationally, alongside more local geographic controls.

Improved isotopic characterization is warranted for the various aquifer types and specific flow pathways, especially those that may serve as a pollutant linkage and pose health risks. For instance, it could be used to assess fault-assisted flows to the surface of deep-sourced groundwater that may drive some of Malawi's salinity [49], fluoride [50] and arsenic [51] risks. Expanding isotope capacity to include tritium (and helium), nitrogen-15 and carbon isotope fingerprinting may help document salinity provenance [52]. The development of isotope capacity and tracer range may likewise assist in the attribution of land-surface sources of groundwater pollution, which are expected to grow—arising, for instance, from agriculture and basic sanitation provision (notably pit latrines)—that have been challenging to attribute in Malawi based on hydrochemical data alone [53]. Furthermore, as IWRM will become increasingly vital, isotopes may assist understanding of the probable mixing of water source types that may occur in, e.g., water transfer, wastewater injection and irrigation schemes.

The influence of land use and climate change on system water resources is of particular concern due to the water system connectivity evident herein and expected in other Rift Valley catchments. It is clear that changes in the management of land around dambo may have significant knock-on influences far downstream, due to its significance as a sustaining dry-season river source. Concerns surrounding increasing agricultural activity around dambo, recognized by Smith-Carington and Chilton (1983) [33] over 35 years, ago remain very valid today. These include the increased channeling of flows, enhanced erosion, higher flood peaks and earlier cessation of dry-season flows. The strategic need to "promote management systems and technologies that protect fragile lands" that include "dambo" areas "is recognized in Malawi's current National Agricultural Investment Plan" [54]. Similarly, the knock-on effects of extensive deforestation across Malawi in the last decade (and longer) upon groundwater and surface water resources and ecosystem services is already a significant concern, and has been observed

to lead to increased occurrence in Malawi of flooding and extreme low-flows that are predicted to persist [25]. Isotopic tools may help improve diagnosis of water-system linkages to furnish the optimal response to deforestation concerns.

4.2. Implication for Policy Implementation

In due course, from this study and its ongoing companion (catchment) studies, the underpinning of Malawian policy implementation is expected on several fronts, important agenda items including:

1. The Government of Malawi should evaluate the sustainability of current catchment management plans to verify if they meet national targets for SDG 6;
2. The Government of Malawi should delineate groundwater recharge zones and protect them from degradation;
3. The Government of Malawi should arrest (and reverse) deforestation in order to sustain groundwater resources and prolong dry-season river baseflows;
4. The Government of Malawi should revisit water-budget calculations (e.g., Water Budget for Lake Malawi) in light of the improved conceptualization and quantification of groundwater contribution to surface water ecosystem services and surface-water resource volumes;
5. The Government of Malawi should prioritize the protection of groundwater resources from pollution;
6. The Government of Malawi should conduct a targeted study of leakage from aging dams in order to enhance dam-safety (e.g., Kamuzu Dam I and II);
7. The Government of Malawi should be part of a network of partners with critical mass to confront today's groundwater issues for the benefit of the present and future generations, by conducting research and building capacity in all aspects in the areas necessary to achieve IWRM;
8. Climate Change is likely to intensify our dependence on groundwater, so the need for increased access to water isotope tracer tools for technical solutions is becoming critical. There is a need to conjunctively manage the surface water and groundwater resources that include transboundary aquifers, as, without coherent policies, attaining many of the UN's Sustainable Development Goals will be a challenge.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/11/12/2600/s1, Tables S1–S3 providing statistical summaries of isotopic composition of local precipitation, groundwater and surface water sampled, and the details of the field survey sampling sites and the isotope and hydrochemical datasets obtained.

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Supplementary Research Article 2

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Mixed method analysis of anthropogenic groundwater contamination of drinking water sources in Malawi

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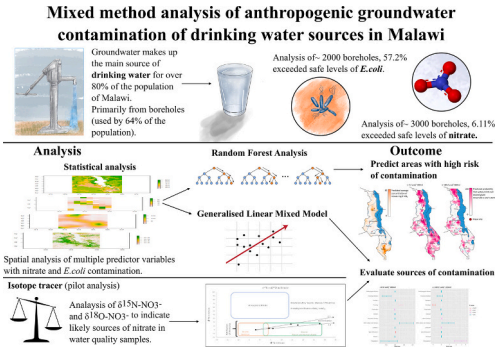
HIGHLIGHTS

- Large scale evaluation of nitrate and *E. coli* contamination in Malawi
- Sanitation variables most significant drivers of microbial and nitrate contamination
- Pilot isotope tracer analysis: sanitation as major source of nitrate contamination
- In particular, high densities of pit latrines result in groundwater contamination.
- Contamination a particular concern around peri-urban areas

GRAPHICAL ABSTRACT



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ABSTRACT

Groundwater contamination poses significant challenges to public health and sustainable development in Malawi, where approximately 80 % of the population relies on groundwater sources for drinking water. This study investigates the presence and drivers of nitrate and *E. coli* contamination in groundwater used for drinking. Analysis was conducted on results from 3388 boreholes/tube wells for nitrate contamination and 2418 drinking water sources drawn from groundwater for *E. coli* contamination. Overall, 6.11 % and 57.2 % of water-points did not meet WHO guidelines for safe drinking water quality for nitrate and *E. coli* contamination, respectively. Through a mixed-method approach, utilizing generalised linear mixed models and random forest regression modelling, the study identifies factors relating to sanitation usage as critical drivers of both nitrate and *E coli* contamination. Pit-latrine usage was identified as a particularly important factor in contamination; accounting for pit latrine density specifically, rather than population density, resulted in better model prediction for both nitrate and high *E. coli* contamination indicating that consideration of the specific type of sanitation is important in predicting water quality. In addition, a stable isotope tracer analysis method to validate predictions and monitor nitrate in drinking water was piloted, identifying human waste as a likely source of nitrate

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contamination. Overall, this study underscores the urgency of addressing sanitation-related contamination of drinking water sources to ensure access to safe drinking water in low-income settings.

1. Introduction

Groundwater is a critical resource, supplying safe and accessible drinking water for over 2 billion people internationally (Kundzewicz and Döll, 2009). Globally, 1.23 million deaths are attributed to unsafe water resources each year, with the burden of unsafe water twice as high in low-income countries (IHME, 2019). As a result, groundwater contamination poses an important concern for human health (Karunanidhi et al., 2021). Alongside human health repercussions, safeguarding groundwater quality is essential for environmental and ecosystem preservation (Li et al., 2021).

Contaminants are commonly categorised as deriving from natural or anthropogenic sources (Li et al., 2021). Anthropogenic sources of contamination, including agriculture and domestic wastewater (Li et al., 2021), pose a particular concern as population growth, urbanisation, industrialisation, and agricultural intensification are resulting in increasing levels (Li et al., 2021). As contamination from anthropogenic sources continues to accelerate, protecting groundwater is becoming an ever-more pressing issue.

Nitrate is one contaminant of concern related to human activities. Whilst nitrate does naturally occur in the environment as part of the nitrogen cycle, anthropogenic sources, predominantly from agriculture and domestic wastewater but also from mining activity, are major causes of nitrate contamination in groundwater (Morrissy et al., 2021; Harper et al., 2017; Morin and Hutt, 2009). Alongside being an ecological contaminant of concern, particularly in contributing to eutrophication of water systems (Nyenje et al., 2010), high nitrate levels have been associated with health risks including increased infant methemoglobinemia 'blue baby' syndrome as well as some cancers (Puckett et al., 2011; Rahman et al., 2021).

Emphasis is often placed on agricultural sources for nitrate contamination, with high nitrogen fertiliser application rates resulting in diffuse nitrate contamination of groundwater resources (Harper et al., 2017; Wick et al., 2012). However, other sectors can be as significant on water contamination. An analysis of the sources of nitrate contamination across Africa found that population density was a better indicator of groundwater nitrate contamination than fertiliser application on a continental level, with a lack of sanitation hypothesised to be the cause of elevated contamination in areas of high population density (Ouedraogo et al., 2019).The assessment of groundwater nitrate loads from human waste sources is thus essential in consideration of water contamination.

Alongside nitrate contamination, inadequate sanitation and domestic wastewater management has also been identified as a critical driver of microbial groundwater contamination (Back et al., 2018). A lack of sanitation infrastructure, resulting in open defecation, has been linked to contamination of groundwater used for drinking water in Asia and Africa (Kayembe et al., 2018; Okullo et al., 2017). However, poor sanitation can itself also cause groundwater contamination where wastewater is inappropriately discharged or leaked (Sridhar and Parimalarenganayaki, 2024) or where there is direct contamination from the sanitation infrastructure itself. Pit-latrines provide one example of how sanitation can result in direct microbial groundwater contamination. Serving as the primary source of sanitation for 1.8 billion people globally, pit-latrines are an integral component of sanitation internationally (Gwenzi et al., 2023). However, unless safely managed, pit-latrines can result in groundwater contamination (Banks et al., 2007; Chidavaenzi et al., 2000; Dzwairo et al., 2006; Escamilla et al., 2013; Graham and Polizzotto, 2013; Gwenzi et al., 2023; Islam et al., 2016; Ndoziya et al., 2019; Tillett, 2013; Wright et al., 2013), a particular concern when they are used in contexts with a high reliance on groundwater sources of drinking water (Graham and Polizzotto, 2013).

As well as contributing anthropogenic \ contaminants to water systems, human activities can also play a part in contamination pathways by influencing other components of the water cycle, such as climate-change related rainfall intensity (Adhikari and Nejadhashemi, 2016). In areas of high fertiliser application, heavy rainfall can result in groundwater contamination of nitrate through the leaching of nitrate from fertiliser (Bijay-Singh and Craswell, 2021). Heavy rainfall can also result in increased surface runoff, which may be contaminated with waste from pit latrines or open defecation, which can infiltrate boreholes and result in heightened microbial contamination (Aralu et al., 2022). In addition, the increased water table height following heavy rain can result in greater pit latrine effluent leaching into groundwater and contamination of boreholes (Rivett et al., 2022). Not only does this highlight the significance of a system's environmental context on anthropogenic contamination, but presents a potential growing challenge due to increased extreme weather events under climate change. *Building resilience to climatic extremes will require greater understanding of groundwater quality from human activities accounting for both sources of contamination and consequences of hydroclimatic extremes.*

Malawi represents a particularly pertinent case study in the consideration of groundwater quality management with one of the lowest levels of access to safe drinking water globally (UNICEF and WHO, 2024). Within Malawi, groundwater provides the main source of drinking water for almost 80 % of the population (NSO, 2021), making groundwater quality essential to providing safe drinking water provision. Boreholes/tubewells provide the main points of access of drinking water and range from under 10 m to over 60 m deep, with most boreholes 40-50 m deep (Kalin et al., 2019). Contamination is a major barrier to safe drinking water access; currently over 60 % of the population access drinking water from contaminated drinking water sources (NSO, 2021). Poor quality water infrastructure worsens the contamination crisis; the infiltration of polluted surface run-off into boreholes is increased in damaged or poor-quality boreholes due to cracks in the concrete apron (Rivett et al., 2022). This is particularly concerning in Malawi due to high rates of borehole non-functionality and minimal borehole maintenance (Truslove et al., 2019, 2020; Kalin et al., 2019) placing water infrastructure itself at a greater risk of contamination.

The health consequences of groundwater contamination at drinking water sources are exacerbated by a low level of water treatment, which is practised by under 40 % of the population (NSO, 2021). Even where water treatment is conducted, it is largely through inefficient treatment processes such as bleach chlorination (Nielsen et al., 2022). This makes microbial contamination of groundwater sources likely to result in direct consumption of contaminated drinking water by the 60 % of the population accessing water from contaminated sources (NSO, 2021). As such, inadequate groundwater quality is undermining Malawi's aim to provide 100 % of the population with clean water sources by 2030 (NPC, 2021).

The consequences of high levels of contamination of drinking water sources can be seen in the scale of waterborne disease challenges within Malawi, estimated to account for over half of the national disease burden (Chavula, 2021). Malawi's deadliest cholera outbreak on record occurred from 2022 to 2023 and was reported to be partially due to widespread drinking water contamination (Freeman et al., 2024). There have been growing concerns of faecal groundwater contamination from pit latrines as a factor in the high burden of waterborne disease (Pritchard et al., 2007, 2008). This is likely to worsen as, under current population growth scenarios, there is projected to be a three-fold increase in the number of water-points at high risk of pit latrine contamination due to proximity (Hinton et al., 2024b).

Yet despite the gross burden of groundwater contamination in

Malawi, no national level evaluation of the extent and sources of groundwater contaminants has been conducted. Previous studies exploring groundwater contamination in Malawi have been limited to sub-national scales (Rivett et al., 2022; Addison et al., 2020; Back et al., 2018; Pritchard et al., 2007, 2008; Mussa and Kamoto, 2023; Dzinjalamala et al., 2024; Mkandawire, 2008) and often do not empirically evaluate the sources of contamination (Pritchard et al., 2007, 2008; Mussa and Kamoto, 2023; Dzinjalamala et al., 2024; Mkandawire, 2008). This limits current understanding on the extent, spatial distribution, and origins of contaminated groundwater, restricting appropriate protection measures of groundwater. *National level analysis of groundwater contamination is needed to develop a representative picture of the scale of challenge of groundwater contamination, studies that explore not only the level of sources but apply various methods to investigate likely sources will be critical in developing appropriate management measures (Kalin et al., 2022a).*

Statistical models including Generalised Linear Mixed Modelling (GLMM) and Random Forest Regression (RF) can provide insight to the relationships between predictor variables and measured groundwater contamination. These models can be applied to enhance understanding of the sources of groundwater contamination (Ouedraogo et al., 2019) as well as predict areas likely to have high levels of contamination (Charulatha et al., 2017; He et al., 2022). Managing anthropogenic groundwater contamination requires both greater understanding of the sources of contamination as well as enhanced prediction of areas at risk of contamination requiring different statistical modelling techniques to achieve different goals. Both GLMM and RF models are particularly useful in their application to a broad range of data types and capacity to handle non-linear relationships (Liu, 2016; Louppe, 2014). GLMM models, alongside other linear regression models, have been used widely to explore sources of contamination of groundwater (Charulatha et al., 2017; Nolan and Hitt, 2006). They have benefit in robustly exploring the relationship between a response variable and predictor variables particularly as GLMMs can account for random effects as well as fixed effects (Rabe-Hesketh and Skrondal, 2008; Muschelli et al., 2014). As such they have been widely used to explain patterns in data in multiple fields (Goldstein and de Valpine, 2022; Zhu et al., 2007). However, as with all linear regression models, GLMM models are held back by their limited capacity to handle collinearity of variables (Hendrickx and Nutricia, 2018). This is a common challenge when investigating anthropogenic sources where multiple variables, e.g. population density and sanitation usage, are highly correlated, reducing model efficiency and making them less useful for accurate prediction.

RF models provide another tool to analyse and predict contamination trends. They have high predictive performance power (Couronné et al., 2018) particularly for spatial data (Hengl et al., 2018). The RF model functions as a combination of multiple decision trees with each tree applying a different subset of predictor variables to predict the response variable of the training dataset (Rokach and Maimon, 2015; Nath et al., 2022). They are particularly useful for collinear variables (Louppe, 2014). Whilst RFs indicate which predictor variables are most important in a specific model prediction (Ishwaran, 2007) variable importance must be interpreted with caution and cannot necessarily be used to indicate which are the most important predictor variables for the phenomena being studied (Louppe, 2014). As such, RFs have limited capacity in analysis of sources of contamination but are valuable for efficient prediction. In recognition of their specific strengths and limitations, combinations of GLMM and RF models have been utilised to enhance analysis and prediction (Bernaisch, 2022) and have been applied to studies of groundwater contamination (Ouedraogo et al., 2019; Charulatha et al., 2017; He et al., 2022; Nolan and Hitt, 2006).

Isotope hydrology is another commonly used method to evaluate groundwater contaminants and has been widely used for tracing sources of nitrate contamination which can be challenging to examine as they can be retained in groundwater for extended periods of time (Canter, 1996; Kendall et al., 2007; Jung et al., 2020, Nikolenko et al., 2018). By analysing the relative abundance of nitrogen and oxygen isotopes, likely sources can be identified due to characteristic patterns of isotope abundance, developing 'signatures' of the source of contamination. Whilst this method is highly effective, the need for specialised analytical facilities, not normally available in low-income countries, often makes application of the method non-feasible. In addition, this method has limited capacity to identify whether sources are from animal manure or human faecal waste due to their similar isotopic signatures (Kendall et al., 2007). *Applying mixed method analysis through the incorporation of statistical models alongside isotope hydrological analysis can enhance understanding of the extent and sources of groundwater contamination, developing understanding to enhance management approaches.*

This study adopts a mixed method analysis, using both GLMM and RF models to explore national groundwater contamination from multiple anthropogenic sources; both exploring sources of contamination (using GLMM) and predicting areas at high risk of contamination (using RF). Both methods are applied to two examples of contamination that are of concern in Malawi, microbial contamination (*E. coli* groundwater contamination) and nutrient contamination (nitrate contamination). Analysis is further enhanced through a pilot isotope analysis study of the sources of high nitrate levels. Specifically, this work addresses the following research questions and objectives: (1) What are the primary sources of nitrate and microbial groundwater contamination in Malawi? (2) What areas are predicted to have highest nitrate and microbial contamination? (3) Evaluate the use of stable isotopes of nitrate as a tool for nitrate source evaluation and verification of the model results in Malawi. These inferences provide valuable insight into groundwater management, informing decision making on contamination sources as well as identifying areas of concern for contamination and guiding areas for future water quality testing.

2. Methodology

2.1. Context and study area

Malawi is a country in South-Eastern Africa which experiences a tropical-continental climate, with a wet season from November to April and a dry season from May to October (Kalin et al., 2022a,b) (Fig. 1). Malawi's water supplies are dominated by Lake Malawi, both in the proportion of the country's water resources contained in Lake Malawi and in narratives around national water security and water resource management. In contrast, despite providing 82 % of water abstracted for agricultural, domestic, and industrial purposes, groundwater is an often overlooked facet of water security in Malawi (Fraser et al., 2020). Alongside being the biggest source of water for abstraction, groundwater underpins much of surface water security with baseflow from groundwater central to maintaining river flows (Kelly et al., 2020). This is particularly true for the dry season where over 90 % of all river flow comes from groundwater discharge (Kelly et al., 2020). Agricultural intensification is impacting Malawi's land and water management. Currently, the majority (over 80 %) of the population are employed in rain-fed, subsistence farming (NPC, 2021), however, planned governmental economic and agricultural development involves increased irrigation and fertiliser usage (MAIWD, 2018), placing growing pressure on water resources, notably groundwater.

Malawi is undergoing rapid demographic change with its current population of 21 million (World bank, 2024) anticipated to reach almost 60 million by the end of the century (United Nations, 2024). Urbanisation is also resulting in dramatic demographic shifts, with the 84 % of the population currently residing in rural areas anticipated to reduce to 40 % by 2063 (NPC, 2021). Groundwater forms the main source of drinking water for 80 % of the population (Kalin et al., 2022a,b; NSO, 2021) with water from boreholes/tubewells providing the main source of drinking water and used by 64 % of the population (NSO, 2021). Access to safely managed drinking water, defined as an 'improved water source that is accessible on premises, available when needed, and free

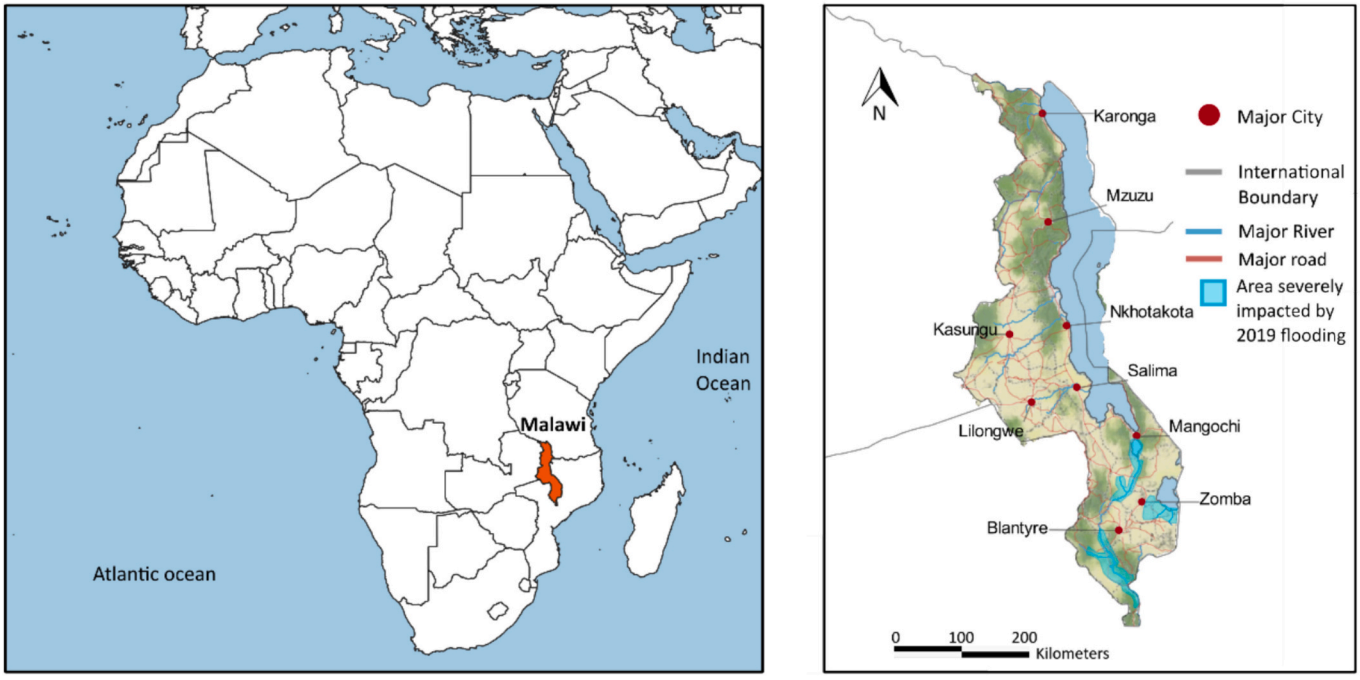

Fig. 1. Study location of Malawi showing major cities and rivers. Water quality data from across the country is analysed. Figure was produced in QGIS with Stamen Terrain background (QGIS, 2024).

from contamination' (WHO and UNICEF, 2017) is low; only 18 % of Malawi's population meet international guidelines for a safely managed drinking water source (UNICEF and WHO, 2024). Contamination is one of the major barriers to access of safely managed drinking water access with over 60 % of the population's source of drinking water having measurable *E. coli* contamination (NSO, 2021).

2.2. Water quality data collection

2.2.1. Nitrate analysis

Groundwater quality samples for nitrate analysis were collected from 3717 boreholes across Malawi. Samples were collected by Government of Malawi water laboratory staff through borehole construction contractors after drilling of a new borehole/tubewell. Information on borehole depth was not available for all boreholes but most water-points in Malawi have a depth between 40 and 50 m (Kalin et al., 2019). Samples were collected between 2000 and 2022, with most data collection from 2015 to 2022 due to an increased drilling effort. Data was provided by the Government of Malawi, Ministry of Water and Sanitation for this study. Out of the collected samples, 3388 were chosen for analysis after removing duplicate responses.

Water samples for nitrate analysis were collected in polyethylene bottles that were rinsed with distilled water, un-acidified, and stored at 4 °C during transportation to the government water laboratory in Malawi. The water samples were filtered through 0.45 μm Whatman filters prior NO_3-N analysis and measured against known laboratory standards. Before 2019, the HACH Chromotropic acid method was used with a HACH spectrophotometer. After 2019, samples were analysed using Ion Chromatography (Ion Analyzer—Model: IA-300). The NO_3-N analysis was performed following the International Standard Methods (APHA et al., 2005), and the accuracy of the results was confirmed through a series of quality assurance and control procedures specified in the International Standard Methods (APHA et al., 2005). The threshold of 50 mg NO_3^-/l was considered high nitrate according to the Malawi Standard (MS733:2005) for drinking water from boreholes and protected shallow wells as well as the WHO guideline standards (MBS, 2017; WHO, 2017).

2.2.2. E. coli analysis

Water quality *E. coli* levels were obtained from the Multiple Indicator Cluster Surveys (MICS); a nationally representative survey between December 2019–August 2020 of 26,882 households in 1111 clusters. This survey was conducted by the Government of Malawi National Statistical Office in collaboration with UNICEF (UNICEF, 1995). The survey sample was based on the 2018 Population and housing Census designed to provide representative clusters across the country. These surveys gathered household level information on a range of topics relevant to child, maternal, and family well-being. In addition to household survey responses, the MICs survey conducted water quality testing data at households' sources of drinking water, evaluating *E. coli* levels in household and source drinking water (Bain et al., 2021; NSO, 2021). Water quality testing was conducted at 2810 waterpoints within the 1111 clusters nationally. Georeferenced water quality data was provided by the Malawi National Statistical Office, UNICEF Malawi, and Global MICs team. Following data cleaning, 2801 complete and unique datapoints were selected. In this work, we evaluate only water-points drawn from groundwater, including boreholes/tubewells, dug wells, and protected springs. In total, water quality assessments for 2418 water-points drawn from groundwater were analysed.

E. coli water quality analysis followed a protocol outlined in the 2016 MICS Water Quality Testing Manual (UNICEF, 2016). A 100 ml water sample was obtained at sources of drinking water reported to be used by households. Prior to collection from the source, water was flushed for 30 s. Water samples were collected in sterilized 'Whirl Pak Bags', the water sample was subsequently filtered through a filter which was placed on an agar growth medium and incubated for 24 to 48 h and bacterial colony growth counted and recorded (UNICEF, 2016). The number of *E. coli* in a 100 ml sample of water was evaluated with values between 0 and 100 *E. coli* recorded as the number of *E. coli* and values exceeding >100 *E. coli* classed listed as 101 *E. coli*/100 ml.

As values exceeding 100 *E. coli* were not quantified, for the purposes of this study, binary classifications of *E. coli* contamination of water-points were created with water-points classified as any *E. coli* contamination (>0 *E. coli*/100 ml) and cases of very high *E. coli* contamination (≥100 *E. coli*/100 ml). Whilst *E. coli* contamination indicators were

available for both source and household drinking water, we consider only source contamination as household drinking water is also significantly influenced by post-abstraction behavioural patterns such as water collection and storage methods as well as the types of containers being used for collection (Wright et al., 2004) and as such are not representative of groundwater contamination itself.

2.3. Water quality data visualisation

For data visualisation, binary contamination data of the presence of nitrate and *E. coli* contamination was rasterized to 10 km resolution using the rasterize() function within the raster package, R (Hijmans, 2024). The percentage of surveys conducted within each cell that exceeded given thresholds of contamination were calculated and summarized.

2.4. Statistical model variable selection

A range of socioeconomic and biophysical 'core' variables were selected for analysis within statistical models of groundwater contamination. Variables were selected based on the variables analysed in published methods (Ouedraogo et al., 2019; He et al., 2022) or where the literature suggested that greater exploration into specific variables (e.g. sanitation infrastructure) was needed (Ouedraogo et al., 2019).

The selected variables are summarized in Supplementary Information Table 2. Summary plots of spatial data used are shown in Supplementary Information Figs. 2 and 3.

The spatial distribution of different types of sanitation was identified as an area of interest. The types of sanitary facility provision considered were pit-latrine use, flush toilet use, and open defecation (no facility) as these make up the majority of sanitary access (Hinton et al., 2023). National spatial data regarding the type of sanitation was only available for pit-latrine usage.

For flush latrine usage and open defecation, spatial sanitation use data was produced following the methodology outlined in (Hinton et al., 2024b). A high resolution, 100 m, gridded population distribution of Malawi obtained from WorldPop population distribution (Worldpop, 2024) was defined as rural or urban areas based on the urban fraction outlined in (Hurtt et al., 2011). The rural and urban population for each district was multiplied by the respective level of sanitary facility use (or open defecation) for rural and urban populations as outlined in the 2015/16 DHS survey (NSO and ICF, 2017). Population density (Worldpop, 2024) and deprivation index (CIESIN, 2022) were also included as socioeconomic variables.

Another variable of interest was flooding extent. The 2019 Cyclone Idai flood was taken as a flooding event of interest as it was representative of other flooding events observed and was close to when most analysed data was collected. Flooding data was generated as a binary raster of areas impacted by flooding in 2018–2019, corresponding to the years leading up to water quality survey sampling. The raster was created in QGIS (QGIS, 2024), creating a map of flooded areas as reported in flooding report survey data (DoDMA, 2019; Scottish Government, 2019) and informed by stakeholder engagement (personal communication). In addition to flooding, the overall level of precipitation, precipitation trend, was obtained from the RCMRD Geoportal (RCMRD, 2015b).

Individual livestock distribution data was available from the gridded Livestock of the World (GLW 3) database (Gilbert et al., 2018). Total livestock data was calculated by summing the quantity of sheep, cows, pigs, and goats as these are the major mammalian livestock cultivated in Malawi. Cropland data was obtained from the HarvestPortal Database (FAO/NASA, 2024) and spatial data for both fertiliser and manure application was also included (Potter et al., 2010, 2012). In addition, anthropogenic biome was included as a measure of 'wildness' (RCMRD, 2015a).

Water sample specific information including the type of water source (e.g. dug well, borehole/tubewell, or protected spring) and the date of collection (month and year) was also included in model generation, this was only available for water-samples for *E. coli* contamination data and was not given for nitrate contamination data (which only evaluated boreholes/tubewells).

2.5. Multiple linear regression model construction

This study employed generalised linear mixed model (GLMM) structures to explore the relationship between response and predictor variables, accommodating noncontinuous as well as continuous variables with both fixed and random effects (Liu, 2016; Rabe-Hesketh and Skrondal, 2008). Three models of contamination were developed using binary response variables, the response variables in the respective models were the presence of high nitrate, any *E. coli* presence, and high *E. coli*. In each model, the response variable was modelled as a binary variable of whether contamination passed given thresholds.

For NO_3, the threshold for 'high nitrate' was 50 mg/l, with values at or exceeding this considered as high contamination according to national and WHO guidelines (MBS, 2017; WHO, 2017). For *E. coli* contamination, two GLMM models were constructed. The first *E. coli* GLMM model considered the presence of any *E. coli* contamination, therefore exceeding WHO specifications of safe drinking water (UNICEF and WHO, 2024). The second model considered high *E. coli* contamination, exceeding 100 *E. coli*/100 ml and considered as a 'very high' risk (NSO, 2021). All GLMM models used logistic regression as they applied continuous and categorical variables to a binary predictor.

All models were produced using the feGLM function in the fixest package (Bergé et al., 2023) in R (R Core Team, 2023), as this enabled GLMM generation with and without fixed effects (Bergé, 2018). For NO_3 contamination, a GLMM model with no fixed effects was constructed with continuous and categorical predictor variables and a binary NO_3 response variable. For *E coli* contamination, consistent data was available on the water source type and date of collection and were used as fixed effects. Within the *E. coli* contamination GLMM water source and date (year and month) were included as fixed effects. The number of levels for each fixed effect is summarized in the model structure in the Supplementary Information, Tables 9 and 12. Both *E. coli* contamination models therefore had a binary contaminant response variable with categorical and continuous predictor variables with fixed and random effects.

GLMM probabilistic assumptions of linearity, response distribution, independence and multicollinearity were confirmed using the R functions lm and the Variance Inflation Factor (VIF) (Chambers, 1992; R Core Team, 2023; Wilkinson and Rogers, 1973). Diagnostic plots and VIF factors are provided in Supplementary Information, Figs. 4–6 and Tables 4–6.

Where there was high multicollinearity between the predictor variables, two GLMMs were generated for each contaminant model containing all variables without high multicollinearity as well as one of the identified variables with high multicollinearity. The model performance of the two GLMMs, each containing one of the highly collinear variables, was evaluated and the model with best overall performance, for each contaminant, is summarized within the results.

Data was subset into training and testing data, using 60 % training to 40 % testing data. The GLMM model was applied to predict testing data outcomes using the R predict function (R Core Team, 2023), predicted contamination was compared to measured data and a confusion matrix produced. Metrics for model evaluation are summarized in Eqs. (1)–(4). Model performance metrics are accuracy (proportion of cases correctly categorised) (Eq. 1), precision (proportion of positive cases identified) (Eq. 2), sensitivity (proportion of predicted positives that were true positives) (Eq. 3), and specificity (proportion of negatives that were true negatives) (Eq. 4). Model fit was also evaluated using the McFadden pseudo R^2 (McFadden, 1974) (Eq. 5), calculated within the feGLM function, fixest package (Bergé et al., 2023), R. For McFadden pseudo R^2

values between 0.2 and 0.4 represent an 'excellent fit'(McFadden, 1977).

$$Accuracy = (TP + TN)/(TP + TN + FP + FN) \quad (1)$$

$$Precision = TP/(TP + FP) \quad (2)$$

$$Sensitivity = TP/(TP + FN) \quad (3)$$

$$Specificity = TN/(TN + FP) \quad (4)$$

$$R^2_{McF} = 1 - ln(L_M)/ln(L_0) \quad (5)$$

where TP is true positive (the number of cases correctly predicted as positive), TN is true negative (the number of cases correctly predicted as negative), FP is false positive (the number of cases incorrectly predicted as positive), and FN is false negative (the number of cases incorrectly predicted as negative). R^2_{McF} is the McFadden pseudo R^2, L_M is the likelihood of the fitted model and L_0 is the likelihood of the null model.

For the models of NO_3 contamination and high *E. coli* contamination presence, there was imbalance in the dataset with only a small percentage of samples exceeding the given thresholds. To improve model development, the minority class was upsampled using the upsample() function under the caret package in R (Kuhn, 2008) to make class distributions equal.

2.6. Random Forest model construction

For spatial prediction of areas of contamination, random forest modelling was applied using the package randomForest in R (Breiman, 2001; Liaw and Wiener, 2002). The number of decision trees was set as 500, considered to be an appropriate balance to limit overfitting. All given spatial predictor variables were included in the model for both NO_3 and *E. coli* level. For NO_3 contamination, a continuous response variable for NO_3 was predicted, therefore a regression random forest model was generated. For *E. coli* contamination, two binary models of *E. coli* contamination were produced: presence of any *E. coli* contamination and *E. coli* contamination of 100 *E. coli*/100 ml and above. For the generation of these random forest models, unsupervised random forest models were produced.

Data was split into training and testing datasets, using 70 % for model training and 30 % for testing. Model performance was evaluated by calculating the Root Mean Square Error (RMSE), summarized in Eq. (6), and R^2 coefficient for the continuous, regression model, of NO_3, Eq. (7).

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(y_i - \hat{y})^2} \quad (6)$$

$$R^2 = 1 - \frac{\sum (y_i - \hat{y})^2}{\sum (y_i - \bar{y})^2} \quad (7)$$

where N is the number of data points, y_i is the given value of y, $\hat{y}$ is the predicted value of y, and $\bar{y}$ is the mean value of y.

For categorical model prediction of *E. coli* contamination, model performance was evaluated using a confusion matrix to calculate model accuracy, precision, sensitivity, and specificity (Eqs. 1–4). Feature importance was evaluated by calculating Shapley values of variables in the Random Forest Model, comparing model predictions with and without features being included, model simulations were iteratively run to give different feature orders. Shapley values were calculated using a randomly assigned 5 % subset of the data due their computationally intensive nature. The kernelshap() function, within the kernelshap package in R (Mayer et al., 2023), was used to calculate Shapley values. Shapley values were visualized as a beeswarm plot using the shapviz() and sv_importance() functions within the shapviz package, R (Mayer and Stando, 2024).

For visualisation of predicted contamination, the random forest models were applied to create a raster of predicted contamination. The NO_3 model generated a predicted NO_3 concentration raster for the average level value of NO_3 contamination for a water-point within a given 10 km cell. For the *E. coli* models, the percent for waterpoints within a given 10 km cell that would exceed thresholds of *E. coli* was predicted. Predicted rasters were produced by applying the random forest model to a raster stack of all predictor variables using the predict() function under the raster package in R (Hijmans, 2024). Maps of predicted contamination were produced in QGIS for visualisation (QGIS, 2024).

2.7. Isotope analysis

A pilot study using nitrate isotope analysis was undertaken within the Linthipe river sub-catchment (Kalin et al., 2022b) in the central region of Malawi. The dominant aquifer type within the Linthipe subcatchment is a colluvium overlying weathered and fractured basement (Kalin et al., 2022b) with extensive groundwater-surface water connections within the region. Pilot samples were collected as part of an International Atomic Energy Agency (IAEA) national project (MWL-7002 TC project). Targeted groundwater and surface water samples were collected at 15 locations suspected of high nitrate concentrations between May and June 2015 and shipped to the IAEA (Vienna) for analysis of $\delta^{15}N$ and $\delta^{18}O$ of NO_3^-.

Water samples were collected in 60 ml HDPE bottles tapped tightly to prevent evaporation and exchange with atmospheric water vapor and stored in cool conditions (4 °C) during transportation and holding at the Isotope Hydrology Laboratory of the IAEA (Vienna, Austria). The $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- were measured using dual isotope approach and results were reported in per mil (‰) relative to atmospheric air (N_2) and Vienna Standard Mean Ocean Water (VSMOW) standards for nitrogen and oxygen, respectively. International reference materials (IAEA-NO_3^-, USGS34 and USGS35) were used for data calibration and instrumental monitoring. Analytical precision was less than ±0.2 ‰ for $\delta_{15}N$- NO_3^-, and ±0.5 ‰ for $\delta^{18}O$-NO_3^-, respectively.

3. Results

3.1. Spatial distribution of groundwater contaminants

Fig. 2 summarises the percent of water quality surveys conducted within 10 × 10 km grid cells which surpassed water quality thresholds. A map of surveying intensity is provided in the Supplementary Information, Fig. 2.

Of the 3388 complete water quality tests surveying NO_3, 207 (6.11 %) exceeded the WHO threshold of 50 mg/l (WHO, 2017) with an average NO_3 level of 3.1 mg/l. There were 322 cases of contamination over 10 mg/l, exceeding historic Malawi Standards guidelines (Pullanikkatil et al., 2015; MBS, 2017), and 212 cases exceeding the current Malawi standards guidelines of 45 mg/l (Chidya et al., 2016; MBS, 3017). Overall, of the 2418 MICs water quality surveys, 1383 (57.2 %) water-points had *E. coli* contamination surpassing WHO guidelines of 0 *E. coli*/100 ml (NSO, 2021) and. 361 (14.9 %) water-points had 100 or more *E. coli*/100 ml.

3.2. Multiple linear regression contamination model selection

There was high multicollinearity between population density and (pit) latrine density for all models. To meet the assumption of collinearity, one of the variables with high multicollinearity (latrines and population) was removed. For NO_3, there was also high multicollinearity between the predictor variables flush toilet use and open defecation. To resolve this case, flush toilet use was removed, VIF values before and after the removal of flush toilet usage are shown in the

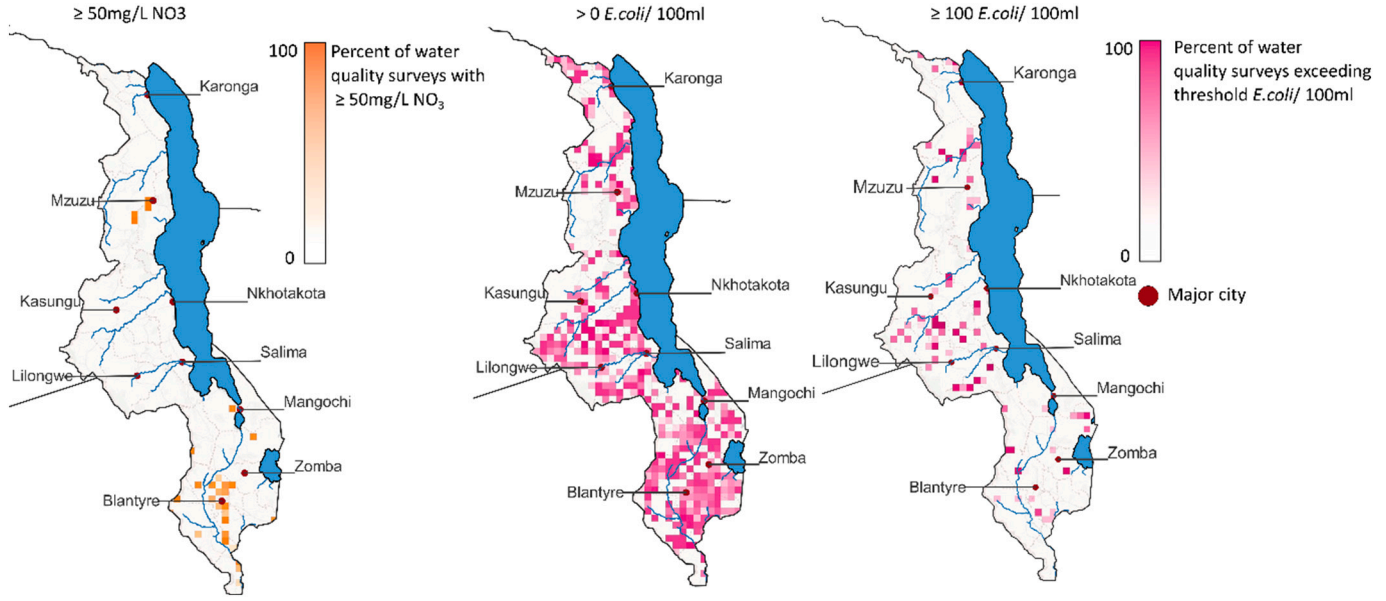

Fig. 2. The percent of groundwater samples within a 10 × 10 km grid exceeding thresholds of drinking water quality for nitrate and *E. coli*. Figure produced in QGIS (QGIS, 2024).

appendix. Flush toilet use did not have high multicollinearity in the *E. coli* contamination model and therefore was included. Following the removal of variables with high multi-collinearity, all VIF values were below 3 and met the assumption of collinearity (James et al., 2013). For each contamination model, models were produced for all variables excluding latrines and another model with all variables excluding population. Model fit was evaluated and is summarized in Table 1. The model with the highest model accuracy was selected as the GLMM model used for further analysis.

For nitrate above 50 mg/l and high *E. coli* contamination (≥100 *E. coli*/100 ml), the models including latrine density as a predictor variable had higher accuracy than the model including population density; nitrate dependent variable models had 70.92 % and 68.23 % accuracy where population and latrine density were dependent variables respectively, models with high *E. coli* as the dependent variable had 80.97 % and 78.52 % accuracy for models with population and latrines as dependent variables respectively. For *E. coli* presence (>0 *E. coli*/100 ml) the model with population density as a predictor variable resulted in higher accuracy (57.98 % accuracy) than the model with latrine density (56.02 % accuracy). All diagnostic plots and assumptions for the selected GLMM for each contaminant are provided in the Supplementary Information Tables 4–6 and Figs. 4–6.

3.3. NO_3 contamination GLMM

The binomial GLMM (with no fixed effects) for NO_3 contamination had good model performance with a McFadden Pseudo R^2 value of 0.329 (considered excellent fit), 70.9 % overall model accuracy, 50 % sensitivity and 71.3 % specificity.

Predictor variable estimates are presented in Fig. 3. Precipitation was the significant predictor variable with the highest estimate, with areas with higher precipitation reporting a lower chance of high NO_3 contamination (≥50 mg NO_3/l). A similar effect was also observed for flooding, areas with high flooding had a lower chance of having high NO_3. Areas with higher anthropogenic biome, a measure of 'wildness', with high anthropogenic biome values being further away from both urbanised areas and intensive cropping, had more NO_3 contamination. This was also seen in that cropping intensity, pit-latrine density, and livestock density were negatively correlated with the presence of high NO_3 contamination. Water points in areas with high poverty were also less likely to report high nitrate levels. Areas with a high catchment level density of pit-latrine users (WRU Latrine User Density) had more waterpoints with nitrate values exceeding safe limits. This was the only factor to have a significant positive correlation with the presence of high NO_3 contamination.

3.4. *E. coli* contamination GLMM

Two binomial GLMM (fixed effects of date and water source) were produced for *E. coli* contamination, the results are summarized in Fig. 4. For the presence of *E. coli* contamination (>0 *E. coli*/100 ml), the GLMM model had a McFadden R^2 value of 0.08 and 58.0 % accuracy indicating

Table 1
Model performance for the contaminant models containing either latrine density or population density. Multiple metrics are shown. The highest value for each metric is highlighted in bold. Core variables are Anthropogenic Biome, Cropping Intensity, Fertiliser, Flooding, Manure, Pit-Latrine Density, WRU Pit-latrine density, Livestock, Open Defecation, Poverty, and Precipitation. The fixed effects on sample source and month of collection were included for the *E. coli* models. McFadden Pseudo R^2 values between 0.2 and 0.4 are considered an excellent fit.

Contaminant model	Variables included in model	McFadden Pseudo R^2	Accuracy	Precision	Sensitivity	Specificity
≥50 mg NO_3/l	Core Variables + Population	0.306	**70.92 %**	3.209 %	50.00 %	**71.32 %**
	Core Variables + Pit-latrines	**0.329**	68.23 %	**3.421 %**	**54.17 %**	68.52 %
	Core Variables + Fixed effects + Flush Toilet + Population	**0.0790**	**57.98 %**	72.17 %	**57.58 %**	58.72 %
	Core Variables + Fixed effects + Flush Toilet + Pit-latrines	0.0775	56.02 %	**75.35 %**	47.93 %	**71.00 %**
>0 *E. coli*/100 ml						
	Core Variables + Fixed effects + Flush Toilet + Population	0.2075	**80.97 %**	**41.67 %**	57.25 %	**85.31 %**
	Core Variables + Fixed effects + Flush Toilet + Pit-latrines	**0.2404**	78.52 %	39.07 %	**61.31 %**	81.70 %
≥100 *E. coli*/100 ml						

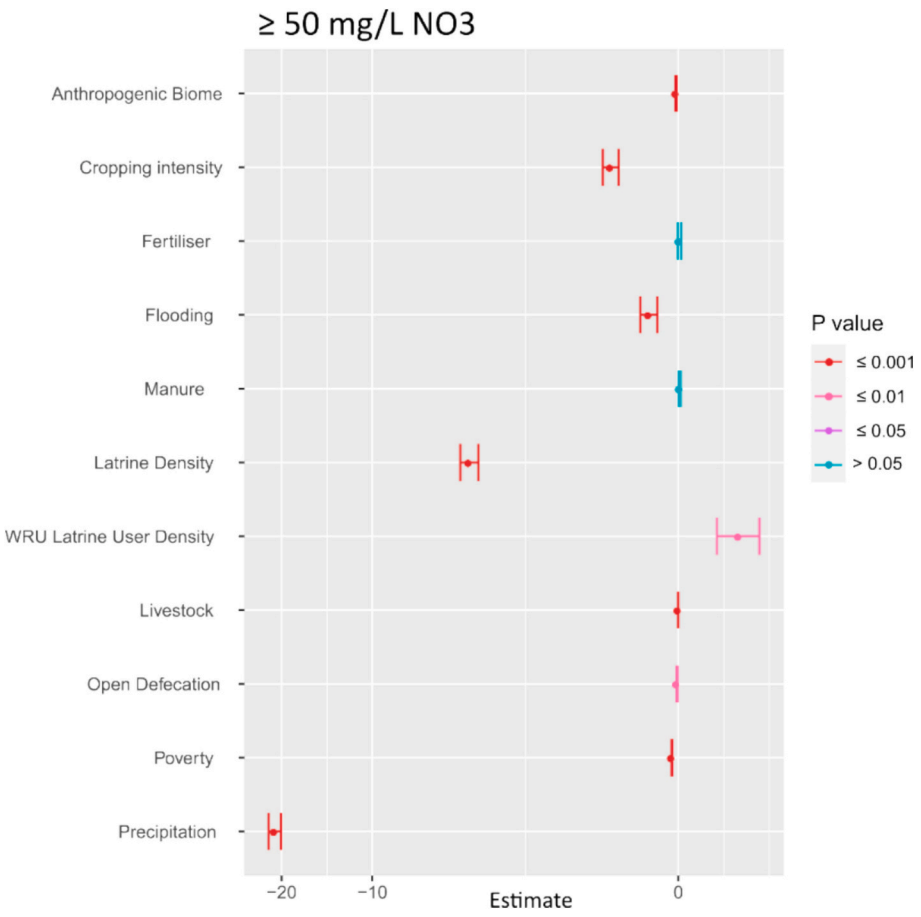

Fig. 3. GLMM model for the presence of high nitrate contamination (≥50 mg NO_3/L) of water-points. Coefficient estimate is shown on the x axis. Significant variables are highlighted in red and pink. Non-significant variables are shown in blue.

moderate performance. The area being impacted by 2019 flooding and the density of people practising open defecation were significantly correlated with an increased presence of *E. coli* contamination. Areas with a high density of flush toilet usage were significantly less likely to have some *E. coli* contamination.

For high *E. coli* contamination (≥100 *E. coli*/100 ml), the model had an 'excellent fit' with a McFadden R^2 of 0.24 and a high accuracy of 78.5 %. Precipitation and pit-latrine density significantly resulted in an increased risk of high *E. coli* contamination. Livestock density and the area being impacted by 2019 flooding were significantly negative drivers of high *E. coli.*

3.5. Random Forest prediction of contamination

A regression RF model for NO_3 contamination was generated for continuous data of NO_3 levels. Overall, the RF model had good model performance with a RMSE of 10.6 and a R^2 fit of 0.87. The plot of predicted vs measured nitrate contamination is shown in the Supplementary Information Fig. 8. Overall, the model underestimated nitrate contamination, particularly in cases where there was very high contamination.

As *E. coli* contamination was predicted as a binary variable (whether contamination was above set thresholds) the *E. coli* contamination RF model was evaluated by confusion matrix model performance metrics (Eqs. 1–4). For predictions of where there was some *E. coli* contamination, the random forest model had an average error rate of 30.0 % (70.0 % accuracy). The model performed better than the multiple linear regression model for all metrics.

For high *E. coli* contamination (≥100 *E. coli*/100 ml) the model had a 19.1 % error rate (81 % accuracy). The model performed better than the multiple linear regression model for accuracy and specificity, as it performed well at identifying areas without high *E. coli* contamination. However, the model failed to identify some of the cases of high contamination and performed worse for precision and sensitivity. Confusion matrices for both *E. coli* models are provided Supplementary Information Tables 7 and 9. The spatial distribution of areas of predicted contamination is summarized in Fig. 5.

The RF model of NO_3 contamination underpredicted some areas with high contamination but had good performance (R^2 0.87). Areas with predicted high levels of nitrate contamination were predominantly surrounding the cities of Blantyre and Mzuzu (Water Resource Areas 1 and 7). For the presence of some *E. coli* contamination, rural areas as well as areas in the north (surrounding Karonga), along the Shire River, and peri-urban areas outside of the major cities were predicted to have high levels of some *E. coli* contamination. The model of whether a water-point had ≥100 *E. coli*/100 ml predicted similar spatial distribution to the presence of any *E. coli* but with regions in the north (surrounding Karonga) as well as areas close to major cities, predicted to have high levels of high *E. coli* contamination. Areas of high NO_3 were typically surrounding population centres with NO_3 levels reducing further away from the population centre. In comparison, *E. coli* contamination was typically more restricted in location with a less clear gradient surrounding population centres and instead regions of high *E. coli* found generally along rounds and the outskirts of major population centres. This is likely due to *E. coli* contamination being highly localised to contamination sources as it cannot survive for extended periods of time in groundwater systems whilst nitrate contamination can travel large distances in groundwater (Canter, 1996).

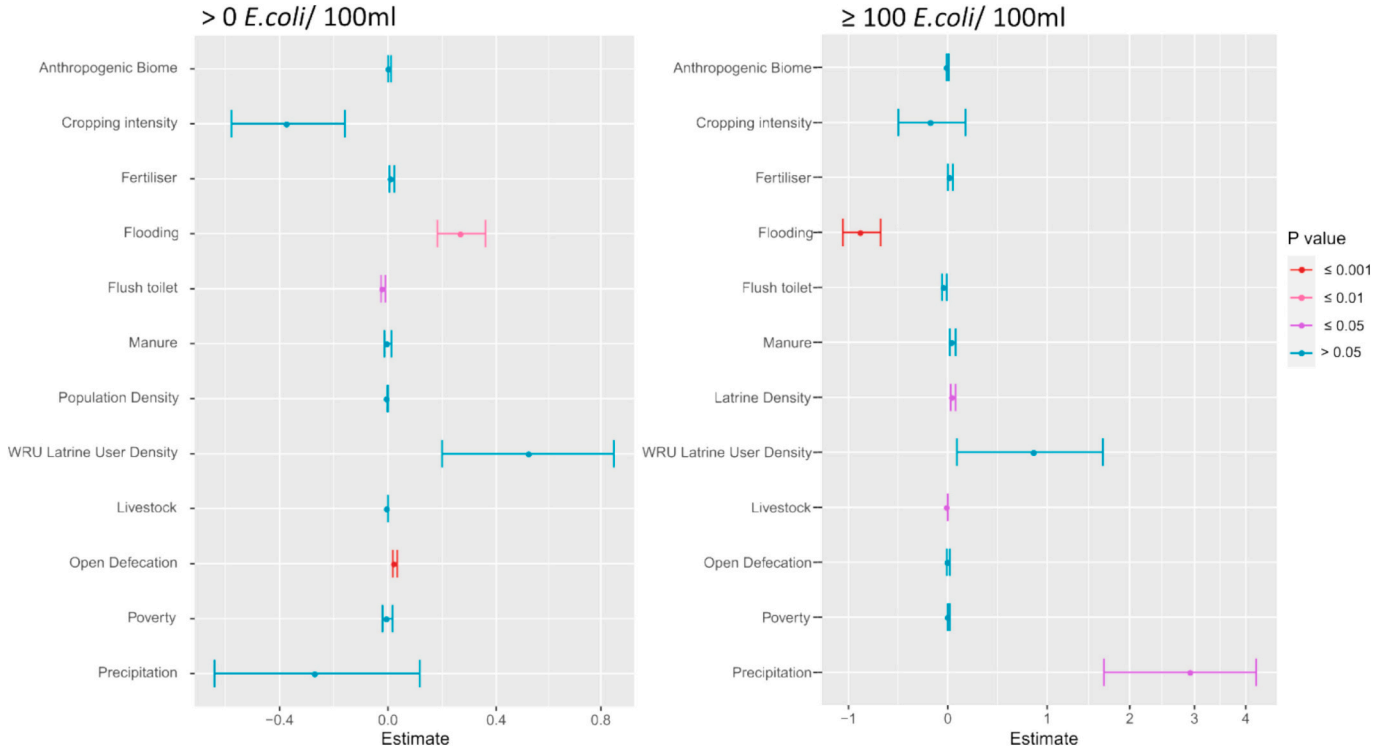

Fig. 4. Fixed effect GLMM models for the presence of any (>0 E coli/100 ml) and high contamination (≥100 *E. coli*/100 ml) *E. coli* of water-points. Coefficient estimate is shown on the x axis. Significant variables are highlighted in red and pink. Non-significant variables are shown in blue.

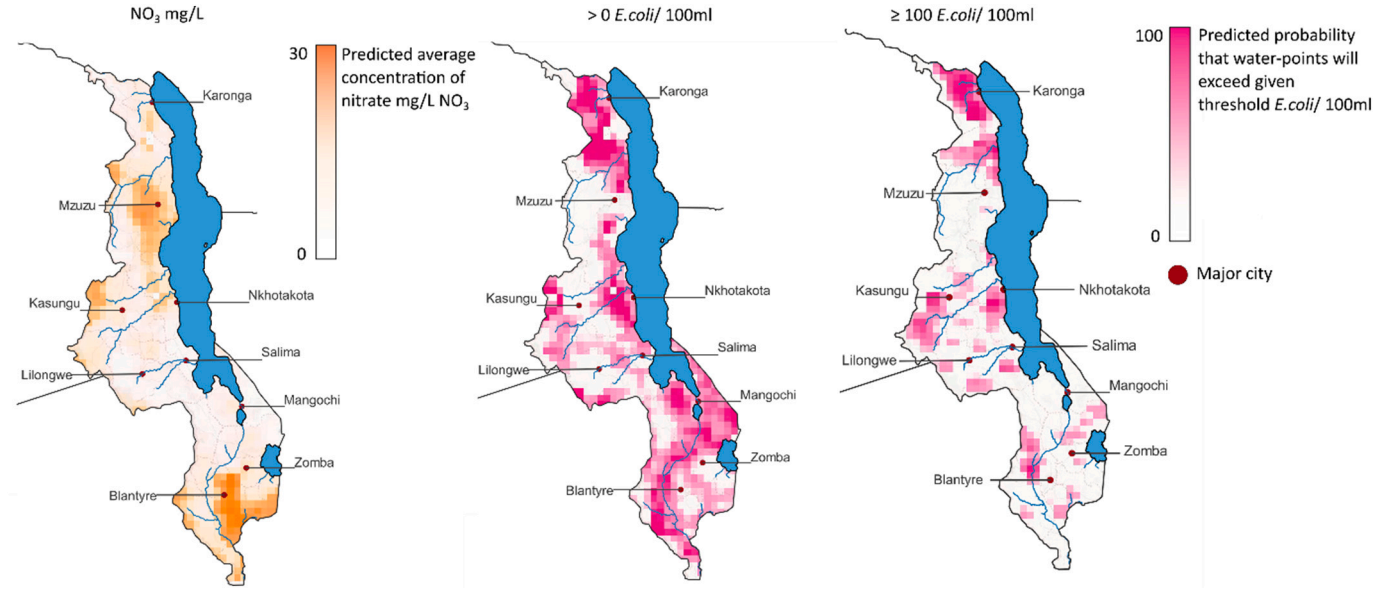

Fig. 5. Predicted contamination from random forest models of NO_3 and *E. coli*. NO_3 contamination was modelled as a continuous response variable with the predicted amount of nitrate contamination given as NO_3 mg/l. The model underpredicted some of the areas with highest contamination but had overall good performance with an R^2 of 0.87. The presence of >0 *E. coli*/100 ml and ≥100 *E. coli*/100 ml were modelled as binary variables with discrete response variables. The model of whether a given water-point had >0 *E. coli*/100 ml had 70 % accuracy. The model of whether a water-point had ≥100 *E. coli*/100 ml had 81 % accuracy. Figure produced in QGIS (QGIS, 2024).

Fig. 6 shows Shapley values, showing the contribution of each feature within the random forest model produced for each contaminant considered. Variables are ordered by their mean feature Shapley value, indicating feature importance. Each point represents the influence of a variable on a given model simulation. For all cases, flooding was the feature with least contribution. For NO_3 and high *E. coli* contamination (≥100 *E. coli*/100 ml), sanitation related variables were the two variables with the highest contributions (WRU latrine user density and latrine density for NO_3 and flush toilet and open defecation for *E. coli*). For *E. coli* presence (>0 *E. coli*/100 ml), cropping and anthropogenic biome had the highest contribution.

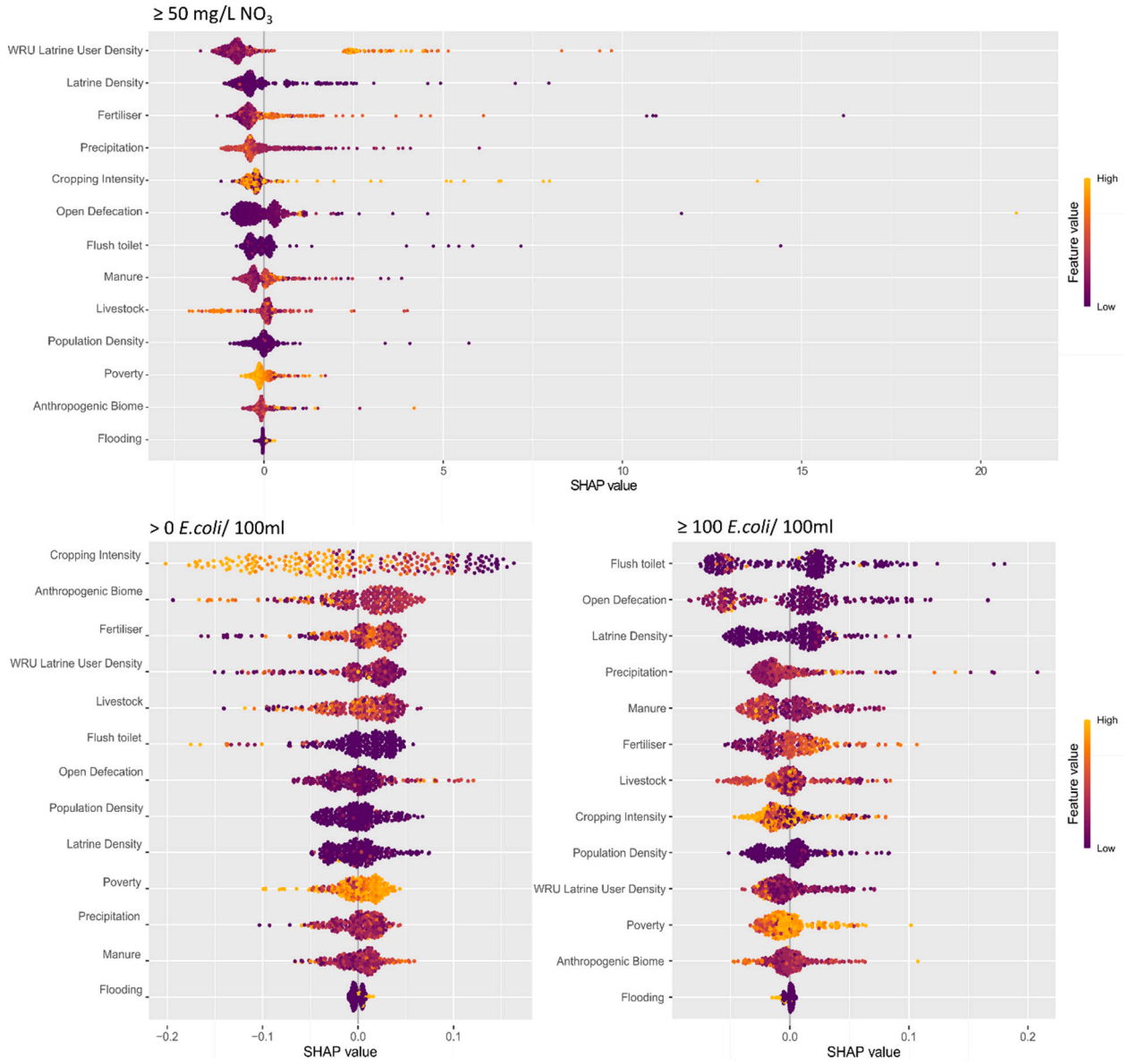

Fig. 6. Shapley values of variables within the Random Forest Regression model. The colour gives feature values with low feature values in blue/purple and high feature values in yellow/orange. SHAP values show the impacts of each feature on the model in each observation run, positive SHAP values indicate that the feature resulted in positive contribution to the chance of contamination whilst negative values respond to a negative contribution of the contamination. Features are ordered by the feature's mean Shapley value (an indicator of feature importance).

3.6. Pilot isotope study

Stable isotope hydrology was introduced in Malawi by the IAEA to enhance monitoring and management of water resources. This pilot study was part of a wider application of stable isotopes across the country (Banda et al., 2019; Banda et al., 2021; Banda et al., 2024). Stable isotopes of nitrate have the potential to validate the sources of nitrogen compounds in the water environment. Of the 15 groundwater and surface water samples collected within the pilot, 40 % (6) had concentrations of NO_3^-N at or above 0.1 mg/l concentration which warrants measurement of δ^{15}N-NO_3^- and δ^{18}O-NO_3^-. Samples were analysed in triplicate, the δ^{15}N-NO_3^- ranged from −1.9 (±1.7) to 27.7 (±1.3)‰ with a mean of 11.4 (±0.6), whilst the δ^{18}O-NO_3^- ranged from 0.0 (±1.0) to 16.3 (±0.3)‰, with a mean of 8.6 (±1), values are shown in Supplementary Information Table 19.

Whilst the dataset is limited, the results hint that the most likely source of nitrate in surface water and groundwater originated as oxidised ammonia (NH_4^+), Fig. 7. The results also suggest that manure or human waste is a likely source of the ammonia (Kendall et al., 2007), Fig. 7. The dataset is not sufficient to track source terms and dynamics (Minet et al., 2017), but it does support the findings of this paper, pointing to pit-latrine derived nitrate in groundwater being a concern, and clearly shows a strong potential for further study to validate the predictions put forward in this paper.

4. Discussion

4.1. Sources of contamination

Nitrate and *E. coli* are two contaminants of concern for Malawi's water provision. Nitrate pollution is a public health concern and has been a growing concern in water quality in Malawi (Chidya et al., 2016; Chimphamba and Phiri, 2014; Nkwanda et al., 2021; Pullanikkatil et al., 2015; von Hellens, 2013.,) with high levels reported in both surface

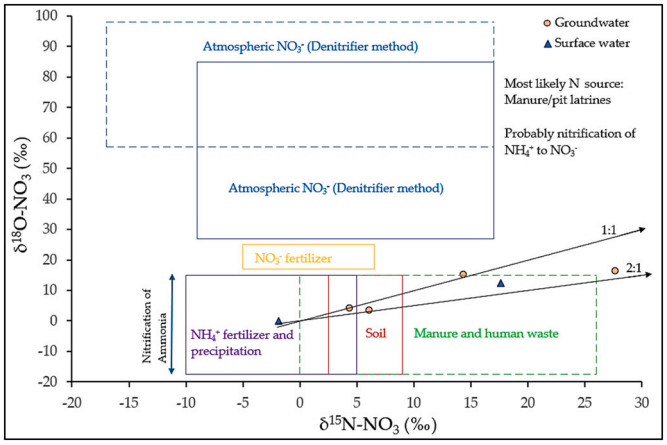

Fig. 7. Results of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ plotted with the likely source of N species and trends added after Kendall et al., 2007.

water (Nkwanda et al., 2021; Pullanikkatil et al., 2015; Sajidu et al., 2007) and groundwater sources (Chidya et al., 2016; Chimphamba and Phiri, 2014; von Hellens, 2013). High groundwater nitrate pollution has been linked to contamination from sanitation sources, both within Malawi (von Hellens, 2013; Back et al., 2018) and beyond (Templeton et al., 2015; Ouedraogo et al., 2019; Rahman et al., 2021). Increasing loading of nitrate to groundwater is a particular concern for safeguarding water quality; nitrate does not undergo reduction in aerobic environments and therefore remains in groundwater for extended periods. When nitrate does not undergo reduction and remains in groundwater it can be transported over large distances, making sources of contamination hard to trace (Canter, 1996).

A GLMM was generated to explore sources of nitrate contamination of over 3000 water sources nationally with 70.9 % accuracy, catchment level density of pit-latrine usage (modelled density of pit-latrine users within WRU) was identified as the only significant positive driver of high nitrate levels. This suggests that there may be a high degree of transport of nitrate from domestic wastewater occurring in groundwater, at catchment levels, in Malawi. Areas with high densities of pit-latrines themselves were significantly less likely to have high levels of nitrate groundwater contamination. High pit-latrine density is mostly found in areas of high population density in which high concentrations of leachate will more likely result in anaerobic conditions in groundwater, enabling denitrification and therefore not resulting in high levels of nitrate. Pit-latrine related variables (WRU pit-latrine user density and pit-latrine density) were also identified as the features with the greatest contributions within the continuous RF model of nitrate contamination (R^2 0.87). As in the case of the GLMM, a high density of pit-latrine users per WRU increased the likelihood of high nitrate in groundwater whilst higher densities of pit-latrines themselves were negatively correlated with nitrate contamination within the model, although care should be taken in interpretation of RF variable importance. The relationship between population density/pit latrines and nitrate in groundwater was validated via the results of the pilot study of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in groundwater and surface water samples that indicates manure and/or pit-latrines present the major source of nitrate contamination.

Collectively considering these results, our findings strongly support previous examinations of nitrate contamination sources which identified sanitation sources as key drivers of nitrate pollution (Chidya et al., 2016; Chimphamba and Phiri, 2014; Ouedraogo et al., 2019; von Hellens, 2013). Ouedraogo et al., 2019, found that population density was a better predictor of pan-African nitrate levels than fertiliser, suggesting that the lack of sanitation in large areas of the African continent may be the reason for population density resulting in greater nitrate contamination (Ouedraogo et al., 2019). We build upon this inference, suggesting that pit-latrines themselves, more specifically pit-latrine density on a catchment/sub-catchment scale, is a major source of groundwater nitrate contamination. A nation-wide study that monitors nitrate and stable isotopes is recommended to monitor the projected growth of pit-latrine usage within Malawi (Hinton et al., 2023) and consequent growing risk of high densities of faecal waste loading (Hinton et al., 2024b).

In addition to anthropogenic factors, nitrate concentration was also significantly influenced by precipitation and flooding events, with lower nitrate concentrations reported in areas with high precipitation and being impacted by flooding, as shown in Fig. 3. This is likely due to high precipitation resulting in dilution of groundwater nitrate, as has been widely recorded (Wick et al., 2012; Nakagawa et al., 2021; Boumans and Fraters, 2010; Mas-Pla and Menció, 2019). Alternative studies have identified instances of high precipitation increasing nitrate concentrations where precipitation events have been suggested to enhance leaching of nitrate from soils (Liu et al., 2024), the absence of an apparent increase in soil nitrate leaching with precipitation perhaps further points to soil nitrate not being a major source of nitrate within this case study.

E. coli contamination is a significant barrier to achieving access to safe drinking water within Malawi (NSO, 2021; Mkandawire, 2008; Dzinjalamala et al., 2024; Mussa and Kamoto, 2023). Nationally, 57.2 % of drinking water sources drawn from groundwater were found to have some presence of *E. coli* and therefore not meet WHO guidelines for safe drinking water. Of particular concern were the 14.9 % of drinking water sources drawn from groundwater that show exceptionally high levels of *E. coli* contamination with 100 or more *E. coli* in a 100 ml sample. To evaluate drivers and provide spatial prediction of *E. coli* contamination in drinking water sources drawn from groundwater, we applied categorical GLMM and RFR models. We considered two cases of *E. coli* contamination, evaluating both the presence of any *E. coli* in drinking water (exceeding WHO guidelines) and another model evaluating very high levels of *E. coli* contamination ($\geq$100 *E. coli*/100 ml). Both cases were modelled as binary variables of the presence/absence of any/very high *E. coli* contamination.

For the presence of both any and high *E. coli* contamination, sanitation related variables were identified as critical drivers. A high density of people practising open defecation was a significant positive indicator of the presence of any *E. coli* contamination whilst flush toilet usage was negatively correlated with the presence of any *E. coli* within the GLMM. In areas where there is a high level of open defecation, environmental contamination because of open defecation may result in contamination of drinking water sources drawn from groundwater. Such environmental contamination by open defecation can result in contamination of groundwater water-points through contaminated surface water and runoff (Rivett et al., 2022). Water-point contamination from contaminated surface runoff alongside an elevated groundwater table promoting increased pit-latrine groundwater contamination has also been reported during flooding (Rivett et al., 2022). The geographic areas most impacted by heavy flooding in 2019 typically in the south of the country near the Shire River (approximately 1 year prior to water quality testing), were more likely to have evidence of *E. coli* contamination. Conversely, areas impacted by 2019 flooding, were significantly less likely to have very high *E. coli* contamination. This may be due to the flooded areas having been impacted by floods a year prior to the water quality tests being conducted and cases of exceptionally high *E. coli* may have undergone intervention over this time.

These findings underline the importance of community wide approaches in ending open defecation to prevent drinking water contamination (Hinton et al., 2024b). Unless safe sanitation for all is provided (as outlined in SDG 6.2), safe drinking water provision may be undermined. Water-points which are damaged or partially functional are more vulnerable to contamination from contaminated surface water (Rivett et al., 2022); a particular concern in Malawi due to limited maintenance and high non-functionality of water-points (Kalin et al., 2019; Kalin et al., 2022a,b). Combating groundwater *E. coli* contamination should

involve not only sustainable progress towards ending open defecation but also ensuring improved borehole maintenance and functionality (Kalin et al., 2019) such as promoting community-led solutions to borehole functionality alongside ending open defecation (Hinton et al., 2021).

4.2. Predicted spatial distribution of contamination

Prediction of the distribution of nitrate and *E. coli* contamination using RFR models enabled greater spatial investigation of areas at high risk of contamination. Spatial prediction of areas susceptible to nitrate contamination identified water-points within water resource areas (WRA) 1 and 7, around the cities of Mzuzu and Blantyre, to be more likely to have high nitrate contamination. These areas have a high density of pit-latrine users within these catchments and also have limited precipitation. Spatial prediction of areas with any *E. coli* contamination (70 % accuracy) predicted that areas with any *E. coli* contamination were more likely to be in rural or peri-urban areas with a high density of people practising open defecation and susceptible to flooding. Spatial prediction of the highest contamination cases, where there were 100 or more *E. coli* per 100 ml, had 81 % accuracy. Cases of high contamination were mostly predicted in densely populated, non-urban areas with high pit-latrine density and high precipitation, typically in peri-urban towns or along roads.

4.3. Study limitations

Samples used for statistical analysis of nitrate contamination were gathered through the Government of Malawi when new boreholes were established. Overall, a national dataset of 3388 boreholes was analysed. To gather such an extensive dataset, samples collected over a 22-year period were analysed, although most samples were collected after 2015. For statistical analyses, spatial rasters of given predictor variables were used, these were typically circa 2020, although ranged from circa 2010. Selecting only samples taken within a smaller time window would have resulted in smaller sample sizes as well as samples that were not nationally representative thereby reducing the statistical power of the analysis. This limitation was deemed appropriate considering that spatial patterns of predictor variables were consistent over time. Future campaigns gathering national, extensive samples of nitrate contamination, as was seen for microbial contamination in the 2019/20 MICs survey, should be prioritised to enable increased analysis.

The level of *E. coli* contamination was provided as a binary variable for samples up to and including 100 *E. coli*/100 ml, however, when contamination was >100 *E. coli*/100 ml, this was marked as a binary measure. As such, for the purposes of this analysis, *E. coli* contamination was considered as a binary (presence of any *E. coli* contamination, and 100 or more *E. coli*/100 ml). This limitation was a result of the sampling method used for which it is hard to count >100 *E. coli* within a sample. This restricted analysis to binary methods or to only considering cases below 100 *E. coli*/100 ml. As this work was particularly interested in high contamination, binary analysis was completed. Further insights could be facilitated, including providing a better prediction of the level of *E. coli* contamination, through analyses with continuous variables. Considering the high number of water-points with exceptionally high *E. coli* contamination, alternative sampling methods enabling high *E. coli* concentrations to be measured, should be explored. The binary discretisation of the presence or absence of *E. coli* may also be a reason for the relatively poor model performance for the presence of any *E. coli* contamination.

Here we present a pilot study of isotopic analysis of nitrate contamination sources of a sample region in the Linthipe river sub-catchment. Whilst the results do indicate nitrate sources from manure and domestic wastewater, only 6 samples underwent isotopic analysis. This limitation was due largely to resources, with the isotopic analysis unable to be conducted in Malawi and having to be conducted at the IAEA in Vienna, Austria. As such, only 15 samples were considered for isotopic analysis. Of those samples, only 6 had nitrate levels with sufficient nitrate to conduct the analysis. To not further restrict the results, 2 of the 6 samples were surface water, this was considered relevant for inclusion due to the high connectivity observed in Malawi between groundwater and surface water (Kelly et al., 2020).

4.4. Policy recommendations and future work

This study supports previous findings within Malawi, and on a continental scale, that sanitation infrastructure is a critical consideration for both nitrate (Templeton et al., 2015; Ouedraogo et al., 2019; Rahman et al., 2021) and microbial (Pritchard et al., 2007, 2008) groundwater contamination. The study emphasises the importance of community wide improvements in sanitation access as open defecation and poor sanitation infrastructure can result in contamination of community-based water resources. This echoes the ethos of programmes such as Community Led Total Sanitation (CLTS) which emphasise the environmental health component of enhanced sanitation provision (Chambers and Kar, 2008; Hinton et al., 2024a). However, whilst these initiatives push to end open defecation at the community level this work highlights the importance of community wide changes in sanitation not only focusing on eliminating open defecation but also on evaluating appropriate pit-latrine usage and management (Hinton et al., 2024a). *Ending open defecation on a community level is important but environmental health perspectives of inappropriate sanitation should also be emphasised.*

This work highlights a paradox in Malawi's progress in sanitation and water; open defecation must be eliminated to improve sanitation and water access but pit-latrines, which often form 'starter sanitation' (UNICEF, 2018) may cause contamination themselves unless appropriately managed. *Appropriate pit-latrine use will be important in ensuring an end to open defecation without resulting in widespread water contamination.* To ensure progress in both spheres of water and sanitation, enhanced policy frameworks to foster cooperation between stakeholders should be promoted. Sanitation infrastructure development must consider groundwater contamination consequences. Critically, this involves guiding long-term investment into higher quality waste management that minimizes contamination considering future projections of high population growth and increasing pit-latrine usage (Hinton et al., 2024b).

Our findings support initiatives to target water quality monitoring in areas of concern. Further expansion of isotope analysis may facilitate tracing of groundwater contaminant sources and develop evidence for source contamination management. Further understanding of contamination, both nitrate and microbial contamination, is needed to guide intervention. Understanding sanitation use will be critical (pit-latrine density was a better predictor of contamination of nitrate and high *E. coli* contamination than population density). Future work and modelling efforts should account for additional factors such as soil type (He et al., 2022) and permeability, as well as localised groundwater dynamics to enhance understanding of areas at high risk of contamination.

5. Conclusion

We apply a mixed method approach to identify drivers of microbial and nitrate contamination of groundwater drinking sources in Malawi. A pilot application of isotope hydrology was used to validate likely sources of nitrate contamination of groundwater. Statistical analysis was used to further enhance understanding of sources of nitrate contamination with catchment level pit-latrine usage identified as a significant driver of areas with high nitrate groundwater contamination. These findings support previous analyses of groundwater in Malawi and across Africa of sanitation sources being a major driver of groundwater nitrate contamination (Templeton et al., 2015; Ouedraogo et al., 2019; Rahman et al., 2021). Pit latrines were noted as a specific concern, highlighting the need for understanding of how sanitation derived contamination

occurs. The results raise concerns for future groundwater contamination with projected increases of pit-latrine usage in Malawi driven by a move to end open defecation alongside high population growth (Hinton et al., 2021).

Sanitation related factors were significant considerations for microbial groundwater contamination. The density of open defecation was found to be a significant driver in cases of any *E. coli* contamination whilst in areas with very high *E. coli* contamination, pit-latrines are most likely the source of contamination. Policy and research efforts need to navigate how appropriate sanitation can be provided to ensure an end to open defecation without coming at the cost of groundwater quality. We also found that flooding risk is an important predictor of microbial borehole contamination, however, more research with higher quality flood risk predictive data would enhance understanding of the future risks of water-point contamination due to climate-change enhanced flooding.

CRediT authorship contribution statement

Rebekah G.K. Hinton: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Robert M. Kalin:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Formal analysis, Conceptualization. **Limbikani C. Banda:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Formal analysis, Data curation, Conceptualization. **Modesta B. Kanjaye:** Writing – review & editing, Conceptualization. **Christopher J.A. Macleod:** Writing – review & editing, Conceptualization. **Mads Troldborg:** Writing – review & editing, Conceptualization. **Peaches Phiri:** Writing – review & editing, Conceptualization. **Sydney Kamtukule:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Robert Kalin reports financial support was provided by Scottish Government. Robert Kalin reports financial support was provided by International Atomic Energy Agency. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Georeferenced *E. coli* data was provided from the Malawi 2019/20 MICs Survey was provided by the UNICEF Malawi and the Global MICs team on behalf of Malawi National Statistical Office (MNSO). Nitrate borehole water quality samples were provided by the Government of Malawi, Ministry of Water and Sanitation. The pilot nitrate isotope tracing work was conducted as part of an International Atomic Energy Agency (IAEA) national project (MWL-7002 TC project).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.177418.

Data availability

Data will be made available on request.

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Hydrogeochemistry and Water Quality Index for Groundwater Sustainability in the Komadugu-Yobe Basin, Sahel Region

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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 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^{2+}, Mg^{2+}, 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 the groundwater chemistry. Groundwater is predominantly Ca^{2+}-Mg^{2+}-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)

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1. 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, live stock farming, and recreation [1–4]. The main source water supply in most developing economies is groundwater from shallow wells [1,2,5–10]. The semi-arid to arid North-East region of Nigeria relies heavily on groundwater for various uses [11–14]. 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 [15–17]. 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 [18]. Thus, the quality of the groundwater determines its usability [19,20].

Groundwater hydrogeochemical analysis provides an in-depth understanding of hydrochemical characteristics and the overall quality of groundwater [20–24]. 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 [5,25–28]. Water quality is assessed and monitored using hydrogeochemical and statistical analysis, as well as the estimation of water quality indices [28,29]. 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 [4,23,29–33]. Many researchers employed the WQI in water quality studies because of its flexibility, adaptability, and simplicity in groundwater quality assessment and monitoring [2,22,24,34–37]. 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 [36–38].

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 [8,30,39]. GISs are widely used for developing groundwater quality maps, which are essential for managing groundwater for various uses [2,4,33]. They are cost-efficient and transform large hydrochemical datasets into spatial information [8,39]. 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 [4,33,34,38,39]. The IDW method is commonly employed as it uses a deterministic model approach [2,8,23,25,33,34,39,40].

Management of the water quality is needed for ecosystem health [7,22] and is critical for environmental quality management [35]. 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 [22,41]. 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 [19,34,42]. Moreover, municipal solid waste, industrial wastewater, and domestic wastewater impact groundwater quality [13,43]. Ganiyu et al. [7] 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 [13,44–48]. 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.

2. Materials and Methods

2.1. 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 1). The basin covers an approximate area of about 150,000 km^2, with an elevation of 294 m 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 [49–51].

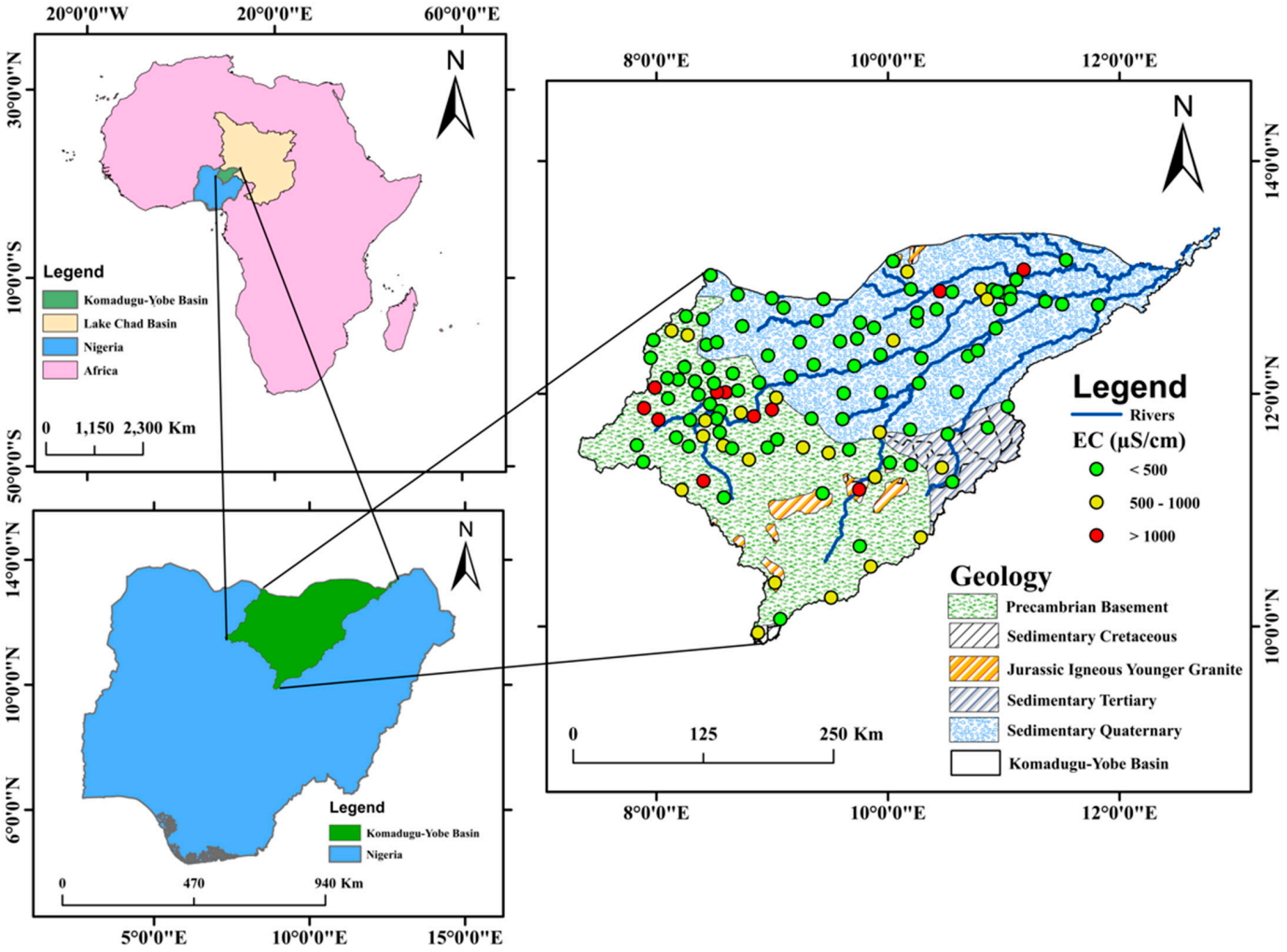

Figure 1. Groundwater sampling location, geology type, and electrical conductivity (EC) concentration in Komadugu-Yobe basin.

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 [52]. 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 [49,52]. 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 [50]. The basin is dominated by dense grasslands, shrubs, and scattered tree-type vegetation [53].

2.2. 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 [54]. Several factors influence the occurrence of faults including the presence of pre-existing lines of weakness formed during the Pan-African orogenic event [55]. The basin is underlain

by basement-complex rocks and sedimentary quaternary formations (Figure 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 [54]. 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. [54], Obaje et al. [56], Obaje [57], Lopez et al. [58], and Bura et al. [59].

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 [18,55,59]. 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 [59–61]. 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 [59,62]. The Gongila formation is characterized by the presence of substantial layers of calcareous gray to dark shales and silty sandstone, which were deposited in a marine setting. Furthermore, the Fika formation consists of dark-gray to blue-black shale. It has been dated as Turonian-Maastrichtian in age by Obaje [57]. The upper part of the formation infrequently has glauconite, gypsum, and fine-grained sandstone [59].

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 [58,59,63–65]. According to Akujieze et al. [66], 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 [65,66]. 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 [67,68]. 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 [11,68]. Carter and Alkali [69] 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. [64] in the Komadugu-Yobe basin.

2.3. 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 [70]. 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).

2.4. Laboratory Analysis

Groundwater samples were analyzed following the standard procedure given by the American Public Health Association [70]. 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).

2.5. Accuracy of Chemical Analysis

The ionic balance error (*IBE*) shown in Equation (1) was employed to check the accuracy of the chemical analysis:

$$IBE\% = \frac{\sum c - \sum a}{\sum c + \sum a} \times 100 \quad (1)$$

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%.

2.6. 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 [2,33,71].

2.7. 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 [2,25,35]. 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 [2,25,34,35].

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 [34]. 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 [33,35]. Sodium and potassium were given the least weight because they are less significant in groundwater quality assessment. Table 1 shows the weights assigned to each groundwater quality parameter.

- Computation of relative weight: Equation (2) below was used to calculate the relative weight (*Wi*):

$$Wi = \frac{wi}{\sum_{i}^{n} wi} \quad (2)$$

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 *i*th 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 [72], all multiplied by 100. The *qi* for all the parameters was computed using Equation (3) below:

$$qi = \frac{ci}{Si} \times 100 \quad (3)$$

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 (4) and (5):

$$SIi = Wi \times qi \quad (4)$$

$$GWQI = \sum_{i=0}^{n} SIi \quad (5)$$

where *SIi* denotes the sub-index of the *i*th water quality parameter; *qi* denotes the quality rating of the *i*th 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 2.

Table 1. Groundwater quality parameters weighing for groundwater quality index computation.

Parameters	Units	WHO [72]	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 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

2.8. 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 [33,34] to understand the various principal mechanisms controlling groundwater chemistry. The Gibbs diagrams are based on two ratios and are calculated using Equations (6) and (7):

$$\text{Gibbs ratio}^{-}\text{I} = \frac{Cl^-}{\left(Cl^- + HCO_3^-\right)} \quad (6)$$

$$\text{Gibbs}^{-}\text{II} = \frac{Na^+ + K^+}{\left(Na^+ + K^+ + Ca^{2+}\right)} \quad (7)$$

Ionic concentrations in meq/L.

3. Results and Discussion

Groundwater quality determines its usability. Various groundwater quality parameters analyzed with their descriptive statistics are presented in Table 3. The results of the analyzed groundwater quality parameters were compared with the WHO [72] guidelines (Tables 1 and 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 2–4).

Table 3. Statistical summary of the physicochemical parameters of groundwater samples of KYB compared with WHO [72] guidelines.

Parameters	Units	Maximum	Minimum	Mean	WHO [72]		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^{2+}	mg/L	220	0.2	39	75	200	2
Mg^{2+}	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
$SO_4{}^{2-}$	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.

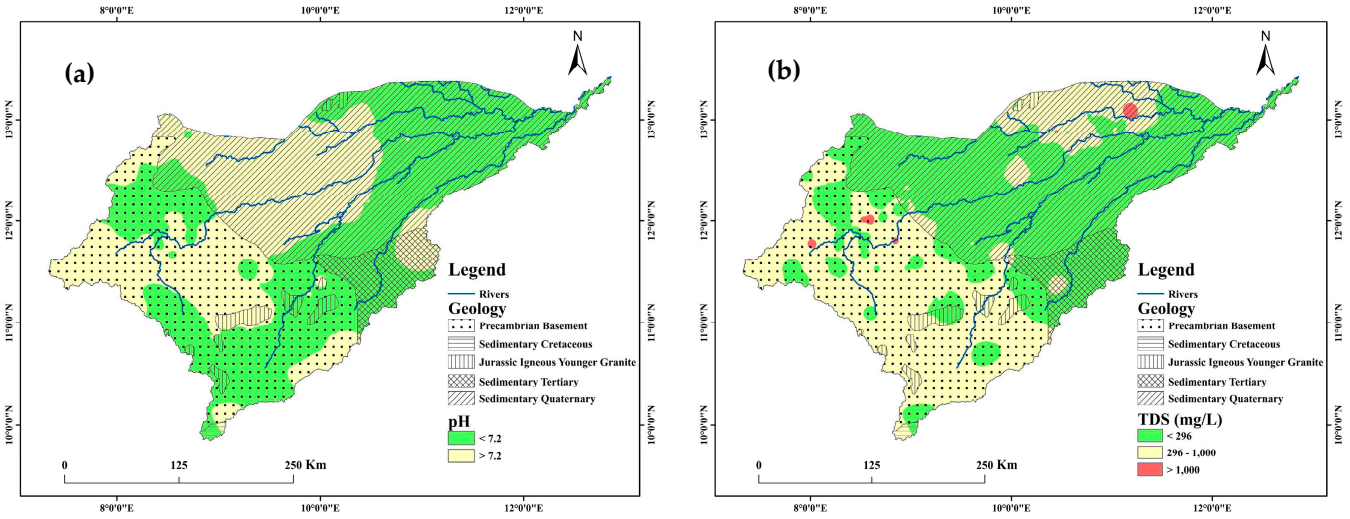

Figure 2. Spatial distribution of groundwater quality parameter in Komadugu-Yobe basin. (**a**) pH; (**b**) TDS.

3.1. Hydrogen Ion Concentration (pH)

pH is an important groundwater quality parameter [34,73]. The pH of the groundwater ranged from 5.52 to 8.24 (Figure 3a), 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 [72]. 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 [71]. Figure 2a shows the eastern part of the basin that is dominated by a 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 [74]. 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.

3.2. Total Dissolved Solids (TDS)

The groundwater in the Komadugu-Yobe basin show variation in concentrations of total dissolved solids (TDSs) (Figure 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 [34]. The method prescribed by Davis and DeWiest [75] was used to classify the groundwater of the study area based on TDS values (Table 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 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.

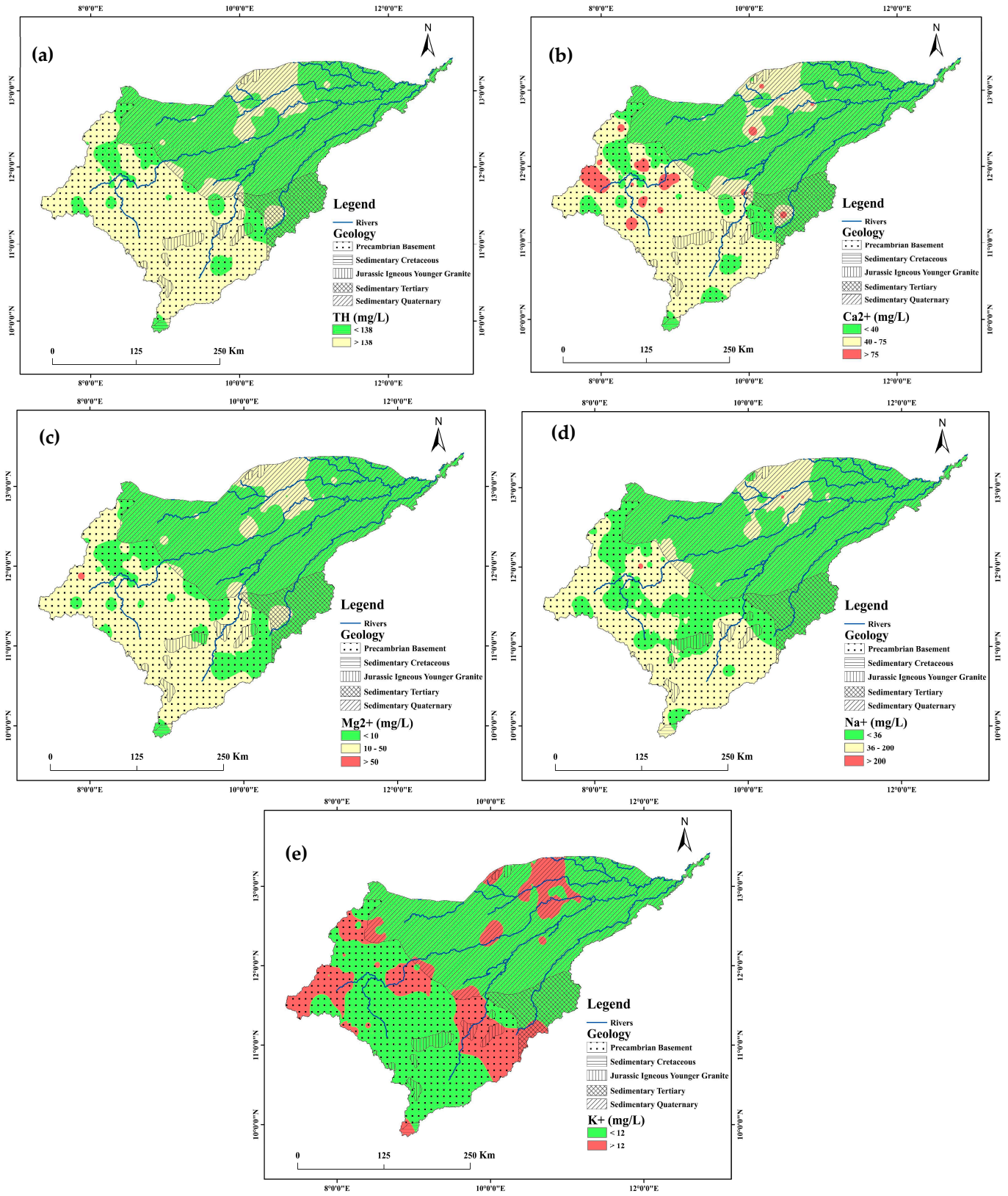

Figure 3. Spatial distribution of groundwater quality parameter in Komadugu−Yobe basin. (**a**) TH; (**b**) Ca^{2+}; (**c**) Mg^{2+}; (**d**) Na^{+}; (**e**) K^{+}.

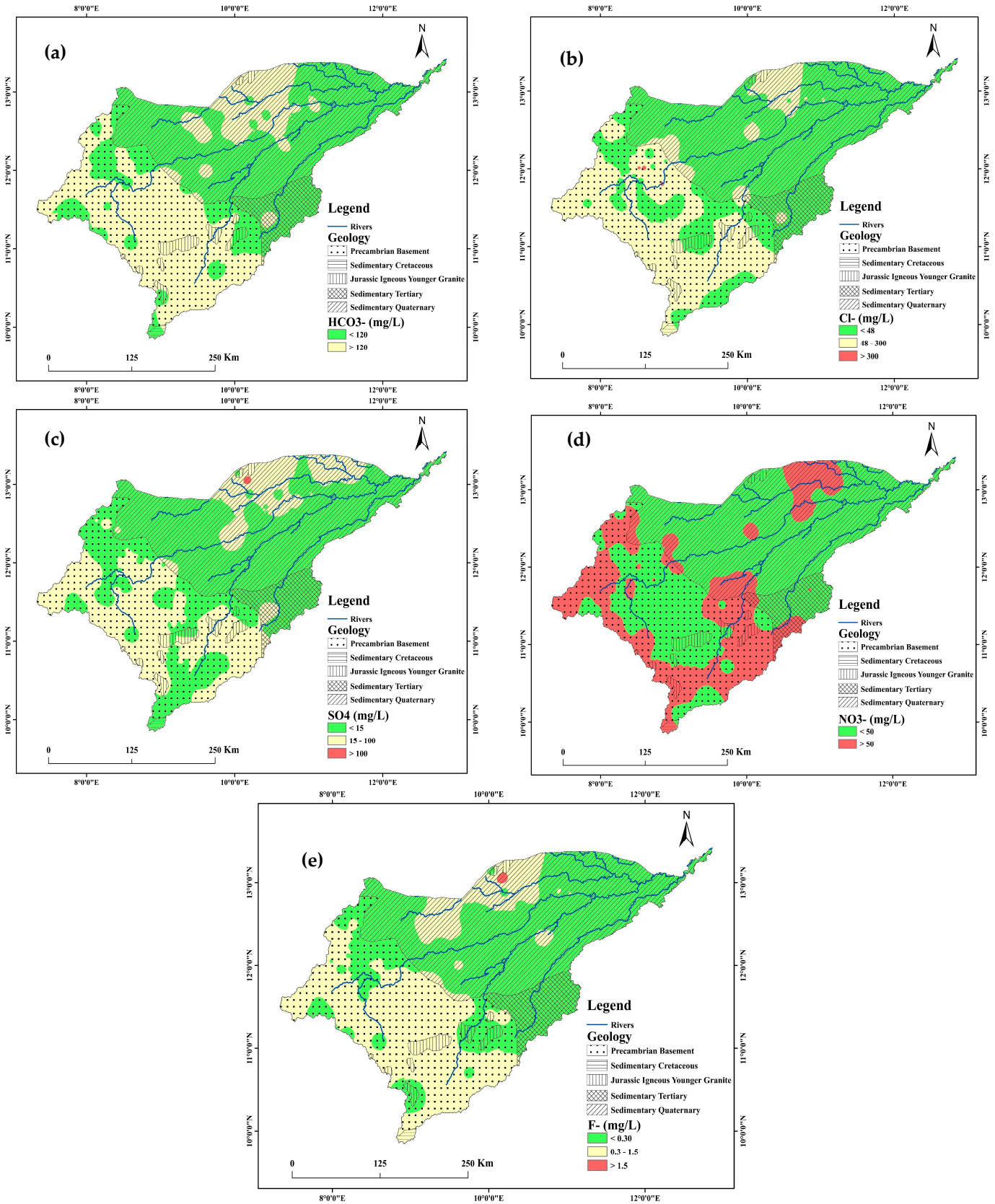

Figure 4. Spatial distribution of groundwater quality parameters in Komadugu−Yobe basin. (**a**) HCO_3^-; (**b**) Cl^-; (**c**) SO_4^{2-}; (**d**) NO_3^-; (**e**) F^-.

Table 4. Groundwater classification based on TDSs [75].

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	/

3.3. 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 [34,51]. 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 2). About 98% of the groundwater samples in the study area were below the maximum permissible limit of 500 mg/L (Table 2). Sawyer and Sawyer & McCarthy [76] classified groundwater based on the concentration of total hardness TH as mg/L of $CaCO_3$ (Table 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 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.

Table 5. Total hardness classification based on Sawyer and McCarthy [76].

Water Class	TH as $CaCO_3$ (mg/L)	% of Samples
Soft water	<75	43
Moderately hard water	75–150	18
Hard water	150–300	26
Very hard water	> 300	13

3.4. Calcium (Ca^{2+}) and Magnesium (Mg^{2+})

Calcium (Ca^{2+}) and magnesium (Mg^{2+}) 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 2). About 2.5% of the groundwater samples were above the World Health Organization [72] maximum permissible limit of Mg^{2+} of 150 mg/L (Table 2). Calcium is derived from cation exchange processes and carbonate dissolution [34]. Therefore, Ca^{2+} variations in groundwater samples could be due to carbonate rock dissolution and ion exchange processes in the Precambrian basement parts of the basin (Figure 3b). Figure 3c depicts the spatial variation in Mg^{2+} in the study area. Furthermore, the lower value of Mg^{2+} 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^{2+} than Mg^{2+}, which could be due to the influence of ion exchange mechanisms and dissolution of mafic minerals in the groundwater system [77]. This is evident in the Precambrian basement parts of the study area.

3.5. 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 2). About 2.5% of the groundwater samples are above the maximum permissible limit, while 74% of the groundwater samples have concentrations below the mean concentration (Table 2). A high Na^+ concentration above 200 mg/L

give an unacceptable taste and make water unsuitable for domestic purposes [2,33,70]. 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 2). Approximately 6% of groundwater samples have K^+ concentrations above the WHO [72] maximum permissible limit (Table 2). Potassium is the most important element for human nutrition, with 10 mg/L in natural water [34,70]. Figure 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 3d), and low Ca^{2+} (Figure 3b). The cation exchange process of Na^+ with cations on the surface of minerals that replaces Ca^{2+} 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.

3.6. 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 2). Bicarbonate in groundwater is known to have no adverse health effects [33,34]. The WHO [72] 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 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 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 [78].

3.7. Chloride (Cl^-) and sulfate ($SO_4{}^{2-}$)

The concentration of chloride (Cl^-) and sulfate ($SO_4{}^{2-}$) 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 2). Excessive chlorine in drinking water imparts a salty taste and signifies contamination from various natural and anthropogenic sources [34]. Chloride concentrations in about 2.5% of the groundwater samples exceeded the WHO guidelines for drinking water (Table 2). However, most of the groundwater samples have a 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 [33,70]. The spatial distribution of chloride concentration in the groundwater of the study area is presented in Figure 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 4c. The WHO [72] guideline value for sulfate $SO_4{}^{2-}$ in drinking water is 250 mg/L. All the groundwater samples are below the maximum permissible limit (Table 2, WHO, [72]). 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 [79].

3.8. Nitrate (NO_3^-) and Fluoride (F^-)

Groundwater NO_3^- contamination is an important water quality issue globally [33–35,72]. Nitrate in the groundwater arises from synthetic fertilizers and organic manures, leachate from dumpsites, septic tanks, landfills, and industrial and municipal waste [73]. The nitrate concentration in Komadugu-Yobe basin varies from ND to 314 mg/L, with a mean value of 42 mg/L (Table 2). The maximum permissible limit of NO_3^- concentration in drinking water is 50 mg/L [72]. Groundwater with nitrate concentrations higher than the maximum permissible limits have been linked to an increased risk of methemoglobinemia [34,72]. 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 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 2). About 2% of the groundwater samples have a F^- concentration exceeding the maximum permissible limit (Table 2, WHO, [72]), which renders them unsuitable for drinking purposes. Figure 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. [80], Giwa et al. [81], Malago et al. [82], and Waziri et al. [83] 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 [84,85]. Therefore, there is a need for further study of the risks associated with groundwater fluoride in the study area.

3.9. Geochemical Mechanism of Groundwater

Gibbs [86] showed that groundwater chemistry is controlled by three main natural processes: rock weathering/rock–water interaction, evaporation, and atmospheric precipitation. A Gibbs plot [86] reveals the interaction between groundwater, soil, and host rock [25,73,87]. Figure 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 [33,82]. 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.

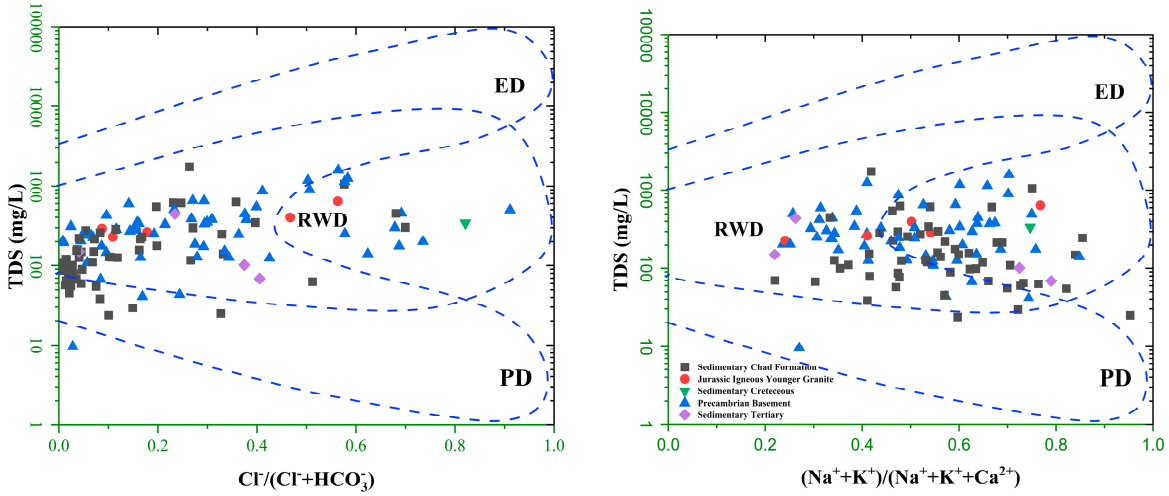

Figure 5. Gibbs plots showing the dominant geochemical mechanisms in KYB, (**left**): anions ratio and (**right**): cations ratio vs. TDS (mg/L). ED: evaporation dominance. RWD: rock weathering dominance. PD: precipitation dominance.

3.10. Groundwater Types and Hydrogeochemical Evolution

3.10.1. Piper Plot

The Piper trilinear diagram (Figure 6) for the Komadugu−Yobe basin uses major ions to classify groundwater into various hydrochemical types and identify influential factors involved in groundwater chemistry [23,24,88]. Figure 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^{2+}-Mg^{2+}-HCO^{-}_{3} water type. The order of dominance of the groundwater type in the basin is Ca^{2+}-Mg^{2+}-HCO^{-}_{3} > Na^{+}-Cl^{-} > Na^{+}-HCO^{-}_{3} > Ca^{2+}-Mg^{2+}-$SO_4{}^{2-}$-Cl^{-}. These show 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 [23,33,70].

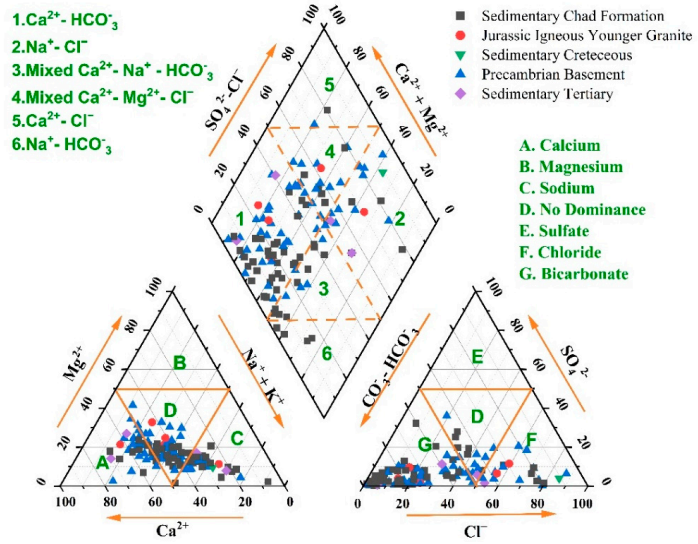

Figure 6. Piper diagram showing various water types in Komadugu−Yobe basin.

3.10.2. Chadha Diagram

The Chadha diagram was employed to assessed the geochemistry of groundwater and various groundwater types in the Komadugu-Yobe basin. The Chadha plot shows the presence of Ca^{2+}-Mg^{2+}-HCO^{-}_3, Ca^{2+}-Mg^{2+}-$SO_4{}^{2-}$-Cl^{-}, Na^{+}-Cl^{-}, and Na^{+}-HCO^{-}_3 water types in the study area (Figure 7). The Chadha diagram is a composite representation that integrates the Piper plot and the extended Durov diagram [23]. The Chaha plot best describes the permanent and temporary hardness domains of water [73]. Figure 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^{2+}–Mg^{2+}– 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^{2+}– Mg^{2+}– 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 6).

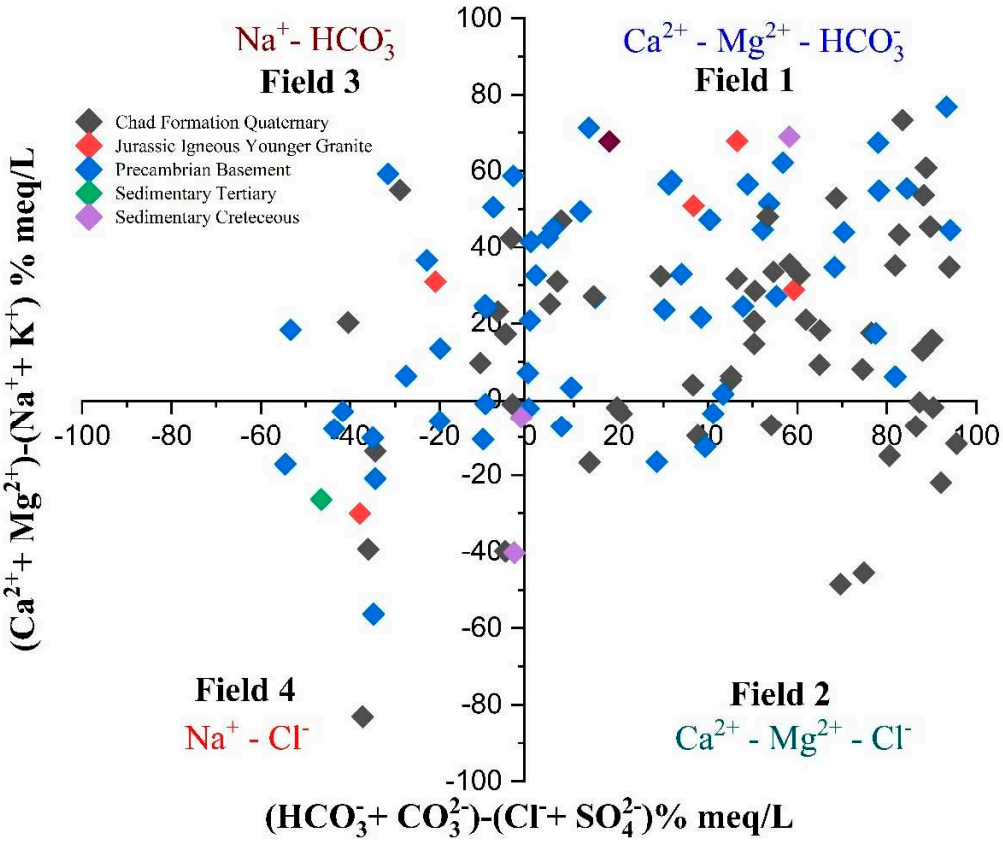

Figure 7. Chada plot showing groundwater evolution in Komadugu−Yobe basin.

3.11. Groundwater Quality Index

The spatial distribution of the groundwater quality index in the Komadugu−Yobe basin is presented in Figure 8 and varies from 9 to 170, with an average value of 48 (Table 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) [33,34]. The majority of the groundwater in KYB is excellent, constituting about 63%, with good and poor water classes constituting 27% and 10% respectively (Table 2, Figure 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.

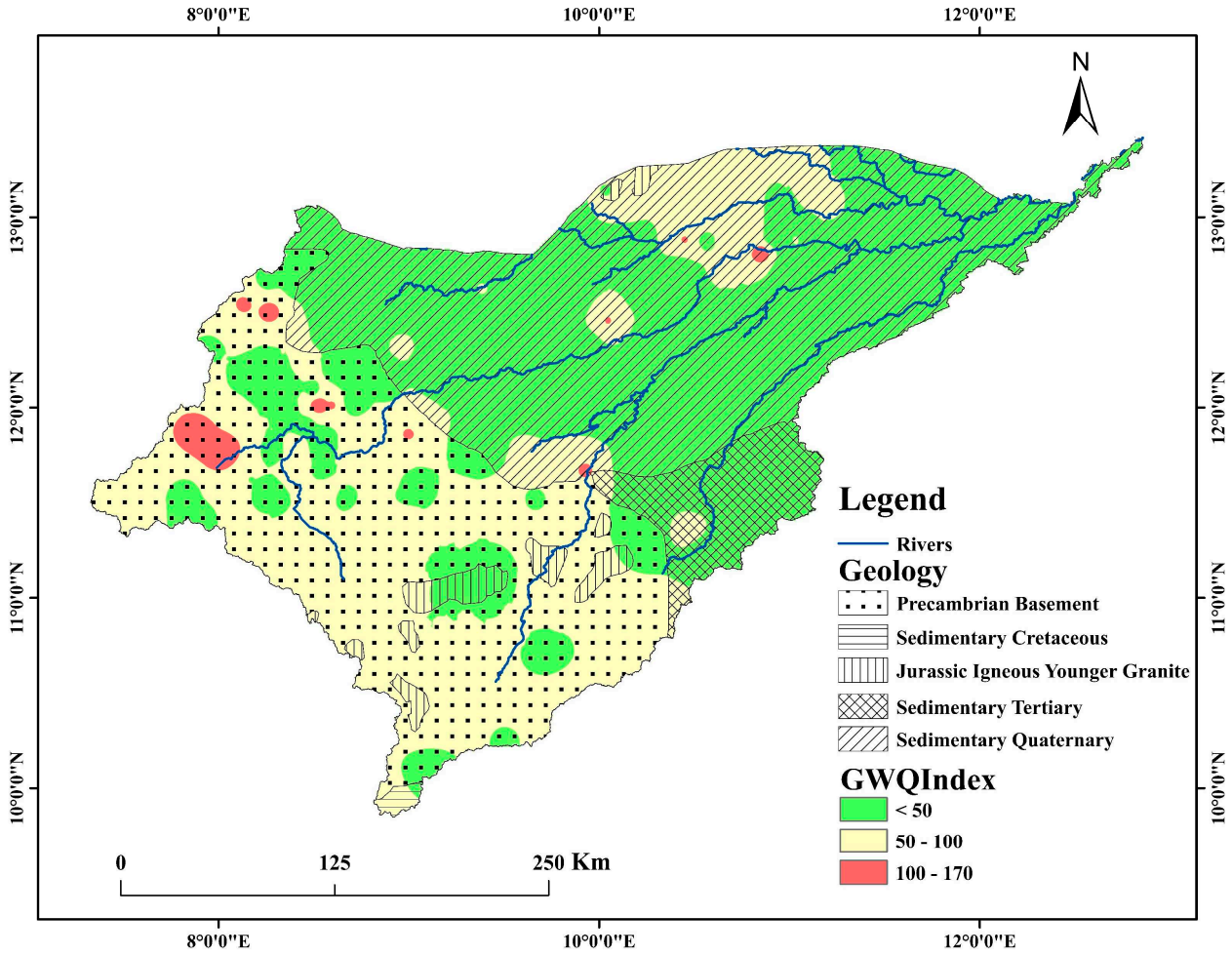

Figure 8. Spatial distribution of groundwater quality index in Komadugu−Yobe basin.

Table 6. Groundwater quality index (GWQI) in Komadugu−Yobe basin.

Sample Numbers	GWQI	Water Type	Sample Numbers	GWQI	Water Type
L1	79	Good Water	L63	74	Good Water
L2	49	Excellent Water	L64	51	Good Water
L3	74	Good Water	L65	125	Poor Water
L4	104	Poor Water	L66	76	Good Water
L5	41	Excellent Water	L67	9	Excellent Water
L6	82	Good Water	L68	62	Good Water
L7	20	Excellent Water	L69	15	Excellent Water
L8	18	Excellent Water	L70	20	Excellent Water
L9	24	Excellent Water	L71	62	Good Water
L10	82	Good Water	L72	46	Excellent Water
L11	39	Excellent Water	L73	38	Excellent Water
L12	29	Excellent Water	L74	61	Good Water
L13	18	Excellent Water	L75	41	Excellent Water
L14	17	Excellent Water	L76	49	Excellent Water

Table 6. *Cont.*

Sample Numbers	GWQI	Water Type	Sample Numbers	GWQI	Water Type
L15	19	Excellent Water	L77	61	Good Water
L16	14	Excellent Water	L78	73	Good Water
L17	156	Poor Water	L79	37	Excellent Water
L18	20	Excellent Water	L80	67	Good Water
L19	31	Excellent Water	L81	91	Good Water
L20	25	Excellent Water	L82	38	Excellent Water
L21	19	Excellent Water	L83	14	Excellent Water
L22	15	Excellent Water	L84	79	Good Water
L23	31	Excellent Water	L85	52	Good Water
L24	59	Good Water	L86	64	Good Water
L25	91	Good Water	L87	38	Excellent Water
L26	134	Poor Water	L88	15	Excellent Water
L27	170	Poor Water	L89	18	Excellent Water
L28	49	Excellent Water	L90	15	Excellent Water
L29	36	Excellent Water	L91	16	Excellent Water
L30	28	Excellent Water	L92	13	Excellent Water
L31	107	Poor Water	L93	17	Excellent Water
L32	150	Poor Water	L94	107	Poor Water
L33	14	Excellent Water	L95	58	Good Water
L34	37	Excellent Water	L96	30	Excellent Water
L35	27	Excellent Water	L97	14	Excellent Water
L36	65	Good Water	L98	14	Excellent Water
L37	107	Poor Water	L99	32	Excellent Water
L38	101	Poor Water	L100	26	Excellent Water
L39	23	Excellent Water	L101	103	Poor Water
L40	22	Excellent Water	L102	24	Excellent Water
L41	38	Excellent Water	L103	23	Excellent Water
TL42	83	Good Water	L104	50	Good Water
L43	34	Excellent Water	L105	18	Excellent Water
L44	64	Good Water	L106	40	Excellent Water
L45	49	Excellent Water	L107	30	Excellent Water
L46	32	Excellent Water	L108	33	Excellent Water
L47	58	Good Water	L109	28	Excellent Water
L48	71	Good Water	L110	52	Good Water
L49	23	Excellent Water	L111	25	Excellent Water
L50	32	Excellent Water	L112	19	Excellent Water
L51	39	Excellent Water	L113	18	Excellent Water
L52	27	Excellent Water	L114	24	Excellent Water
L53	40	Excellent Water	L115	58	Good Water
L54	54	Good Water	L116	16	Excellent Water
L55	110	Poor Water	L117	12	Excellent Water
L56	35	Excellent Water	L118	11	Excellent Water
L57	33	Excellent Water	L119	35	Excellent Water
L58	72	Good Water	L120	94	Good Water
L59	24	Excellent Water	Maximum	170	/
L60	36	Excellent Water	Minimum	9	/
L61	33	Excellent Water	Mean	48	/
L62	84	Good Water			

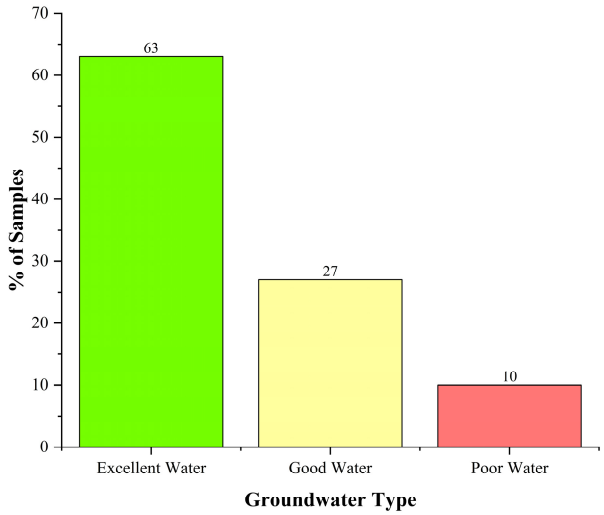

Figure 9. Groundwater quality index (GWQI) classification in Komadugu−Yobe basin.

4. Conclusions

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 a Gibbs plot, 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: $Ca^{2+} > Na^{+} > K^{+} > Mg^{2+}$ and $HCO^{-}{}_{3} > Cl^{-} > NO_{3}{}^{-} > SO_{4}{}^{2-} > F^{-}$, respectively. More than 90% of groundwater samples have Na^{+}, Ca^{2+}, Mg^{2+}, K^{+}, Cl^{-}, and $SO_{4}{}^{2-}$ and total hardness within the WHO [72] 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^{2+}-Mg^{2+}-$HCO^{-}{}_{3}$ 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^{2+}-Mg^{2+}-$HCO^{-}{}_{3}$ > Na^{+}-Cl^{-} > Na^{+}-$HCO^{-}{}_{3}$ > Ca^{2+}-Mg^{2+}-$SO_{4}{}^{2-}$-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.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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Conflicts of Interest: The authors declare no conflicts of interest.

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10.2 Peer-Review Comments and Remarks

Research Article 1

water-1272967

AUTHOR RESPONSE TO REVIEW COMMENTS
(incl. Cover Letter)

F.A.O. Dragana Markovic, Assistant Editor, WATER

Dear Dragana,

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

We note that the Review Comments were comprehensive and generally supportive of our work and its publication. This is especially true for almost all the reviewers who provides the more in-depth technical review, and comments:

We have produced a positive response, with only minor exception, to the perceptive comments that have allowed manuscript enhancement. The scientific comments have been addressed by providing clarity and additional presentation and interpretation of the results. This is especially true for data analysis focusing on the dual wet season of Malawi in response to the Reviewer 1 Scientific Question and additional Comments 17 and 19 on the specifics. We have further highlighted the novelty of the data and potential impact of the research in response to the Reviewer 1's main scientific comment 2. Above all, we have managed to respond to all the comments raised by the four reviewers and adopted recommended text edits as well as structural revision where we deemed applicable.

We trust that you may find this revised manuscript suitable for publication. Please do contact myself if any aspects require further clarification etc.

Our detailed review response follows below or is attached.

Kind regards,

Limbikani Chitsundi Banda

1. Response to Reviewer 1

Comments and Suggestions for Authors

In this paper Banda and colleagues present the third paper in a series introducing and establishing the National Stable Isotope Baseline in Malawi. The first two other papers focused on groundwater and also appeared in Water in 2019 and 2020. This is a very important and worthwhile project and I wish it every success.

A quick disclaimer on my person expertise. I am a climate scientist working in southern Africa with extensive experience in stable isotopes, but less so in isotopes of precipitation. My review therefore comes from that viewpoint. A thorough review of the stable isotopes in precipitation should be provided by another reviewer.

Overall, I think this is a very nice introductory paper describing new and important results. There is very little that I am concerned about, and the majority of my comments are about making the paper clearer to the reader, or other minor corrections. For example: In a few places in the manuscript is vague about tangential issues. These either need to be explained more clearly and precisely or be removed to keep the manuscript focused. I also think some of the supplementary material could be brought into the manuscript.

- Thank you for the positive sentiments and supportive comments on our work and its publication
- Some sentences have been re-written and/or re-phrased and removed for explanatory clarity and precision as recommended.

Main Scientific Comments

1) My main scientific query relates to whether there is an isotopic signal between the early and late wet season rainfall. As Malawi appears to have a dual wet season with contrasting atmospheric circulation regimes between Dec/Jan rainfall and Feb/Mar rainfall (Nicholson et al., 2014) this feels like a missing piece of data analysis. Whether such a relationship exists (or not) would be an interesting and important result for both modern and paleoclimate communities, and greatly enhance the citations of this paper.
- We have addressed this comment. However, we note that in Nicholson *et al*., 2014, the early rainy season is from December – February and late rainy season is from March – April. Therefore, our response followed that pattern.

2) Additionally, I am slightly worried that the data presented here is not novel, having previously already been published in section 3.1.1, figure 3 and figure 5 of Banda et al., 2020 also in Water. I am not overly worried as this paper has a very different focus, but the authors should be careful of over slicing this data and/or be aware of publication order of several closely spaced papers.
- We would like to indicate that the data sets presented our previous papers is considerably different to this one as the current dataset includes a lengthy period and additional sampling stations.

Overall, I recommend accepting this paper, pending inclusion of analysis on the dual wet season, and other minor revisions.

Scientific Questions:

1) Section 3.5 and Figure 6 discuss the peak months using December and January data only. In 2014, Nicholson et al. (International Journal of Climatology) describe the climatology of Malawi and "introduce/define" a double wet season with a minor break or lull in rainfall and February and March rainfall being effectively derived from a different rainfall regime to that in December and January. It would be extremely interesting to see if this relationship is also seen in precipitation isotopes. If there is not yet sufficient data to determine whether the second half of the wet season has its own isotopic relationships, then this should still be mentioned.

- We have addressed this comment. However, we noted that in Nicholson et al., 2014, the early rainy season is from December – February and late rainy season from March – April. Therefore, our response followed that pattern.

Additional Comments:

1) Line 54: the great-lake influence on East African regional climate is vague, even with a reference. An extra sentence explaining what this influence is would be appreciated.
- Balagizi *et al* (reference 18) concluded the Malawi great lakes exerted influence on the regional climate, and we have added a brief addition.
2) Line 70 and 74: "global issues" is vague, and I don't really know what you are talking about here. You should either be more precise, or trim down this section.
- We are at a loss, as the term 'global issue' is widely used and is one that affects the entire population, this may include environmental, political, health, social and economic issues, therefore this section provides the background setting of challenges in Malawi.
3) Figures 1, 2 and 3 contain lots of repetitive information. You have five panels here, but all the necessary information could be included in just three panels, either as one or two figures. I'm not sure figure 2 is even referenced in the text.
- The figures 2 and 3 have been combined. We now have figures 1 and 2 only.
4) Lines 142-169 is confusingly structured and could do with rewriting in a more structured way, delineating spatial and temporal variability better.
- Completed as requested.
5) The sentence beginning line 142 seems out of place.
- The sentence has been deleted
6) All of these individual sentences in the paragraph beginning on line 147 are fine, but the narrative jumps around a lot through time and space and is difficult to follow.
- Adjusted as requested.
7) I don't quite understand why the paragraph beginning line 164 is here. I think this could be incorporated into the introduction or deleted.
- The paragraph has been shifted to introduction.
8) Paragraph beginning line 186: You don't mention headspace, which should be mentioned briefly.
- We have indicated that isotope samples were collected in air-tight containers with no head space to maintain representativeness.
9) Line 198: Having the deuterium excess defined here is a little confusing. Is there anywhere else to put it.
- The deuterium excess definition has been deleted in line 198 and defined in lines 249-250

10) Paragraph beginning line 234: this feels out of place too, maybe move this paragraph up to keep it with the other physical methods.

- This paragraph has been moved up to methods section as proposed

11) Table 1 and 2: add WMO codes

- WMO codes have been added where applicable (i.e., in Table 2 only as Malawi stations do not currently have such codes) as advised

12) Figure 4 and 5: please be consistent with your colour and symbol choices. MNIP samples change color and shape between figures, which makes it hard to follow.

- Previously, we provided color codes in legends of figures 4 and 5 to make it easy to follow. But as per your suggestion, we have modified the colour and symbol for MNIP samples in figures 4 and 5 and are now the same.

13) The term "offset of the wet season" is confusing and not one that I'm familiar with. Do you mean shoulder season?

- We have replaced the term "offset" with "end" as in "end of the wet season"

14) Section 3.6 is nicely done.

- We are grateful for the positive remark

15) I think SM-Figure 2, SM-Figure 3 and SM-Figure 4 could possibly be included in the main text, if there is space. (See comments on figures 1,2,3). Though they likely would need some work to make them as publication ready as the current figures. e.g., making box plots in SM-figure 4 to include spread, etc.

- There is a need for longer (time series) information to draw strong conclusions for this data, however for the sake of academic transparency, these figures are included in the Supplementary Material. It is anticipated that future publications will develop the concepts shown in these figures with a longer dataset.

16) Paragraph starting line 377 and line 429: you switch to winter/summer here and use boreal winter summer rather than local. This is confusing. I would stick with the wet/dry season delineation you use in the rest of the paper.

- The paragraph has been revised and we have maintained the wet/dry delineation in this paragraph and also throughout the paper where applicable.

17) Paragraph beginning line 399: I think this section could be expanded slightly

- We do not wish to inadvertently draw conclusions that are speculation, we believe a longer time series across a number of stations in Malawi will allow for a future, more detailed focus (and further un-packing of the likely sources of moisture). We are comfortable with the level of interpretation based on the existing data.

18) Section 3.8: should this be its own section 4 as you move from interpretation of results to climatic interpretation.

- Section 3.8 has been re-numbered to section 4 as recommended

19) The existence or not of evaporative signals is confusing e.g., where it exists in line 412, but does not in line 419. I would take some extra time to explain the differences between different evaporative signals.

- In line 419, we intend to indicate that the evaporative effects are **NOT** significant and not necessarily indicating absence of it. This is well presented by way of prediction bands in Figure 4 of this paper which clearly shows sample deviations being within the band. Such similar interpretations are also presented in Boschetti *et al*, 2019. doi:10.3390/w11040791.

Minor corrections:

1) Line 11: "with the resurgence"
   - Changed "With resurgence" to "with the resurgence" as recommended.
2) Line 12: "establishing a stable isotope baseline"
   - Changed "Establishment of a stable isotopic baseline" to "establishing a stable isotope baseline"
3) Line 15: "through the establishment"
   - Changed "Through establishment" to "through the establishment" Revised as recommended.
4) Line 26: "help understand uncertainties"
   - Revised as recommended.
5) Line 26: "This pioneering study"
   - Revised as recommended.
6) Line 44: "baseline signatures in precipitation"
   - Revised as recommended.
7) Line 62/423: isn't it the Congo Air Boundary now
   - Changed "Zaire Air Boundary" to "Congo Air Boundary" as recommended
8) Line 78: 3% of what? Per year, per decade?
   - The 3% has been qualified with annul scale.
9) Line 152: "Interannual monthly" (delete the")
   - Revised as recommended.
10) Line 153: "by Indian Ocean Sea Surface Temperatures:
   - Revised as recommended.
11) Line 154: "El Niño" (with tilde)
   - Revised as recommended.
12) Line 175: delete "on the map of Malawi"
   - Revised as recommended.
13) Line 213: "generating"
   - Revised as recommended.
14) Line 234: missing brackets opening
   - Added opening brackets.
15) Line 235: "spectrometer, specifically a Picarro"
   - Revised as recommended.
16) Line 237: delete "based on laser spectroscopy method"
   - Revised as recommended.
17) Line 325: delete "influencing"
   - Revised as recommended.
18) Line 338: "result in less depleted"
   - Revised as recommended.
19) Line 395: change "is expected to largely confirm" to "will test" and rephrase the rest of the sentence. You shouldn't expect future results to do or show anything.
   - Changed "Is expected to largely confirm" to "will test" as recommended.

1. Response to Second Reviewer

Comments and Suggestions for Authors

Dear Authors, Dear Editor

This work represents an important contribution for mapping the isotopic composition of precipitation in Africa; up to date, no isotope-in-precipitation data are available for Malawi. This study contributes to the Integrated Water Resource Management of the state, establishing the first Malawi Network of Isotopes in Precipitation (MNIP) and also providing useful data for GCM models with isotope diagnostic at global scale. The aim of this study is to provide a LMWL at national scale which could be used as a benchmark for future isotopic studies in the region, and to assess the geographical and seasonal variability of rain isotopic signal. While providing a good description of the state climate and of the main circulation systems governing climatic variations, the study could benefit from the inclusion of back-trajectories for tracking the sources of precipitation for the different sites in different periods. I wonder if Lake Malawi, which represents 23% of the state area, is also a moisture source for at least the mountain area on the west side of the lake. This work could also benefit from the expansion of the rain collector network and from the inclusion of the dry season samples, which could make the LMWL more robust. English is good,but needs a minor revision as some errors are present especially in the first part. I reported some in the list below, but the whole paper has to be read again and slightly adjusted in language.

- We find *"inclusion of back-trajectories for tracking the sources of precipitation for the different sites in different periods"* an interesting recommendation and plan to focus on that in our follow-up studies.

- We are pleased to mention that our follow up studies are already focusing on *"expansion of the rain collector network and inclusion of the dry season samples"* to make the LMWL more robust"

- We plan to investigate more on issues like *"I wonder if Lake Malawi, which represents 23% of the state area, is also a moisture source for at least the mountain area on the west side of the lake"* in our follow up studies as this paper is deemed foundational.

I think this manuscript needs a minor revision before publishing.

1) Showing also a graph (maybe box plots) of the amount of precipitation collected for each month could help understanding precipitation distribution and its inter-annual variability.
- The data set used is available on monthly scale. However, our follow up studies are focusing on obtaining such data on daily scale.

Specific comments:

2) Line 17 – reinforcing THE understanding. Change "country's" with "country"
- Revised/edited as recommended

3) Line 26 – change "help understand resolve uncertainties" with "help understanding and resolving uncertainties"
- Revised/edited as recommended

4) Line 35 – change "source waters" with "water sources"
- Revised/edited as recommended

5) Line 73-74 – change "are almost exclusively reliant on groundwater" with "almost exclusively relying on groundwater"
- Revised/edited as recommended

6) Line 74 – change "dogged" with "affected"
- Revised/edited as recommended

7) Line 79 - "each DISTURBING hydrological systems and DISRUPTING"
- Revised/edited as recommended

8) Line 80 – "A significant vulnerability"
- Revised/edited as recommended

9) Line 81 – "AN associated"
- Revised/edited as recommended

10) Line 156-157 – change "highlands receive highest and lowlands least precipitation" with "highlands receive the highest and lowlands the lowest precipitation amount"
- Revised/edited as recommended

11) Line 159 – change "much" with "most"
- Revised/edited as recommended

12) Line 186 - change "Between the period 2014 and 2019" with "Between 2014 and 2019"
- Revised/edited as recommended

13) Line 192-193 – Why you only show monthly values?
- Because the corresponding precipitation amount data available are on monthly scale.

14) Line 193 – "being THE main focus"
- Revised/edited as recommended

15) Line 237-249 – From my experience, is better to use only isotopic standards which are close to the samples that will be analysed; Picarro is affected by a memory effect and the ampler the isotopic range of the standards, the higher the memory effect that you will get on standards and samples. Preparing the instrument running two samples of deionized water is ok only if that water has a similar isotopic composition to the following samples. The analytical precision (0.2 and 2 ‰ for ◎18O and ◎D, respectively) is not as good as expected using that instrument.
- Our analysis was done based on the IAEA project recommendations as per the isotope hydrology laboratory in Vienna Austria. However, we have taken note of the constructive observation and will apply that in our subsequent analyses and check for any significant variations from the current standard procedure.

16) Line 328 – change "tend to become heavier" with "increase"
- Revised/edited as recommended

17) Line 338 – change "lowly depleted" with "less depleted"
- Revised/edited as recommended.

18) Line 369-375 – I think it could be useful to calculate this correlation using monthly values instead of mean annual values and to use single station data instead of averaging them all.

- The focus of the paper was on isotope data generated from monthly samples. Going forward the suggested approach will be adopted.

19) Line 456-458 – How is the intercept at +13 (slightly above the GMWL) an indicator of equilibrium conditions during condensation?

- The sentence has been revised and indicated the slope (8.0 (±0.03)) as an indicator of equilibrium conditions other than the intercept at +13.

20) I think that the difference between this LMWL and the GMWL is negligible (notice that you have an analytical error of 2‰ on deuterium excess);

- This thought has been well noted and taken into consideration.

21) At the same time, having basically just summer precipitation (wet season) is not the ideal condition to calculate the LMWL, which normally relies on a full 12-month sampling period.

- We would like to indicate that the rainfall pattern in Malawi is largely characteristic of wet season months unlike in other countries where a full-12-month sampling period can be achieved. At the same time, we would like to state that, as an on-going research, we are currently aiming to generate data for the dry season months whenever we have rains during such times.

Supplementary materials

1) SM-Figure 2 - How do you explain the inverse altitude effect observed in February, contrary to January and December which both show a direct correlation?

- These observations are well noted and acknowledged. However, we intend to investigate more on those in our follow up studies (as this is an ongoing research) and this is meant to be foundational paper.

2) SM-Figure 4 – How do you explain the high d-excess value in April, which is the end of the wet season (and not as rainy as the previous months) also characterized by the highest $\delta^{18}O$ and δD values? I would expect a lower d-excess value compared to Dec, Feb and Mar. It would be interesting to see where that precipitation came from.

- We did not wish to draw a conclusion from one data point and we believe a longer time series across a number of stations in Malawi will allow for a future, more detailed focus (and further un-packing of the likely sources of moisture). We are comfortable with the level of interpretation based on the existing data and this is why this data was provided in the Supplementary Materials and not provided in the body of the publication.

20) Line 409: delete “The”

- Revised as recommended.

21) Section 5: this should be section 4 if the current numbering system is kept. Or keep this if you renumber section 3.8 as 4 (see above).

- Re-numbered section 3.8 as section 4 and retained section 5 as it is.

22) Reference 38: I assume this is incorrect and is referring the groundwater Shire River catchment paper?

- The correct reference on 38 has been inserted

1. Response to Fourth Reviewer

Comments and Suggestions for Authors

Dear Authors, Dear Editor

The manuscript (*Banda et al., National Stable Isotope Baseline for Precipitation in Malawi to underpin Integrated Water Resources Management*) provides a valuable dataset and presents the first systematic assessment of the stable isotope baseline for precipitation in Malawi. The study is principally well written although there are some sentences which needs rephrasing to clarify the meaning or to avoid unnecessary complications. In addition, some repetitive parts can be revised. These are pointed out among the specific comments.

Although I marked few language issues among the specific comments, I note that I cannot provide a detailed linguistic review since I'm not a native English speaker.

Major comments:

1) Deuterium excess is defined in lines 198-199 and later in lines 249-250. Since there are mistakes in the definition at the first place and the text flows better, I suggest removing the first version and keeping the version in lines 249-250.
   - The deuterium excess definition has been deleted in line 198 and defined in lines 249-250

2) Figure 2 and Figure 3 should be combined.
   - The figures 2 and 3 have been combined. We now have figures 1 and 2 only.

3) The only structural change can be suggested for consideration is to move the last paragraph of 3.7 (lines 399-404) to the beginning of this section.
   - Last paragraph of 3.7 (lines 399-404) has been moved up to the beginning of this section.

4) The study refers several times to d-excess>10 to be characteristic for vapor recycling and d-excess<10 to be characteristic of raindrop evaporation. These statements need supporting references. See details below.
   - These statements have been referenced accordingly as proposed.

5) The study mentions significant relationship several times referring to the R2 values (e.g., lines 333, 341). However, I think, if you write "significant" you should add p-value instead of (or beside to) the R2.
   - This has been adjusted accordingly

6) Formatting the reference list needs careful checking. The year of publication is not in the required format at many instances.
   - The references have been revised and year of publication put in the required format

Specific comments:

1) line13: „continue to grapple with" can be replaced with a simpler expression e.g., „struggle with" line15: „strides in its quest" can be replaced with a simpler expression e.g., „advance"
   - Revised/edited as recommended

2) line 20: the first part of the sentence sounds strange.
   - Revised/edited as recommended

3) lines 21-22: The text needs checking. I think the higher intercept implies considerable continental moisture recycling as mentioned in the last part of this sentence.
- Revised/edited as recommended

4) lines43-44: The text needs revision. Stable-isotope baselines should be established for the isotope-hydrological regions. National boundaries usually do not correspond to the borders of the isotope hydrological regions.
- Revised/edited as recommended

5) line78: "…rapidly increasing population (c. 3%)," On which temporal scale? annual or decadal?
- The 3% has been qualified with annual scale

6) lines125-126: You don't need to list these dams if they are not shown in the map of Fig1.
- Revised/edited as recommended

7) lines183-184: Note here that the optimal network design could be planned by geostatistical tools see e.g., https://www.sciencedirect.com/science/article/pii/S0160412020322182
- We have indicated that expansion of the MNIP to achieve optimal network design will be informed by geostatistical evaluation as recommended.

8) line 190: "mL" is recommended instead of "ml"
- Revised/edited as recommended

9) line 263: I suggest replacing "meteoric" with "isotope hydrometeorological"
- The authors have opted to maintain "meteoric" as it is a more relevant term in the present context and a standard term that is commonly used.

10) line 264: I suggest removing the text about the regression coefficient. It is enough to present in the figure.
- Revised/edited as recommended

11) line 267: "by Craig (1961)" can be omitted. The ref in squared brackets is enough.
- Revised/edited as recommended

12) lines 267-272: The same info is repeated in these sentences. Please rephrase these sentences. In addition, a reference is required supporting the statement that d-excess>10 is characteristic for vapor recycling. e.g.: Gat and Matsui 1991 https://doi.org/10.1029/91JD00054.
- Revised/edited and provided references as recommended

13) line 273: Similarly, as above: a reference is required supporting the statement that d-excess<10 is characteristic of raindrop evaporation. e.g., Stewart 1975 https://doi.org/10.1029/JC080i009p01133, Salamalakis et al., 2016 https://doi.org/10.1016/j.scitotenv.2015.11.072.
- Revised/edited and provided references as recommended

14) lines 314-317: This is a rather long sentence. I suggest a full stop after the word "excess" and replacing "due to" with "This feature might indicate".
- Revised/edited as recommended

15) lines 322-327: Since both isotopes follow the same seasonal pattern they could be described in the same sentence. It might help to present the same complete scientific information in a more compact description.
- Revised/edited as recommended

16) line 344: if you write significant you should add p-value instead of the R2 (see major comments above). In addition, in this case I'm sceptic whether R2=0.28 based on 5 data points will reach any meaningful significance level.
- P-values have been provided. The "5 data points" are presentative of 5 MNIP stations' mean values. But appropriate revision has been made following the comments.

17) line 353: Gonfiantini et al., 2001 (https://doi.org/10.1016/S0009-2541(01)00279-0) or Kern et al., 2020 (https://doi.org/10.3390/w12061797) are more relevant references for isotopic "altitude" effect than the current citation. I suggest replacing the current citation with the mentioned ones.
- Revised/edited and provided references as recommended

18) line 364: I think "such as the one" can be omitted.
- Revised/edited as recommended

19) lines 378-379: I think it is a strange sentence with ambiguous notation. A possibly suitable rephrasing "The mean and standard deviation calculated from data of the MNIP stations (13.3‰, SD:3.80) compare to the ones (11.2‰, SD:5.48) calculated from the data of the GNIP stations."
- Revised/edited as recommended

20) line 396-398: Extension of the MNIP is rewarding, however I note again that, searching for the optimal location for additional MNIP stations could be done by geostatistical tools see e.g., https://www.sciencedirect.com/science/article/pii/S0160412020322182.
- We have indicated that expansion of the MNIP to achieve optimal network design will be informed by geostatistical evaluation as recommended.

21) lines 409 and 411: I think the last character should be subscript in the acronym.
- Revised/edited as recommended

22) line 473: maybe "principally" or "basically" could be a more suitable adjective to replace foundationally.
- Revised/edited as recommended

Figures

23) Figure 2 and Figure 3 should be combined.
- Figures 2 and 3 have been combined

24) Figure 4: Please consider this rewording in the first sentence of the caption: ".... monthly precipitation stable isotope data..."
- Revised/edited as recommended

References:

1) ref9: The last part of the bibliographic details belongs to a different paper: Rozanski et al., 1993. Please, check it.
- Revised/edited as recommended

2) re11: incomplete bibliographical details. Please, complete it.

- Revised/edited as recommended

3) ref17: The bibliographic details should be corrected, because it is a book chapter and not a journal paper.
- Revised/edited as recommended

4) ref30: authors' names are not presented in the required format.
- Revised/edited as recommended

5) refs 37 and 38 seem to be repetition.
- A corrected reference has been provided for 38.

water-1272967

AUTHOR RESPONSE TO PROOFREADING COMMENTS
(incl. Cover Letter)

F.A.O. Dragana Markovic, Assistant Editor, WATER

Dear Dragana,

Please be advised that we have responded to the proofreading comments via track changes on the live manuscript uploaded for your attention.

Kind regards,

Limbikani Chitsundi Banda

On behalf of the authorship

Encl.

1. Response to Reviewer 3

Comments and Suggestions for Authors

This paper describes the isotopic variability of precipitation in Malawi, Africa. it is well presented covering the main aspects for describing country-specific isotope hydrology.

At this stage, I recommend 'minor revision'. I have only a comment regarding the 'isotope-amount effect'.

Specific Comments

1) Section 3.4: please add the linear regression lines in the cross plots of stable water isotopes and precipitation amount.

- Linear regression lines in the cross plots have been added.

2) Also, regarding 'the amount effect' - the slope of the observed relationships, did you find similarities with other regions-countries with similar climatic characteristics.

- Currently, our data set is limited and there is on-going sample collection including expanding sampling to specific / individual events that will further our understanding of the amount effect, which will in turn provide a data set that can be more directly compared with other data sets with similar climatic characteristics.

3) How ITCZ or other factors contribute to the amount effect in Malawi. Please be more specific since it is the only effect that contribute to the observed isotopic variability (as you present in the article, temperature and altitudinal dependencies are not reflected in the isotopic patterns).

- This has been addressed

water

MDPI

Article

National Stable Isotope Baseline for Precipitation in Malawi to underpin Integrated Water Resources Management

Limbikani C. Banda [1,*], Michael O. Rivett [2], Anold S. K. Zavison [3], Sydney Kamtukule [3] and Robert M. Kalin [1]

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Abstract: With the resurgence of water-isotope tracing applications for Integrated Water Resource Management in developing countries, establishing a stable isotopic baseline is necessary. Developing countries, including Malawi, continue to struggle with the generation of consistent and long-term isotopic data-sets due to non-existent or inadequate in-country water-isotope capacity. Malawi has made significant advances in its quest to establish a stable isotopic baseline through the establishment of the Malawi Network of Isotope in Precipitation. This study provides the first results for the isotopic characterization of precipitation in Malawi with a view to reinforcing understanding of the country's hydrological cycle. Error-in-variables regression defined a Local Meteoric Water Line as $\delta^2H = 8.0 (\pm 0.3) \delta^{18}O + 13.0 (\pm 2.0)$ using stable isotopic records of 37 monthly samples from 5 stations between 2014 and 2019. Local precipitation (isotopic composition) is consistent with global precipitation expectations, its condensation-forming process occurring under equilibrium conditions and ~~with~~ a higher intercept (d-excess) above the 10‰ for Global Meteoric Water Line~~,~~ implying that air moisture recycling significantly influences local precipitation. Wider variations observed in local precipitation isotopic signatures are largely attributed to different moisture-bearing systems and diverse geographic factors across the country. Additional stations are recommended to improve spatial coverage that, together with longer temporal records, may help understanding and resolving uncertainties such as the altitude effect. This pioneering study is expected to facilitate Malawi's ambition to achieve integrated use and improved protection of its surface - water and groundwater resources in response to mounting climate change, growing population and land-development concerns.

Keywords: Precipitation; Stable Isotope Baseline; Local Meteoric Water Line; Integrated Water Resources Management; Deuterium excess; Malawi

Citation: Banda, L.C.; Rivett, M.O.; Zavison, A.S.K.; Kamtukule, S.; Kalin, R.M. National Stable Isotope Baseline for Precipitation in Malawi to underpin Integrated Water Resources Management. *Water* **2021**, *13*, x. https://doi.org/10.3390/xxxxx

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1. Introduction

Integrated Water Resource Management (IWRM) requires an understanding of the provenance of the various water sources contributing to a resource that may enable their protection. Establishing the stable-isotopic signature of these waters~~,~~ and mixed waters subsequently occurring within water resources~~,~~ provides diagnostic insight into the physical processes the water has been subjected to over time, the identification of possible water sources~~, and~~ and the improved understanding and conceptualization of the local or regional hydrological cycle; all which underpin IWRM [1–5].

The diagnostic value of ~~surface water~~surface water and groundwater resource stable-isotope signatures is predicated upon the characterization of isotopic signatures present in meteoric (precipitation) inputs [6–9]. It is important to the national-scale

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implementation of IWRM that countries establish stable-isotopic baseline signatures in local precipitation. In developing countries such as Malawi and across Sub-Saharan Africa (SSA), baseline development and wider isotopic tool use ~~has~~ have been hindered by poor socioeconomic conditions, little investment in the science~~, and~~ and a lack of in-house isotope analytical facilities. Reliance to date has been on samples collected and exported by researchers in developed countries leading to sporadic isotope studies in Malawi [10–17].

Malawi has a complex land-locked hydrology. The ~~north–south~~north–south-oriented country spans significant latitude from 9° S to 17° S. Its location at a southern extremity of the East African Rift System (EARS) results in significant topographic variation, from *c.* 30 to 3000 m asl. Lake Malawi covers 23% of the surface area of the country and its setting within the larger African Great L~~l~~akes~~,~~ region (incl. Malawi, Victoria and Tanganyika) results in a predominant great-lake influence (a significant source of moisture) on its East African regional climate [18]. It experiences a sub-tropical climate influenced by altitude, relief and Lake Malawi. It is generally cool in plateau areas~~,~~ but hot in the rift valley, becoming increasingly semi-arid from the north to the southern lowlands. Seasonal contrasts are significant with distinct wet (November~~–to~~–April) and dry (May~~–to~~–October) seasons driven by north-easterly winds (Mpoto) in the former and strong south-easterly winds (Mwera) in the latter seasons. Topographically influenced mean temperatures range from 17 to 37 °C in the hot~~–~~–dry season. Precipitation is influenced by the migration of the Inter Tropical Convergence Zone (ITCZ), Congo Air Boundary (CAB) and Tropical Cyclones [19]. Given the above complexities, spatial–seasonal characterization of variations in precipitation stable-isotope signature across Malawi is vital to assess the expected depletion of heavier isotopes from increased latitude, closeness to the continental interior~~, and~~ and increased altitude due to temperature variations and 'rainout' effects [18]. To date, Malawi has relied upon stable isotopic data records from Global Network of Isotopes in Precipitation (GNIP) stations located outside the country [10–17]. Malawi represents a gap in ~~the~~ SSA's regularly monitored network.

The country is vulnerable to several 'global issues'. Although there are substantial ~~surface water~~surface water resources within Lake Malawi and its Shire River outflow, these only provide pipeline supplies to its urban ~~centres~~centers. Most of ~~the~~ Malawi's population is the rural poor, in common with around half a billion people in SSA [20], almost exclusively reliant on groundwater [21]. Such supplies are affected by functionality concerns, a global issue, with many of Malawi's circa 120,000 water points vulnerable to 'asset stranding'. driving the consideration of IWRM alternatives [22,23]. Malawi's water resources are also vulnerable to a host of development pressures, including irrigated agriculture, urbanization, rapidly increasing population (*c.* 3% annually), increasing (hydroelectric) energy needs and deforestation; each disturbing hydrological systems and disrupting the sensitive balances between runoff and recharge [24–29]. Malawi has a significant vulnerability to climate change and ~~an~~ associated intensification of drought and flood events. ~~–~~Although influence is already probable, evidenced by a series of climatic perturbations in SSA [30–32] and in Malawi [30,33–35], the priority remains to establish current baselines (including stable isotopes) to benchmark further change. Finally, as a landlocked country neighbo~~u~~ring Mozambique, Tanzania and Zambia~~, and~~ and its main Shire River draining into the Zambezi River also influencing Angola, Botswana, Namibia and Zimbabwe, Malawi has significant transboundary aquifer and ~~surface water~~surface water obligations [36].

Malawi is one of the world's most physically vulnerable places to repercussions resulting from climate change [37,38]. The country has recorded climatic evidence of significant temperature variability and increased intensity and frequency of occurrence of floods and drought [29–35]. Climate~~-change-~~change-induced perturbations in the ~~sub-Sahara~~Sub-Saharan precipitation regime causing a rise in numerous severe weather incidents are also asserted [30–32].

Our research is an outcome of the partnership between the International Atomic Energy Agency (IAEA) and Malawi's Ministry of Forestry and Natural Resources that

enabled the 2018 commissioning of an isotope hydrology national facility. This specifically comprises the operationalization of an Isotope Hydrology Laboratory (IHL) and the establishment of the Malawi Network of Isotopes in Precipitation (MNIP). The data collected to date from the MNIP form our focus herein. ~~Objectives.~~ The objectives set were to establish a stable isotopic baseline for precipitation at national scale for Malawi, to understand the factors that may influence spatial and temporal (intra-seasonal) isotopic signature variability~~, and~~ and to develop a Local Meteoric Water Line (LMWL) for Malawi that will act as a benchmark for future isotopic studies assessing water-resource status. The overarching goal was to provide a foundational characterization of precipitation that will reinforce understanding of Malawi's hydrological cycle and thereby underpin future IWRM and policy decision making. This study represents the ~~first~~ first-ever characterization of the stable isotope precipitation baseline for Malawi and hence provides a pivotal step to achieving the long-held ambition to provide isotope-informed IWRM for the country. Study findings have already helped underpin our companion catchment [39] and basin-scale [40]. stable-isotope studies in Malawi and on-going studies of other catchments.

2. Materials and Methods

2.1. Study Area Setting

Malawi occurs as an elongate plateau towards the south-western extreme of the lower EARS that structurally dominates its landform (Figure 1). Its diverse physiography ranges from highlands reaching 3000 m asl, plateau occurring at 750–1300 m covering much of the country, rift valley scarp~~, and~~ and the rift valley and associated plains that decline to around 30–100 m asl in the Lower Shire Valley–Mozambique border. The highland and plateau comprise normal-faulted blocks of Precambrian and Lower Palaeozoic Basement gneiss and granulite rock (the pan-African 'basement rock') with Quaternary colluvium, alluvium and lacustrine basins forming the rift valley plains. These form Malawi's three main aquifer types; the weathered basement rock, the often-underlying fractured basement rock and the valley alluvial aquifer systems upon which rural Malawians extensively rely upon for water supply [21,22,41].

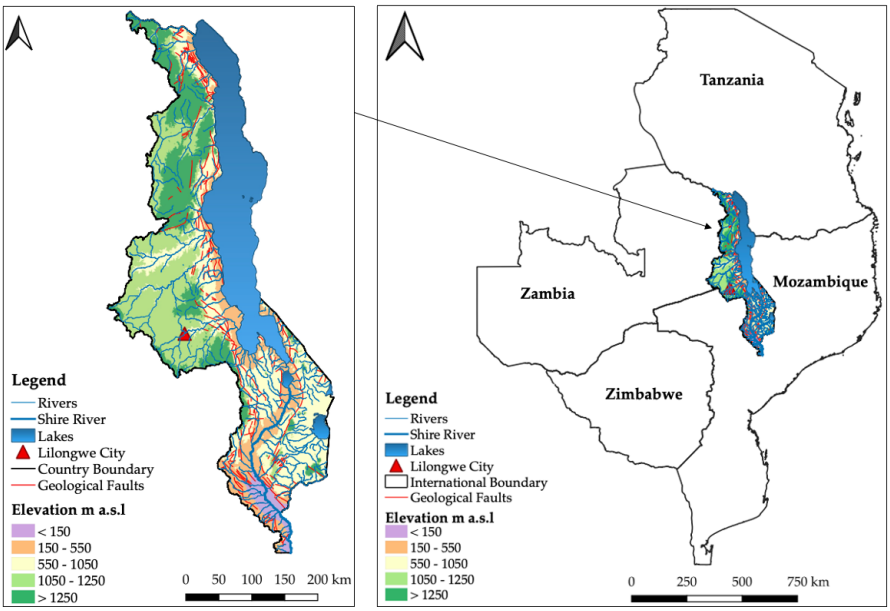

Figure 1. Study area showing topography (various colo~~u~~red zones), major rivers, lakes, fault lines~~, and~~ and neighbo~~u~~ring countries.

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Malawi's drainage system is dominated by the Lake Malawi – Shire River system, into which a vast network of many of its rivers drain (e.g., Ruo, Linthipe, Rukuru and Dwangwa). A few rivers drain to the endorheic Lake Chilwa basin to the east of the rift valley. Other moderately large lakes (Chiuta~~, and~~ and Malombe) also exist, as well as many dams (reservoirs) constructed for water supply. Malawi is a ~~water-~~water-stressed nation, and in particular, groundwater and ~~surface water~~surface water resources during the dry season are significantly stressed, especially in severe drought years [21].

Climate and Precipitation Derivation in Malawi

Malawi's climate is sub-tropical, with generally cool conditions experienced in the plateau and hot, dry conditions in the rift valley. A distinct wet season from November to April and dry season from May to October occurs throughout the country. Based on the revised Köppen-Geiger system, Malawi's climate may be classified as Aw or Savannah, with the following defining criteria; ''~~"~~Not (Af) and~~&~~ Pdry < 100 − MAP/25''~~"~~, where Af is rainforest, MAP is mean annual precipitation~~, and~~ and Pdry is precipitation of the driest month [35]. ITCZ migration southwards between December and January, and northwards between February and March, accounts for the moisture for most of Malawi's precipitation. South-east trade winds blowing across the Indian Ocean from east to west along the Mozambique Channel occasionally bring~~s~~ widespread heavy precipitation in April extending into May in ~~North~~northern Malawi, and infrequent tropical storms that vary in impact and intensity. Due to its proximity to the East African Coast, Malawi experiences rather light precipitation and drizzles (locally known as Chiperoni) mainly during early month of July, particularly in highlands facing south-east. [29].

Malawi's precipitation regime has two distinct features~~:~~; a region with a strong precipitation maximum in austral autumn along Lake Malawi's western shoreline and a brief period of reduced precipitation in mid-February ascribed to a shift in prevailing

precipitation and circulation regime [42]. The precipitation regime is characterized by strong seasonality, inter-annual fluctuations and intra-annual spatial and temporal distribution and variability, which are critical to water resources planning and management [43]. Inter-annual monthly precipitation is influenced by Indian Ocean Sea Surface Temperature (SST) attributed to the El Niño Southern Oscillation Phenomenon [43]. Annual precipitation ranges from 725 mm to 2500 mm and~~,~~ the country's precipitation is largely influenced by diverse topography and proximity to Lake Malawi [44,45]. Generally, highlands receive the highest and lowlands the lowest precipitation amount. Most of the precipitation (*c.* 90%) occurs between November and April [46]. Within this period, precipitation is concentrated between December and March, with maxima occurring in January in most of the country but delayed until March, close to Lake Malawi's western shoreline [42].

2.2. Malawi Network of Isotopes in Precipitation (MNIP): Design, Sampling and Analysis

The Government of Malawi, with funding from International Atomic Energy Agency (IAEA) established a monitoring network of isotopes in precipitation at national scale through the Water Resources Department (WRD) in the Ministry of Forestry and Natural Resources between 2014 and 2018. The monitoring network is known as the '*Malawi Network of Isotopes in Precipitation*' (MNIP), and Figure 2a locates the MNIP stations. The MNIP was commissioned for collection of systematic data on isotopic signatures of precipitation for the establishment of a stable isotopic baseline for precipitation at national scale. Currently, it comprises five (5) stations (sited at (3) and near (2) meteorological service stations) equipped with a rain collector "' dip-in sampler"' and access to meteorological equipment for measuring meteorological parameters (e.g., rain gauge for measuring precipitation amount). The siting rationale of the MNIP stations aimed at providing ~~national balanced~~balanced national coverage and ~~to~~ capturing influences of different weather systems affecting precipitation across the country. This was a fledgling starter network meant to be expanded (by geostatistical tools to achieve an optimal network design) with additional stations for spatial and temporal enhancement of the isotopic data records [47].

Between 2014 and 2019, a total of 40 monthly water stable-isotope samples were collected from the MNIP stations (Table 1) using dip-in samplers designed to prevent evaporation (and eliminate the need for paraffin) [48]. The water stable-isotope samples were collected on a daily and a weekly basis and thereafter mixed to provide integrated monthly samples. Samples were contained in 25 mL brown (light-proof) bottles with airtight caps and no headspace and kept at 4 °C during transportation and holding. Laboratory analysis involved daily, weekly~~, and~~ and monthly precipitation samples, with monthly samples being the focus of this study. A sub-dataset (n = 37) (from stations with precipitation amount data) generated from monthly precipitation amount weighted samples ~~was~~ were then used to derive a national Local Meteoric Water Line (LMWL) using error-in-variables regression analysis denoted EIV-LMWLw. The EIV-LMWLw equation included standard errors (representing mean deviation of isotopic values from the EIV-LMWLw) for its slope and intercept [39,49]. The weighted EIV-LMWLw equation was then compared with a non- EIV-LMWLw equation derived from a regressed entire non-weighted dataset (n = 40) to check any variations in extent of slope and intercept that were found to be insignificant. Summary statistics of precipitation isotopic data ~~was~~ were computed based on the entire dataset (weighted and non-weighted), but the LMWL and other isotope-related graphs focused only on the precipitation amounts weighted dataset.

Analysis of oxygen ($^{18}O/^{16}O$) and deuterium ($^{2}H/^{1}H$) ratios was undertaken using an automated cavity ring-down spectrometer, specifically a Picarro isotopic water analyzer (Model: L2110-I, Picarro, Santa Clara, CA, USA) at Ministry of Forestry and Natural Resources Isotope Hydrology Laboratory (IHL). Daily calibration of light and heavy standards encompassing the expected ranges of isotopic signatures in the samples was undertaken, alongside the use of a daily control mid-range intermediate standard. The Picarro

isotopic water analyzer was prepared by running two vials of ~~deionised~~ deionized water, and accuracy of measurement was checked by inspecting concentration peaks, with adherence to an acceptable range of 19,000–21,000 ppm for abundance of isotope ratios for both deuterium (δ^2H) and oxygen-18 ($\delta^{18}O$). The isotopic analysis precision (2σ) was set at ±0.2‰ for oxygen-18 and ±2.0‰ for deuterium, while quantification and validation of results ~~was~~ were accomplished via dedicated Laboratory Information Management System (LIMS) software. The processed isotopic analysis results were reported in delta values (δ^2H and $\delta^{18}O$) representing parts per thousand (‰) deviations from the international Vienna-Standard Meteoric Ocean Water (V-SMOW) [50,51] with precision (2σ) of ±0.2 permil for $\delta^{18}O$ and ±2.0 permil for δ^2H. The deuterium excess parameter was calculated from Dansgaard's equation relating $\delta^{18}O$ and δ^2H of water, defined as $d = \delta^2H - 8\ \delta^{18}O$ [52]. The water stable-isotope chain ~~of~~ of custody (onsite measurements, sample collection, transportation, holding, preparation~~, and~~ and analysis) adhered to International Standard methods [53].

The study focused on the only available stable isotopic data generated during wet season as Malawi's precipitation is largely received during this time of the year. Hence, only intra-seasonal variability of isotopic signatures of local precipitation was investigated, not inter-seasonal variability. Thus, the intra-seasonal variability in stable isotopic signatures of local precipitation has been displayed in Supplementary Material (SM) Figure S1a by way of averaging weighted monthly isotopic values of precipitation for each month of the wet season over the period 2014–2019. The upcoming phase of our work will largely focus on generating seasonal isotopic data for investigating inter-seasonal variability in isotopic signatures of local precipitation.

The local precipitation data were augmented by precipitation isotopic data obtained from neighboring international Global Network of Isotopes in Precipitation (GNIP) stations in Mozambique at Gorongosa (8 monthly samples) and Chitengo (4 monthly samples), Zambia at Ndola (154 monthly samples), Zimbabwe in Harare (188 monthly samples) and in Tanzania in Dar es Salaam (117 monthly samples) ~~in~~ to reinforce the national meteoric water characterization and to capture regional status of isotopic signatures (spatially and temporally) thereby allowing a more complete regional meteoric characterization (IAEA/WMO) (Figure 2b; Table 2). It was deemed vital to have this surrounding boundary defined for a landlocked country (and expected as standard to do so). The MNIP is spatially lacking and needs infilling, and the temporal earlier isotopic data records are useful to ~~providing~~ provide some way of extrapolating time series. Above all, the MNIP was designed to fit into the wider international network contribution. The resultant Regional Meteoric Water Line (RMWL) derived from a sub-dataset of precipitation amounts weighted stable isotopic samples (n = 449) (from stations with precipitation amount data) from MNIP, and the surrounding GNIP stations ~~was~~ were also calculated by error-in-variables regression, denoted EIV-RMWLw.

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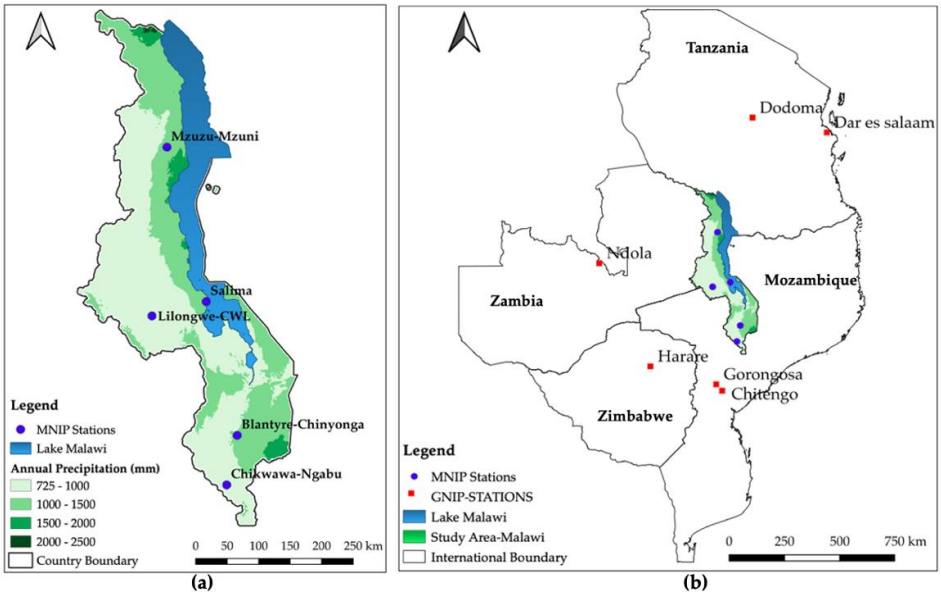

Figure 2. Malawi-network of isotopes in precipitation (MNIP) sStations (**a**) and global network of isotopes in precipitation (GNIP) sStations (**b**).

Table 1: Summary of isotopic sampling undertaken from Malawi Network of Isotopes in Precipitation (MNIP) stations (2014-2019)

*Meteorological Services Station	MNIP Stations	Decimal Degrees		Altitude (m a.s.l)	Monthly Samples
		Latitude	Longitude		
Mzuni	Mzuni	-11.41977	33.9952843	1287	6
Chitedze	*CWL	-13.976628	33.7686897	1046	18
Salima	Salima	-13.75	34.5892292	512	4
Ngabu	Ngabu	-16.536863	34.8912164	80	7
Chichiri	Chinyonga	-15.813924	35.0397645	1127	5

*Meteorological services stations associated with MNIP stations; CWL: Central Water Laboratory

Table 2: Summary of isotopic sampling undertaken from Global Network of Isotopes in Precipitation (GNIP) Stations (1969-2019)

GNIP Stations	WMO Codes	Country	Decimal Degrees		Altitude (m a.s.l)	Monthly Samples
			Latitude	Longitude		
Harare	6777400	Zimbabwe	-17.83	31.02	417	188
Dodoma	6386200	Tanzania	-16.1852	35.7533	1157	18
Dar es salaam	6389400	Tanzania	-6.88	39.2	55	117
Ndola	6756100	Zambia	-13	28.65	1331	154
Chitengo	6729501	Mozambique	-18.9751	34.34842	34	4
Gorongosa	6729502	Mozambique	-18.6717	34.07239	346	8

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3. Results and Discussion

Stable isotope data obtained from the local (MNIP) and regional (GNIP) precipitation stations have permitted comprehensive characterization of Malawi's current local meteoric system.

3.1. Co-Isotopic Relationships of Local Precipitation

Error-in-variables (EIV) regression was applied to the stable isotopic dataset collected from the MNIP stations to calculate a Local Meteoric Water Line (LMWL) that describes Malawi's local meteoric characteristics. The local meteoric water line (EIV-LMWL) is defined as: $\delta^2H = (8.0 \pm 0.3)\ \delta^{18}O + (13.0 \pm 2.0)$ (Figure 3). The EIV-LMWL shows a strong positive correlation between δ^2H and $\delta^{18}O$ values of local precipitation of slope consistent with the Global Meteoric Water Line (GMWL), defined as: $\delta^2H = 8\delta^{18}O + 10$ [50]. The stable isotopic signatures of local precipitation from the MNIP stations registered a mean deuterium excess value of 13.3 ‰, slightly above the GMWL intercept of 10. This is characteristic of local vapor recycling contribution to the local precipitation isotopic signatures [54]. A subset of the MNIP samples that plotted below the GMWL is indicative of the re-evaporation of raindrops during precipitation events (Figure 4) [55,56]. Most of the local precipitation samples scattered along the EIV-LMWL, with almost all the samples plotting within the prediction error band. This corroborates that there ~~was~~ were insignificant evaporative influences on the local precipitation and ~~was~~ were further substantiated by the EIV-LMWL slope (8.0 ± 0.3), which is characteristic of non-evaporated rains.

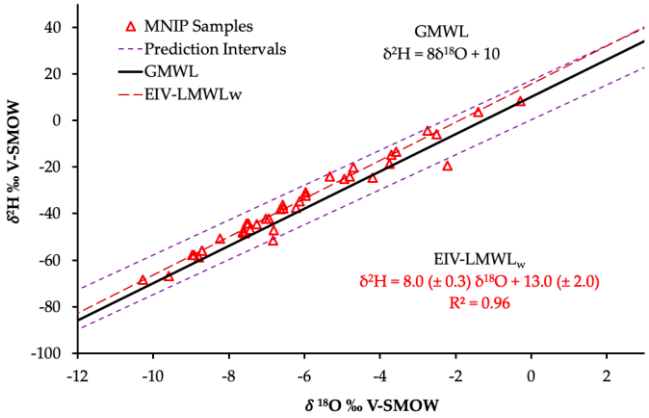

Figure 3. Monthly precipitation stable-isotope data for MNIP stations (n = 37). Error-in-variables local meteoric water line (EIV-LMWLw) represents the weighted local meteoric water line for Malawi (calculated based on ~~error~~ error-in-variables regression analysis). MNIP: Malawi network of isotopes in precipitation; GMWL: Global Meteoric Water Line.

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3.2. Isotopic Signature of Local and Regional Precipitation

The current MNIP stations' dataset was judged insufficient to meet our goals, and hence, characterization of the local meteoric conditions was augmented by surrounding GNIP stations' datasets. This permitted a more regionally representative LMWL relative to the origin of air masses that was defined as $\delta^2H = 7.6 \pm (0.1)\ \delta^{18}O + 10.0\ (\pm 0.5)$ (Figure 4). The EIV-LMWL is quite consistent with the regional meteoric water line defined as $\delta^2H = 7.6\ (\pm 0.1)\ \delta^{18}O + 9.9\ (\pm 0.5)$ (Figure 4) derived from the surrounding GNIP stations datasets. The slopes of both meteoric water lines are identical, but somewhat less than the GMWL slope of 8. This is ascribed to evaporative influence on the isotopic signatures of precipitation events as well as possible isotopic non-equilibrium conditions affecting the ~~rain~~ rain-out process.

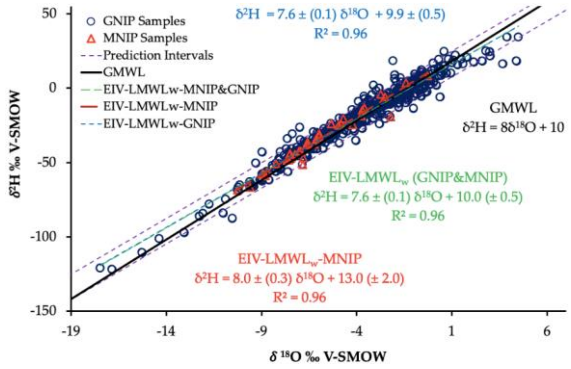

Figure 4. Plot of δ²H and δ¹⁸O for precipitation stable-isotopic samples from MNIP stations (n = 37) and GNIP stations (n = 409). Error-in-variables local meteoric water line (EIV-LMWLw) represents the weighted local meteoric water line calculated based on ~~error~~ error-in-variables regression analysis. MNIP: Malawi network of isotopes in precipitation; GMWL: Global Meteoric Water Line.

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The scenario reinforces the need for continuity and long-term collection of water stable-isotopic data from the MNIP stations to significantly improve both the EIV-LMWL local representativeness and its significance in contributing to the regional global water stable-isotopic meteoric characterization.

3.3. Isotopic Signature Variability of Local and Regional Precipitation

The MNIP stations' monthly dataset displayed wide variations spanning a range of 76.8‰ for δ²H~~, and~~ and 10‰ for δ¹⁸O (Table 3a). This is attributed to distinct rain-bearing systems and varying geographic factors resulting from the country's extremely diverse physiographic zones. The wide variation evident in the water stable-isotopic signatures is consistent with the expected water stable-isotopic signatures of Indian Ocean ~~monsoon~~ monsoon-derived precipitation [57]. The surrounding GNIP stations dataset displayed even wider variation (range: 159 ‰ for δ²H; 22 ‰ for δ¹⁸O) relative to the MNIP stations dataset (Table 3b). This was attributed to spatial and/~~,~~or intra-seasonal variability among other factors such as temporal and geographic scales. Plotting of the MNIP dataset within the prediction band supports evaporative effects on local precipitation were insignificant (Figure 5). A GNIP stations sub-dataset, however, did plot outside the prediction band~~;~~, both below the GMWL, signaling an oxygen-18 excess. This feature might indicate secondary evaporation of raindrops during the fall~~,~~ and above the GMWL (representing excess deuterium), from which precipitation originated from recycled air moisture is inferred.

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Table 3: Summary statistics of stable isotopic signatures of precipitation from (a) MNIP stations and (b) MNIP plus surrounding GNIP stations

(a)

Variable	Count	Min.	Max.	Mean	Median	StDev	Range
δ^2H	40	-68.4	8.40	-35.9	-38.0	18.7	76.8
$\delta^{18}O$	40	-10.3	-0.29	-6.15	-6.61	2.30	9.98
D-excess	40	-1.64	18.6	13.3	13.9	3.80	20.3

(b)

Variable	Count	Min.	Max.	Mean	Median	StDev	Range
δ^2H	489	-122.1	36.4	-20.6	-17.7	23.9	158.5
$\delta^{18}O$	489	-17.5	4.5	-4.0	-3.7	3.2	22
D-excess	489	-17.3	34.6	11.2	12	5.48	51.8

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3.4. Intra-Seasonal Isotopic Signature Variability of Local Precipitation

The stable isotopic signatures of local precipitation varied significantly monthly, with the largest isotopic signatures variation depicted between January and April ascribed to weather systems transitioning Figure S1). The most depleted isotopic signatures of $\delta^{18}O$ and δ^2H were recorded in January, the peak month of the wet season, whereas the most enriched isotopic signatures of $\delta^{18}O$ were recorded in April, the end of the wet season. The enriched isotopic signatures of $\delta^{18}O$ and δ^2H are indicative of drier–-warmer conditions during the end of the wet season (SM-Figure S1b). Overall, the isotopic compositions of rainfall in Malawi increase as the ITCZ migrates northwards around April. Therefore, there is a need for further investigation at a regional scale coupled with the collection of high-resolution isotopic data across various catchments in Malawi to better understand the spatial distribution variation with time across the country.

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3.5. Isotopic Signature and Precipitation Amount Relationship: "'*Amount Effect*"'

A strong correlation ($R^2 = 0.86$) was observed between precipitation amount and stable isotopic signatures of local precipitation at the monthly scale (Figure 5a). An increasing trend in precipitation amounts corresponded to highly depleted isotopic signatures. The "'amount effect"' is generally influenced by actual precipitation amount with precipitation intensity dominating [52]. Thus, several precipitation events of lesser intensity, with a cumulative higher amount, can result in less depleted isotopic signatures, and contrasts with a few precipitation events of higher intensity, with a cumulative low amount, that can exhibit highly depleted isotopic signatures [2]. Peak months of the wet season (December–January) study depicted a stronger relationship ($R^2 = 0.89$), suggestive of precipitation derived considerably more from convective events. This contrasts with the onset and end of wet season months (base months) (November and April, respectively) having a weaker relationship ($R^2 = 0.28$), ascribed to precipitation episodes under the influence of frontal origins (Figure 5a), as echoed by Darling (2003) [2].

The precipitation "'*amount-effect*"' was also investigated considering the dual nature of Malawi's wet season, which, after the early phase (December–February), has a slight break or lull in precipitation, followed by the late phase (March–April). Precipitation during these phases is derived from contrasting atmospheric circulation regimes [42]. During these phases, the stable isotopic signatures of local precipitation are strongly influenced by precipitation amounts (Figure 5b). The amount effect varied considerably at higher precipitation amounts as compared to low precipitation amounts between the early and late phases. Overall, the current dataset has not depicted clear dependencies of the isotopic signatures on altitude or temperature but rather the influence of the ITCZ as it migrates southward and northward in Malawi. Considering the present data records

limitation, especially for the late phase, it will be extremely interesting to further investigate ~~further~~ the nature of the isotopic relationships that exists in local precipitation using more robust temporal and spatial isotopic data records.

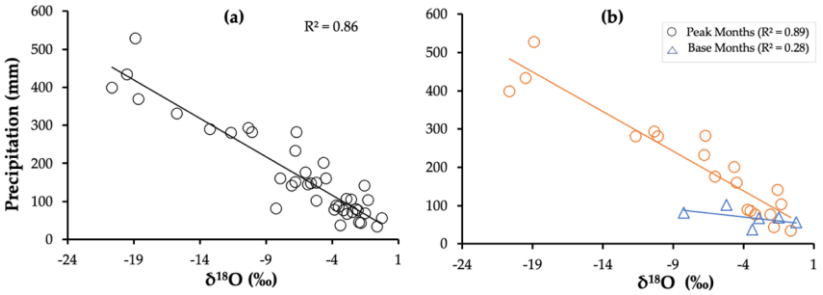

Figure 5a. Precipitation amounts plotted versus $\delta^{18}O$ values for (**a**) all monthly data and (**b**) the intra-seasonal relationship for MNIP stations over the period 2014–2019. The monthly data in (**a**) show a high and strong correlation, while in (**b**), a strong amount effect is depicted for the peak months (December–January), but weak amount effect for base months.

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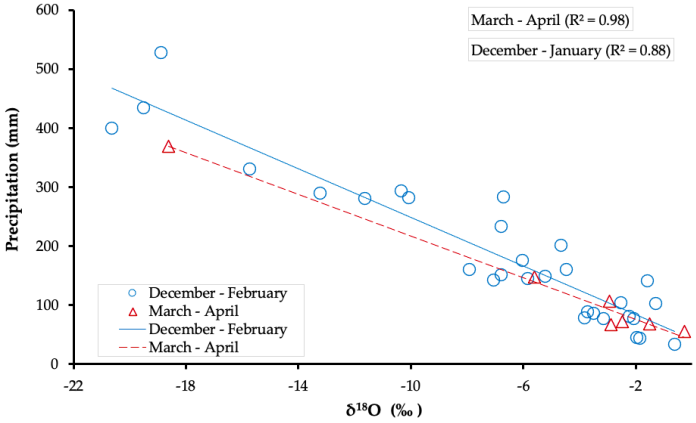

Figure 5b. Precipitation amounts plotted versus $\delta^{18}O$ values for early (December–February) and late (March–April) phases of wet season (depicting intra-seasonal relationship for MNIP stations over the period 2014–2019).

3.6. Isotopic Signature and Altitude/Temperature Relationships

An observed altitude effect is indicative of a temperature effect attributed to cooling air masses with increasing elevation. This has largely been reported to be insignificant in lowlands and significant in uplands/highlands [58,59]. Altitude effects were investigated during the months of December and, January for the period of 2014–2019 (SM—Figure S2). These are the months with good records for all the ~~5~~ five stations. The rest of the months have significant data gaps and do not warrant investigation. Moderately correlated relationships between altitude and $\delta^{18}O$ signatures were observed for December and January precipitation events, but weak correlations for February (SM—Figure S2). In both instances, precipitation tended to be isotopically depleted with increasing altitude. A poor correlation of isotopic signatures ($\delta^{18}O$) with altitude was found and most likely ascribed to the geographical separation of the precipitation stations (Malawi being a long stretch of land from north to south, with contrasting topographic settings) and varying sources

of air moisture. The precipitation stations in sSouthern Malawi are predominantly influenced by Indian Ocean air Masses and El Niño, while other stations in the nNorthern Malawi are mainly influenced by the ITCZ. Thus, it could be that this lack of climatic relationship between some of the stations may potentially render it impossible to conclude on a national altitude effect for Malawi at this stage, but local scale data collection is advised for future study.

A poor correlation between isotopic signatures ($\delta^{18}O$) and temperatures was also observed and attributed to the extreme geographical separation among the precipitation stations as observed for the altitude effect (SM—Figure S3). The other factors attributing to such poor correlation could be the varying air moisture sources influencing rainfall at the stations. Also,Additionally, intense secondary evaporation effects in sSouthern Malawi compared to elsewhere in the country alongside re-evaporation influence may be significant contributing factors to isotopic variation with respect to temperature.

3.7. Deuterium Excess Variability and Frequency Distribution

The monthly variation of deuterium excess in precipitation over the period 2014–2019 shows that, the highest deuterium excess values were recorded during the month of January, while the lowest deuterium excess values were recorded during February. The deuterium excess values are greater than 10‰ for GMWL, indicating that there is a considerable contribution of air masses that generate precipitation by recycling of continental air moisture (SM—Figure S4).

The frequency distribution of deuterium excess of the fledgling MNIP network (n = 40) is compared to the surrounding GNIP station record (n = 489). The mean and standard deviation calculated from data of the MNIP stations (13.3 ‰, standard deviation: 3.80) compare to the ones (11.2 ‰, standard deviation: 5.48) calculated from the GNIP stations. (Figure 6a). Observation of the MNIP peak at 13–15 ‰ is important in assessing the provenance of air masses. The frequency distribution of deuterium excess supports that precipitation from the MNIP station are to some extentis influenced by recycled continental moisture of the atmospheric reservoir. Most deuterium excess values (87.5%) fell within the range of 10–20‰ that are characteristic of wet season rains which are typical of and expected for MNIP stations due to the high wet season precipitation proportion. A few deuterium excess values (12.5%) occur within the range of 2–10 and are characteristic of dry season rains. The surrounding GNIP record (Figure 6b) exhibits a contrasting isotopic fingerprint characteristic of both wet season and dry season rains, more characteristic of the surrounding country localities (shown by precipitation analysis of the GNIP station locations). This is consistent with the slight difference in the characteristics of the LMWL and the regional meteoric water line derived from surrounding GNIP stations datasets. These differences may also provide insight and investigation opportunity opportunities into the varying origin of air masses contributing to the seasonal precipitation events at the surrounding GNIP stations (considered beyond our scope herein). The growing dataset from the MNIP stations in future years will test our initial interpretation that appears consistent with the physical expectations. Additional MNIP stations and long-term isotopic data records are required to achieve both spatial resolution enhancement and temporal records increase. Up-scaling of the MNIP will be informed by a detailed geostatistical evaluation of optimal location for additional MNIP stations [47].

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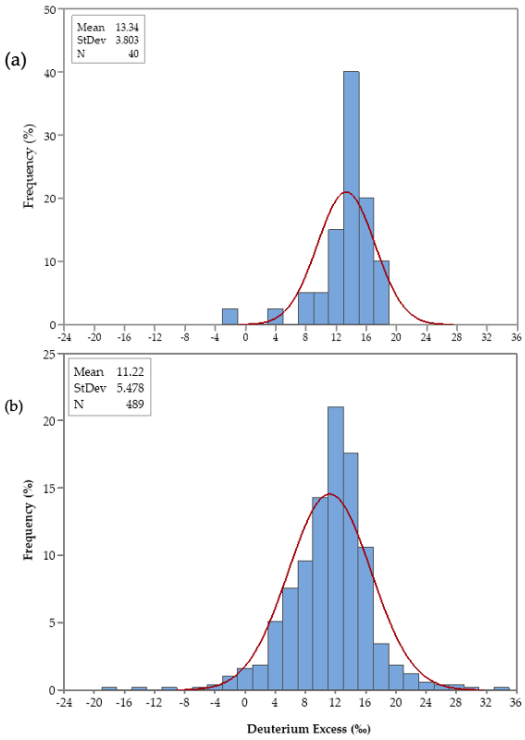

Figure 6. Frequency distribution of deuterium excess signatures for monthly precipitation from (**a**) MNIP stations over 2014–2019 and (**b**) surrounding GNIP stations for the period 1960–2016.

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4. Relationship with Precipitation Moisture Sources

Malawi's Local Meteoric Water Line (EIV-LMWLw) generated $\delta^2H = 8.0 (\pm 0.3) \delta^{18}O + 13.0 (\pm 2.0)$ ‰; confirmed the country's local precipitation was generally consistent with global precipitation expectations, but with the EIV-LMWLw displaying a slight shift above the GMWL, suggesting kinetic fractionation during evaporation [60,61]. The LMWL's intercept (13.0 (± 2.0) ‰) representing the deuterium excess value, greater than the GMWL intercept of 10 ‰, is probably due to the influence of the Salima and Central Water Laboratory station samples in Central Malawi and Chinyonga station samples in ~~South-~~southern Malawi which recorded higher d-excess values. The LMWL's slope of 8.0 (± 0.3) is comparable with 8.0 for the GMWL, from which it is reasonably inferred that a condensation process leading to local precipitation formation occurred under equilibrium conditions~~,~~ and without significant evaporation phenomena [18,62].

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The stable isotopic signatures recorded in local precipitation were clearly distinct and varied widely, suggesting differences in water vapo~~u~~r sources and varying weather systems [61]. This is reasonably ascribed to the country's different precipitation-bearing systems, i.e., the Inter Tropical Convergence Zone (ITCZ), Congo Air Boundary (CAB) and Tropical Cyclones, alongside the influence of geographic controls upon local precipitation variation. This calls for further investigation on how these ~~weather-~~weather-bearing systems link~~s~~ to the varying water vapo~~u~~r sources. The stable isotopic input signatures of local precipitation were found to be less seasonal ~~that-~~than those recorded at the

surrounding GNIP stations. This was attributed to the fact that the available dataset largely covered one season (wet season), a period when the country mostly receives rains (wet season rains). As a result, the seasonal variation in the stable isotopic signatures of local precipitation has not been fully investigated at this stage. Going forward, deliberate efforts will be made to fully capture isotopic signatures of dry season rains to provide meaningful resolution of seasonal variability. ~~Altitude~~ The altitude effect was investigated, considering significant isotopic variations in local precipitation. However, ~~basing~~ based on the available isotopic dataset, evidence of the influence of the altitude effect was rather erratic and contrary to conventional trends. Consequently, there is a need for further investigation requiring enhancement of the MNIP temporal and spatial isotopic data records to provide high resolution of the altitude effect. This can be achieved through continuous generation of isotopic data and expansion of the MNIP station from the existing five (5) to at least ten (10) stations. There is also a need for investigation on how daily/weekly precipitation $\delta^{18}O$ signatures relate to air mass characteristics contribut~~eory~~ to the formation of the local precipitation across the country.

The study findings will largely contribute to the operational component of the MNIP, which was established to collect systematic data on isotopic signatures of precipitation on a national scale, and to establish temporal and spatial variations of environmental isotopes in precipitation. The study provides important foundational isotopic data that will underpin the use of environmental isotopes in hydrological investigations within the scope of water resources management and development.

5. Conclusions

The study successfully established a national-scale deuterium and oxygen-18 stable-isotope baseline for precipitation in Malawi. This is a first for this developing country and was achieved through the sampling of the recently commissioned Malawi Network of Isotopes in Precipitation (MNIP) and isotope analysis at its own recently established national laboratory facility, removing previous hindrances of sample export abroad for analysis. The Local Meteoric Water Line (LMWL) developed is proposed as a reference benchmark for future and more focused hydrological and climatic studies. The study demonstrates the stable isotope composition of local precipitation was consistent with global precipitation expectations; its condensation-forming process occurring under equilibrium conditions evidenced by a slope of 8.0 (± 0.3) quite comparable to a slope of 8.0 for the Global Meteoric Water Line (GMWL). The precipitation-forming process was also closely associated with atmospheric vapo~~u~~r recycling across the region, the LMWL and GMWL slopes being consistent. Variation in stable isotopic signatures of precipitation was attributed to differences in atmospheric vapo~~u~~r sources arising from Malawi experiencing diverse precipitation-bearing systems and distinct geographic–topographic controls within its Rift Valley setting.

The established LMWL will enhance understanding of the hydrological–hydrogeological cycle in Malawi. It is pivotal to providing increased insight into the provenance of meteoric waters, especially of groundwater recharge sources, but also the confirmation of seasonally variant dependency of ~~surface water~~surface water flows on runoff, baseflow and evaporation losses. The latter process may also impact near-surface groundwater resources, especially in Malawi's semi-arid lowlands. ~~Use~~ The use of isotopic tools underpinned by the isotopic precipitation characterization herein is already beginning to provide insight into such processes, as demonstrated in our recent basin- [39] and catchment-scale studies [40].

The characterized precipitation isotopic baseline principally contributes to the newly established national stable isotopic database. Looking forward, this is expected to provide a critical underpinning of IWRM implementation in Malawi due to the resolving power of stable-isotope signatures providing forensic insight into the key challenge of understanding the mixing and provenance of the various possible source waters. This is expected to greatly facilitate Malawi's ambition to achieve integrated use and improved

protection of its ~~surface water~~surface water and groundwater resources in its response to mounting climate change, growing population and land-development concerns. Finally, the study valuably contributes to the global network of isotopes in precipitation (GNIP) database by the infilling of the data-record gap previously existed in Malawi. This allows increased certainty in regional and global hydrological and climatic mode~~l~~lling study predictions. The current isotopic data record is regarded as foundational, and spatial network expansion and increased temporal records are both required to reach its full potential and IWRM goals.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: title, Table S1: title, Video S1: title.

Author Contributions: conceptualization, L.C.B., M.O.R. and~~,~~ R.M.K.; methodology, L.C.B. and~~,~~ M.O.R.; validation, L.C.B. and~~,~~ A.S.K.Z.; formal analysis, L.C.B. and~~,~~ M.O.R; investigation, L.C.B.; resources, L.C.B. and~~,~~ A.S.K.Z.; data curation, L.C.B and~~,~~ A.S.K.Z.; writing—original draft preparation, L.C.B. and M.O.R.; writing—review and editing, M.O.R., L.C.B.~~,~~ and R.M.K.; visualization, L.C.B.; supervision, R.M.K. and~~,~~ S.K.; project administration, R.M.K. and~~,~~ S.K.; funding acquisition, S.K., R.M.K. and L.C.B. All authors have read and agreed to the published version of the manuscript.

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Commented [M22]: Please add more details in Supplementary Material.

Commented [MD23]: Please check that your meaning is retained.

Commented [M24]: In this section, please add the Institutional Review Board Statement and approval number for studies involving humans or animals. Please note that the Editorial Office might ask you for further information. Please add "The study was conducted according to the guidelines of the Declaration of Helsinki, and approved by the Institutional Review Board (or Ethics Committee) of NAME OF INSTITUTE (protocol code XXX and date of approval)." OR "Ethical review and approval were waived for this study, due to REASON (please provide a detailed justification)." OR "Not applicable." for studies not involving humans or animals. You might also choose to exclude this statement if the study did not involve humans or animals.

Commented [M25]: Any research article describing a study involving humans should contain this statement. Please add "Informed consent was obtained from all subjects involved in the study." OR "Patient consent was waived due to REASON (please provide a detailed justification)." OR "Not applicable." for studies not involving humans. You might also choose to exclude this statement if the study did not involve humans.
Written informed consent for publication must be obtained from participating patients who can be identified (including by the patients themselves ...

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Response to Reviewer 1 Comments

The present paper reported the hydrochemical and isotopic characteristics of a lake basin aquifer system and explored the water interaction and the source of recharge. The findings are interesting and show practical value for the local sustainable groundwater management. I would recommend the paper to be published after necessary modifications.

- Thank you for acknowledging the practical value of our research in sustainable groundwater management. We appreciate your endorsement for publication and have made the required adjustments accordingly.

In the abstract, you should make it clear what kind of isotopes were employed in the "isotope hydrology" method. Also, avoid emphasizing too much on the "insights" or contributions of your findings, instead, please include the key data.

- We have identified the isotopes utilized and have taken caution not to overemphasize the significance of the findings.

Section 2: you provided a very detailed background knowledge description. However, only key information related to the water supply and water-rock interaction should be kept.

- The manuscript has been reorganised considering the recommendation.

Line 126: dams should not be regarded as a water resource. Maybe you could use "reservoir water".

- This has been revised as suggested.

Line 129: what's the mean of " groundwater points"?

- Groundwater points have been qualified as community water supply boreholes and protected shallow wells.

Line 257: the number of this heading should be 2.5.

- This has been revised

Figure 2: please note the direction for the arrow.

- Noted and addressed

Section 3.1: please also include the seasons/climate conditions for the sampling campaigns.

- This has been presented in methods section.

The distribution of isotopic sampling sites and how you collected the isotope samples for different waters should be mentioned.

- The sampling rationale is included in the methods section and appropriate methods have been cited that provide a comprehensive description of the international standard methods.

Figure 5: please introduce the percentiles of boxes and whiskers.

- Here we present standard statistical evaluation using interquartile plots. Additionally, it is paired with an accompanying table in supplementary materials section providing specific data on the maximum, minimum, and average values.

The Gibbs diagram and other employed metrics (such as CAI and SI) should be introduced in the M & M section instead of in the Results.

- This feedback has been acknowledged and the manuscript has been revised accordingly. Equations, formulae, and their explanations have been shifted to the methods section.

Please separate the Discussion and Conclusion sections to make them clearer.

- This has been revised in adherence to journal format.

Please check the correct use of sub- and super-scripts for ions (e.g., Line 769, Figure 15) .

- This has been revised throughout the manuscript.

Response to Reviewer II Comments

Water-2981627 - Review

Isotope Hydrology and Hydrogeochemical Signatures in the Lake Malawi Basin: A Multi-Tracer Approach for Groundwater Resource Conceptualisation

The article delves into the hydrological dynamics of the Shire River system, highlighting important findings from using the Eckhardt recursive digital filter and recession analysis. The authors identify Lake Malawi as the main source of the Shire River's baseflow, emphasizing the lake's crucial role in sustaining the river, especially under varying climatic conditions. They report that baseflow significantly contributes to river flow—80% during dry seasons and 76% during wet seasons. This finding is essential for understanding and predicting the river's behavior under different hydrological scenarios. They also found an inverse relationship between baseflow and precipitation, underscoring the importance of baseflow in sustaining river flow during dry periods and demonstrating the self-regulating nature of hydrological systems. They, the study provides a strong foundation for policy-making and the development of management practices that ensure the effective and sustainable use of the Shire River's water resources.

General Considerations

Text

1. Introduction

Lines 57-58: Delete sentence „In Malawi, groundwater plays a vital role in meeting the water supply needs, especially for rural communities". This is indicated clearly in the following sentences.

- The sentence has been deleted as suggested.

Lines 63 to 65: Reformulate the sentence. It is difficult to read

- The sentence has been reformulated as suggested.

Line 83: Isotope Hydrology should all be written in small cases

- Isotope Hydrology has been written in lower case "isotope hydrology" as suggested.

2. Study Area Setting

Line 111: Delete "setting" from the title

- Setting has been deleted to read "Study Area".

Line 122 (and through the entire manuscript): Geographic locations must be shown in the maps (Chizumula and Likoma islands, Kamuzu dam I and II, Lilongwe River, Lunyangwa dam, Lunyangwa River, Bwanje Valley dam, Namikokwe River, Lilongwe city, Mzuzu city, Dedza and Viphya mountains, Dzalanyama range, Mchinji and Nyika highlands, …)

- These geographic locations have been shown in the maps.

Lines 140 to 142: Maintain uniformity for comparison. Either supply capacity or storage capacity for all dams

- "Storage capacity" has been replaced by "supply capacity" to maintain uniformity.

Line 161: You should consider defining "rift valley floor" here and not in line 176

- This has been revised accordingly.

Line 173: Replace "eastern Lake Malawi shoreline" by the "southeastern Lake Malawi shoreline". You do not show the complete eastern shoreline in Figure 2b. Consider this in the complete manuscript

- Here we draw attention to the eastern side of the basin. Therefore, we have replaced eastern Lake Malawi shoreline by western Lake Malawi shoreline which borders the eastern side of the basin.

Line 202: Replace "rocks" by "aquifers"

- Rocks has been replaced by aquifers.

Lines 223 and 226: Replace "transmission" by "flow"

- Transmission has been replaced with flow.

Line 238: Consider rephrasing the sentence in this line

- The sentence has been rephrased

Line 241: Do not repeat the preceding sentence (The unconsolidated sedimentary units overlying weathered basement aquifer). Please rephrase

- The repeated sentence has been replaced by another aquifer unit and the entire sentence has been revised to improve clarity.

Lines 241 to 248: Consider rephrasing. It is unclear as it is now

- This has been rephrased to improve clarity.

Line 245: Rift Valley in lower cases

- Rift Valley has been written in lower cases as "rift valley".

Line 257: The sub-section Climate should be number 2.5. Do not write a full stop after the number for consistency

- The section and sub-section numbers have been updated throughout the manuscript. We have opted to write a comma after a number for uniformity.

3. *Material and Methods*

Line 288: delete the sub-section. You only have one

- This has not been deleted considering we have introduced other sub-sections.

Line 272: Rift Valley Plain in lower cases

- Rift Valley Lake Plain has been replaced by rift valley lake plain.

Line 272: Replace "most rains" by the highest rainfall

- Most rains has been replaced by highest rainfall.

Line 278: Write Rift Valley Lake Shore Plain in lower cases

- Rift Valley Lake Shore Plain has been replaced by rift valley lake shore plain.

Line 281: Start the sentence by "The presence of Lake Malawi moderates the surrounding temperatures…"

- The sentence has been rephrased.

Line 294: Replace "high risk" by "risky"

- "High risk" replaced by "risky".

Line 295: What does "mostly" mean? Did you prove that purge was correct, especially for dug wells?

- This has been revised. Water points were fitted with handpump and is use at the time of sampling. There not in use, the water points were purged properly.

Line 302: Delete "of isotope hydrology samples"

- Delated

Line 306: Which gas did you use?

- Air is used as a carrier gas.

Lines 323 to 326: Move these two sentences to the top of the paragraph (Line 299)

- These sentences are rounding up the prescribed procedures processes described above, hence no change was made to maintain agreement of these sentences.

Line 330: Write the size of the bottles

- The volume of the sampling bottles was 1L and it has been indicated.

Line 332: Did filtering take place in the laboratory? Why?

- Sample filtration was conducted at the holding laboratory with 24 hours of sample collection.

Line 337 sand 337: Where were cations measured? Please indicate

- The analysing laboratory for cation has been indicated.

4. *Results*

Line 348: What does "a median slightly acidic (53.1%)" mean? Which is the value of the median?

- The median value has been indicated and the sentence has been revised to improve clarity.

Line 349: In table SM1, TDS mean is 305 mg/L and median 210 mg/L. Please check

- This has been checked and amended accordingly.

Line 352: Is sulphate dominant or it appears at low concentration? You should clarify. Furthermore, could you include fluoride in figure 5?

- Sulphate is dominant and it has been clarified.

Lines 353 to 358: Move these last three sentences to the top of the paragraph (Line 350, before the sentence starting with "Bicarbonate,…"

- The sentences have been restructured.

Line 364 and 365: Replace "provided details of" by "reported of". Delete comma before "and". Write fluoride with low cases

- The phrase "provided details of" has been replaced by "reported of". Comma deleted and Fluoride written in low cases as fluoride.

Line 366: Replace "at a majority of" by "in most of". Could you write the number of water points containing nitrate?

- The phrase "at a majority of" replaced by "in most of". The number of water points has been indicated as a percentage.

Lines 370 to 374: The ubiquitous presence of nitrate points towards human induced pollution, but not to a model. You suggest building up a model. Please rephrase

- This has been revised accordingly

Line 379: You write either "The Piper plot method was used" or "A piper plot was used" Line 395: Delete comma before "and"

- A piper plot has been used instead of piper plot method. Comma before and deleted.

Line 401: Have you analysed the Lake Malawi water? Why do you conclude that there is a "potential lake water infiltration to groundwater"? Please explain

- The chemistry of Lake Malawi was analysed but not presented in this paper. Hence the evidence of potential lake water infiltration has been shifted to the isotope section where isotope signatures for Lake Malawi has been presented.

Line 413: Delete bracket after TDS

- The bracket after TDS has been deleted.

Line 419: Are all the minerals listed in Table 1 and SM5 present in the aquifers? If so, then write it Line 429: Delete comma after e.g.

- Yes, and it has been indicated. The comma after e.g. has been deleted.

Line 444 and 445: Your write: "A groundwater subset deviates from". From what?

- This has been revised for clarity.

Line 458: Replace "equal to" by "of"

- The phrase "equal to" replaced by "of".

Lines 415 to 419, Lines 427 to 443, Lines 452 to 470: All formulas and explanations belong to Section 3 Materials and Methods. Only results belong to this section. Please correct

- This has been revised accordingly .

Lines 473 to 485, Lines 489 to 494, and all equations with correspondent explanations: Belong to Section 3 Materials and Methods. Only results should be written in this section. Please correct

- This has been revised accordingly.

Line 498 and 499: Write "is associated with groundwater recharge in highlands, which is characterised by low pH"

- This has been revised accordingly.

Lines 501 to 504: Rephrase. Write what you did not measured in-situ to be more clear

- Alkalinity was not measured onsite, and this is indicated in methods section.

Line 520: The end of the sentence should read: "to dissolve in groundwater". Please correct

- This has been revised accordingly.

Line 537: What do you mean with "hidden hydrothermal water"? Please clarify

- This has been revised to hidden hot springs.

Line 550: δ^2H ranges from -111 ‰ to 12.4 ‰ in Table SM2. Please check

- This has been revised accordingly.

Line 552: Write ‰ after -2.2 for consistency. Decide whether you are going to write d-parameter or D-excess. Be consistent throughout the entire article

- We have opted to maintain d-parameter throughout the manuscript for uniformity.

Line 553: Write "shows **that** the recycling…"

- The sentence has been rephrased.

Lines 556 and 577: The last sentence should read: "This isotopic offset ascribed to excess deuterium in precipitation is consistent with the African Great Lakes region isotopic effect"

- The sentence has been rephrased.

Line 567: Ranges are +123 ‰ for $\delta^{2}H$ and 15.3 ‰ for $\delta^{18}O$ in Table SM3. Check and write consistently

- This has been checked and corrected.

Line 572: Minimum $\delta^{2}H$ is -47.4 ‰ and mean $\delta^{2}H$ is -34.4 ‰in Table SM4. Check and correct

- This has been checked and corrected.

Line 574: It should read: "d-parameter ranges from…". Replace "Figure 14b" by "Figure 13b"

- This has been checked and corrected.

Line 575: Clarify the meaning of GWML

- The GMWL has been clarified to Global Meteoric Water Line.

Line 578: It should read: "A subset of samples, Group G2, deviate**s** below the GWML…"

- The sentence has been rephrased.

Line 582: Delete "possibly"

- Deleted.

Line 584: Deep-seated hydrothermal waters with rock minerals? This sentence, as it is, does not have any meaning. I would delete "with rock minerals" or you should rephrase

- The sentence has been rephrased to improve clarity.

Line 585: delete s in line**s**

- Deleted.

Lines 587 to 589: What does it mean for you that the future study of $\delta^{17}O$ in precipitation is "highly warranted"? Please explain

- An appropriate reference has been added.

Lines 596 to 599: You are talking about Figure 13a and not Figure 14a. Furthermore, the fact that Group C shows evaporation indicates rather aquifer recharge with lake water and not the other way around. Please consider.

- This has been revised to improve interpretation of the figures.

Lines 605 to 611: I would delete the first sentence and write the second sentence after the third

- The sentences have been restructured as suggested.

Line 646: The definition of GMWL should came earlier, not here

- This has been revised as suggested.

Lines 645 to 647: Actually, values are very much scattered to conclude as you do

- This has been revised. "Suggest" has been used to avoid much emphasis.

Line 649: Replace "and" by "that" after conductivity. Delete "it might have experienced"

- This has been revised accordingly.

Line 651: Delete s from "plot**s**"

- Deleted.

*5. **Discussions and Conclusions***

Line 675: It is "sodium **in** clay". Delete "materials"

- Deleted.

Lines 669 and 670: Did you measure trace elements? If not, then delete the elements listed between brackets as you have more that those listed there

- The sentence has been revised as suggested.

Line 675: Write "sodium-rich groundwater in clay" instead of "groundwater with sodium on clay materials"

- The sentence has been revised accordingly.

Line 681: Delete comma before "and calcite"

- Deleted.

Line 682: Add comma before “and amphibole”

- Added

Line 704: Write “smectites” and “kaolinite” with low cases

- This has been revised accordingly.

Line 706: Delete “the” after of

- Deleted.

Line 707: Replace “saturated” by “saturation”

- Saturated replaced by saturation.

Line 732: Locate all these areas in the map of Figure 1 or Figure2

- The areas have been added on the Map figures.

Line 769: It should read SO_4 and not SO4

- This has been revised accordingly.

Figures:

Figure 1b: Major rivers, although indicated in the legend, are not plotted. Plot them and add the names of those described in the text. What do the numbers on the map (5, 6, 7,…) mean? They are not described, neither in the legend nor in the figure capture

- The geographic locations have been added and the numbers (5, 6, 7,….) have been qualified by WRA (WRA 5, WRA 6, WRA 7,….).

Figure 2, figure capture: You do not need to write that the topography is indicated by “various coloured zones”. However, you should write the source of elevation data-

- This has been revised accordingly.

Figure 2b: Either draw the WRA boundary with another colour or shade the Plateaux areas with colour. Both have the same symbol in the legend

- The WRA boundary has been removed to draw emphasis on the physiographic zones.

Figure 3: The only difference between the left and right sides in your cross section is the presence of unconsolidated alluvial/colluvial deposits aquifers to the left. The fracture basement is an aquifer on both sides. Indicate accordingly

- This has been revised as suggested

Figure 4, figure caption: Delete “(coloured zones)”. Legends in Figure 4a and 4b should be at the same height

- Figure 4a: Correct “MET Sattions” in the legend
- Figure 4b: Swap the colours for temperature. The hottest area should be in red and the coolest in blue. In the legend, write (°C) in the following line to match the legend of Figure 4a

- This figure has been removed considering one of reviewer’s recommendation.

Figure 5: What do the Whisk-boxes mean? Maxima and minima are not represented. HCO_3 should be written together. Include fluoride, because you describe it in the text. You can delete the columns TA and TH, because you do not refer to them in the text. Could you indicate the mean value in each box?

- Here we present standard statistical evaluation using interquartile plots. Additionally, it is paired with an accompanying table in supplementary materials section providing specific data on the maximum, minimum, and average values.

Figure 6: These two maps do not make any sense. I would suggest that you plot only the map b but setting the limit at 50 mg/L (WHO limit) and not at 5 mg/L as it is now. Be careful to have legends at the same height when you compare maps under the same figure

- Figure 1 sets detection extent of nitrate, while figure b projects impact with reference to the detection extent. The emphasis is not on compliance with WHO limit but rather projected impact on GW.

Figure 7: The left Piper does not help the interpretation, please delete. You have indicated two areas as “4” on the Piper on the right. One of them is “5”. Please correct

- This has been revised as suggested.

Figure 8b: Please, change the colour for the GW type Na-HCO_3-Cl. It is difficult to distinguish in the map. Ensure that both maps have the legend at the same height

- This has been revised as suggested.

Figure 9: As you have the same Y-Axis in both graphs, consider drawing only one. The same for the legend.

- One Y- Axis has been drawn as suggested. However, legends are unchanged for easy reference to the plots.

Figure 11a and b: The line of apparent equilibrium seems to be higher

- Considering figures 11, apparent equilibrium of fluorite with dolomitic carbonates and calcite is derived from common ion effect, hence nature of the apparent equilibrium lines.

Figure 12: Indicate what GMWL and LEL_{Lake} mean

- This has been indicated as suggested.

Figure 13: Which is the Local GW-Line? Why do you draw so many d-lines? This makes the graph to busy

- We have been very careful not to draw a "Local GW line" considering the GW samples are from complex multi-aquifer systems.
- Figure only has 5 D-lines which sets a foundational base for interpretation of our follow-up studies as this paper is part of a wider research.

Figure 14: Consider representing either $\delta^{18}O$ or $\delta^{2}H$. Furthermore, it is difficult to distinguish the colours that you have selected for the representation of the values in the map. Please change

- This has been revised accordingly.

Figure 16: Include the LEL_{Lake} in the legend and indicate in the graph to be consistent with GMWL. Change the Axis' scales to facilitate visualisation

- This has been revised as suggested.

Tables

Table 1: You divide either all columns with a line or none of them Table 2: You divide either all columns with a line or none of them. I wonder whether both tables should not be combined into one as Table 1. You do not need to present Table 2 under Discussions and Conclusions

- This has been revised as suggested

Response to Reviewer III Comments

Article:
Isotope Hydrology and Hydrogeochemical Signatures in the Lake Malawi Basin: AMulti-Tracer Approach for Groundwater Resource Conceptualisation

English is clear and well written with a wordy style that does not fit for scientific or technical articles. The text needs to be condensed and also needs to be better organized. Figures and tables are of good quality.

- We reorganized the manuscript considering the review report feedback.

Remove sentences that say the same with different words and provide more numericalvalues as results.

- We have acknowledged that positive feedback.

Some suggestions of removal of unnecessary wording are shown for the abstract in theattached marked file, however the abstract was not corrected for organization. The abstract jumps from significance to results to significance to discussion without providing any tangible (numerical) values.

- This feedback has been acknowledged such that we have revised the manuscript for uniformity. We have provided numerical values where they were presented in word expressions.

L. 362. I imagine mg/L of TA and TH are in mg CaCO3/L, please correct, as it could be reported as bicarbonate instead of carbonate.

- The TA and TH are reported in mg $CaCO_3$/L, and we have indicated that as suggested.

Capitalization of words should be revised (e.g., Fluoride in line 365)

- This has been addressed throughout the manuscript.

Use numbers instead of qualifiers (…moderate concentration, line 367); write the concentration value and let the reader decide if that value is moderate or not. Correctthe rest of the manuscript.

- This has been addressed throughout the manuscript.

Description of the study area is too lengthy. Please condense and only include those figures that are needed to point out something specific.

- This has been addressed by removing some figures as shown in the revised manuscript.

Avoid repeating the same information, e.g., the same information (water types) is described in the text, in Piperdiagram (Fig 7) and in a map (Fig 8).

- Be advised that Figure 7 depicts groundwater types and figure 8 shows spatial distribution of these groundwater types. We do not regard such a logical presentation as repetition.

Add a reference to the applied methodology, e.g. add. a reference to the processesdepicted in Fig. 10 (Line 441)

- We have added appropriate citations to methods where deemed necessary.

Clean the section of results, discussion, and conclusions from repeated thoughts or those not obtained as a result in this study.

- We reorganized the manuscript considering the review report feedback.

water

MDPI

Article

Isotope Hydrology and Hydrogeochemical Signatures in the Lake Malawi Basin: A Multi-Tracer Approach for Groundwater Resource Conceptualisation

Limbikani C. Banda [1,2]*, Robert M. Kalin [1] and Vernon Phoenix [1]

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[2] Water Resources Department, Ministry of Water and Sanitation, Private Bag 390, Postcode: 207213, Lilongwe 3, Malawi

* Correspondence: limbikanicbanda@gmail.com

Abstract: Reliance on groundwater is outpacing natural replenishment, a growing imbalance that requires detailed and multi-faceted water resource understanding. This study integrated water-stable isotopes and hydrogeochemical species to examine hydrogeochemical processes during groundwater recharge and evolution in the Lake Malawi basin aquifer systems. The findings provide insights into groundwater source provenance, with non-evaporated modern precipitation dominating recharge inputs. Grouped hydrochemical facies exhibit five groundwater water types, prominently featuring Ca-Mg-HCO_3. Modelled hydrogeochemical data underscore dominant silicate dissolution reactions with the likely precipitation of calcite and/or high-Mg dolomitic carbonate constrained by ion exchange. Isotope hydrology reinforces water resource system conceptualisation. Coupled isotopic-hydrogeochemical lines of evidence reveal a discernible spatial-seasonal inhomogeneity in groundwater chemical character, revealing a complex interplay of meteoric water input, evaporative effects, recharge processes, and mixing dynamics. Findings show that measurable nitrate across Malawi highlights a widespread human impact on groundwater quality and an urgent need for detailed modelling to predict future trends of nitrate in groundwater with respect to extensive ~~fertilizer~~ fertiliser use and an ever-increasing number of pit latrines and septic systems arising from rapid population growth. This~~e~~ study not only refined the Lake Malawi basin aquifer systems conceptualisation~~,~~ but also provided isotopic evidence of groundwater and lake water mixing. This~~e~~ study sets a base for groundwater management and policy decisions in support of the Integrated Water Resources Management principles and Sustainable Development Goal 6 objectives for groundwater sustainability in the transboundary Lake Malawi ~~Basin~~basin.

Keywords: isotope tracers; hydrogeochemistry; sustainable development goal 6 (SDG 6); geochemical modelling; groundwater sustainability

Citation: Banda, L.C.; Kalin, R.M.; Phoenix, V. Isotope Hydrology and Hydrogeochemical Signatures in the Lake Malawi Basin: A Multi-Tracer Approach for Groundwater Resource Conceptualisation. *Water* **2024**, *16*, x. https://doi.org/10.3390/xxxxx

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1. Introduction

Access to safe drinking water and sanitation is a fundamental human right, as stated in the United Nations (UN) resolution 64/292 [1]. The p~~P~~rovision of clean water is further enshrined as a critical global priority in Sustainable Development Goal 6, 'Clean water and sanitation'. Despite this, a considerable proportion of the global population lacks access to adequate water services. Recent figures estimate that *ca* 2.4 billion people reside in water-~~-~~stressed countries, and *ca* 2.2 billion people lack access to safely managed drinking water (2020 and 2022, respectively) [2]. This issue is particularly prevalent in many rural and peri-urban communities in sub-Saharan African (SSA) countries, including Malawi. Groundwater plays a vital role in supplying drinking water and supporting domestic

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needs, especially in regions with limited water distribution networks. It constitutes approximately 50% of global freshwater resources, serves about 40% of irrigated agriculture, and provides around one-third of the water supply for industry. Its significance extends to human development and economic growth [3]. However, excessive groundwater extraction and declining groundwater levels present sustainability challenges [4]. Sustainable management approaches are necessary to ensure the long-term availability of groundwater resources. Groundwater has been particularly critical in building resilience to climate change and ensuring water security in the Southern African Development Community (SADC) region [5]. Approximately 65% of Malawi's population heavily relies on groundwater for drinking and domestic use [6,7]. This is even more significant in rural areas where 82% of the population ~~rely~~ relies on groundwater. Considering the unpredictable nature of precipitation and inconsistent surface water flows in Malawi [8], groundwater is viewed as a reliable alternative for water supply provision, especially during drought periods [9]. The significance of groundwater in surface water dynamics in Malawi, through its significant role in base ~~-~~flow, further emphasi~~s~~z~~e~~s the importance of groundwater within Malawi's water security.

Malawi's aquifer lithology influences groundwater quality [6]. Geogenic and geochemical factors influence groundwater quality in Malawi, in some instances leading to elevated levels of salinity, fluoride, iron, sulphate and chlorides [10–13]. Raised levels of sulphate in weathered basements [14] and high salinity in alluvial aquifers have been reported, with the latter resulting in the abandonment of several boreholes [15]. Malawi also faces challenges regarding groundwater supply impacted by aquifer stress and improper infrastructure development by non-governmental ~~organizations~~organisations, resulting in a scourge of stranded groundwater assets across the country [16]. Rapid population growth, changing lifestyles, unpredictable precipitation, higher agricultural demands, water resource degradation, and climate change add to a list of drivers confounding Malawi's water problems [17,18]. The agricultural sector, employing over 80% of the population and driving Malawi's economy, uses a substantial amount of the country's renewable freshwater resources, exerting heavy pressure on Malawi's water resources [19]. To address these issues, Integrated Water Resources Management (IWRM) and sustainable water management techniques such as borehole garden permaculture [20,21], alongside advanced technologies like isotope hydrology tracers, can play a crucial role in understanding and managing groundwater resources sustainably [22]. Notably, isotope hydrology tracers provide insights into the conceptualis~~z~~ation of hydrological ~~–~~–hydrogeological systems [23,24], groundwater dynamics, recharge processes, and water-source provenance [25–28], aiding in science-led policy decisions [29]. Yet, despite their benefits, the use of advanced technologies to facilitate sustainable water resource management is limited in low-income countries, and their potential to inform SDGs (e.g., SDG 6) has not been fully ~~exploited~~ explored [30–32]. Establishing shared laboratories for the routine use of isotope hydrology tracers can significantly improve water resource management in low-income countries.

The overarching aim of this work was to establish a conceptualisation of the groundwater in the Lake Malawi basin (LMB) aquifer systems, focusing on isotope hydrology and hydrogeochemical baseline characteri~~z~~ation, spatial-seasonal effects on groundwater mineral signatures, geochemical controls on groundwater quality and evolution, groundwater-resource provenance, and hydrogeological system conceptualisation. Specifically, thi~~s~~e study addressed the following research questions: (a) What are the background isotope hydrology and hydrochemical signatures of groundwater in the LMB?~~;~~ (b) How are the LMB aquifer systems recharged, and what are the isotope hydrology and hydrochemical signatures of distinct recharge inputs? (c) What are the geospatial and seasonal effects on groundwater quality and mineralisation? (d) What are the key geochemical controls on groundwater quality and evolution? and (e) How do isotope hydrology, hydrogeochemical and geospatial characteristics help refine the conceptualisation of the LMB aquifer systems? Thi~~s~~e study is consistent with the IWRM principles and SDG 6

objectives, with the potential to underpin sustainable groundwater resource management in Malawi and the wider region. Thise study aligns with the International Atomic Energy Agency (IAEA) Technical Cooperation (TC) project objectives (RAF7021 regional project) for sustainable water management and supports transboundary water management initiatives under the 2004 ZAMCOM agreement and was supported by the Scottish Government's Climate Justice Fund Water Futures Programme (CJF).

2. Study Area

The Lake Malawi basin (LMB) is a transboundary region that covers Lake Malawi and its surrounding surface areas in Malawi, Mozambique, and Tanzania, (Figure 1a). It lies within a seismically active belt at the southern mostsouthernmost region of the East African Rift System (EARS), with a combined lake and land surface area of *ca.* 126,500 km², 97,740 km² of which is land surface [6]. The study area is constrained to the Lake Malawi basin section within Malawi's international boundary (Figure 1b), spanning *ca.* 64,785 km² of land surface, with *ca.* 32,955 Km² of land surface occupied by Mozambique and Tanzania. The study area covers 13 water resources areas (WRAs) of national significance, mainly focusing on the 11 major 11 water resource areas with a substantiallly contribution to lake Lake Malawi hydrology (Figure 1b). It leaves out two minor WRAs encompassing Chizumula and Likoma islands in the middle of Lake Malawi with minimal contributions to the Lake Malawi hydrology.

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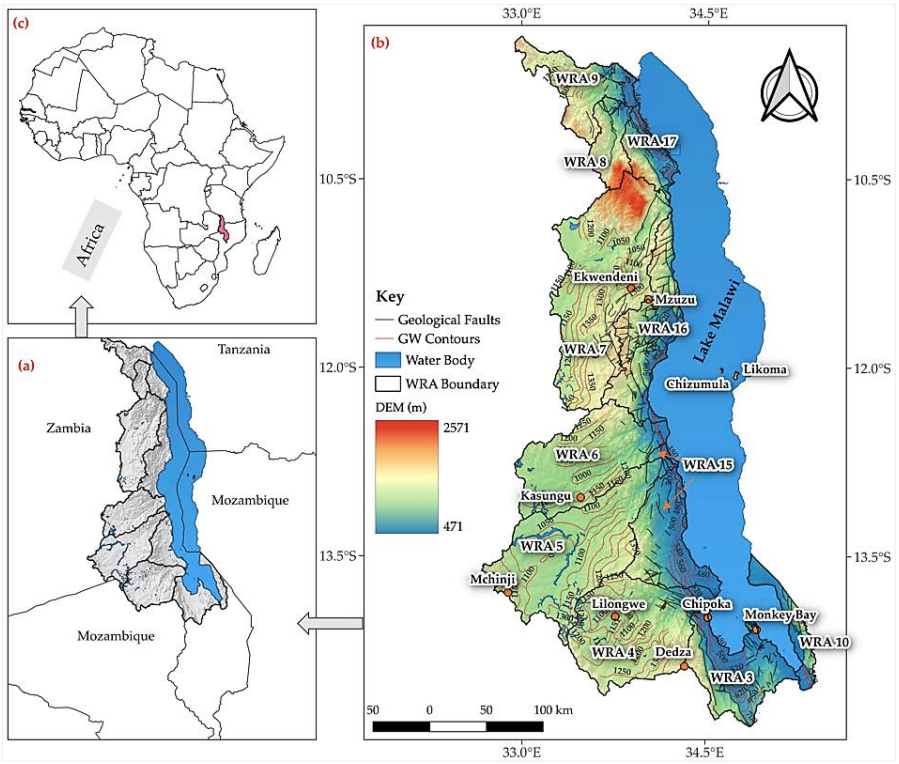
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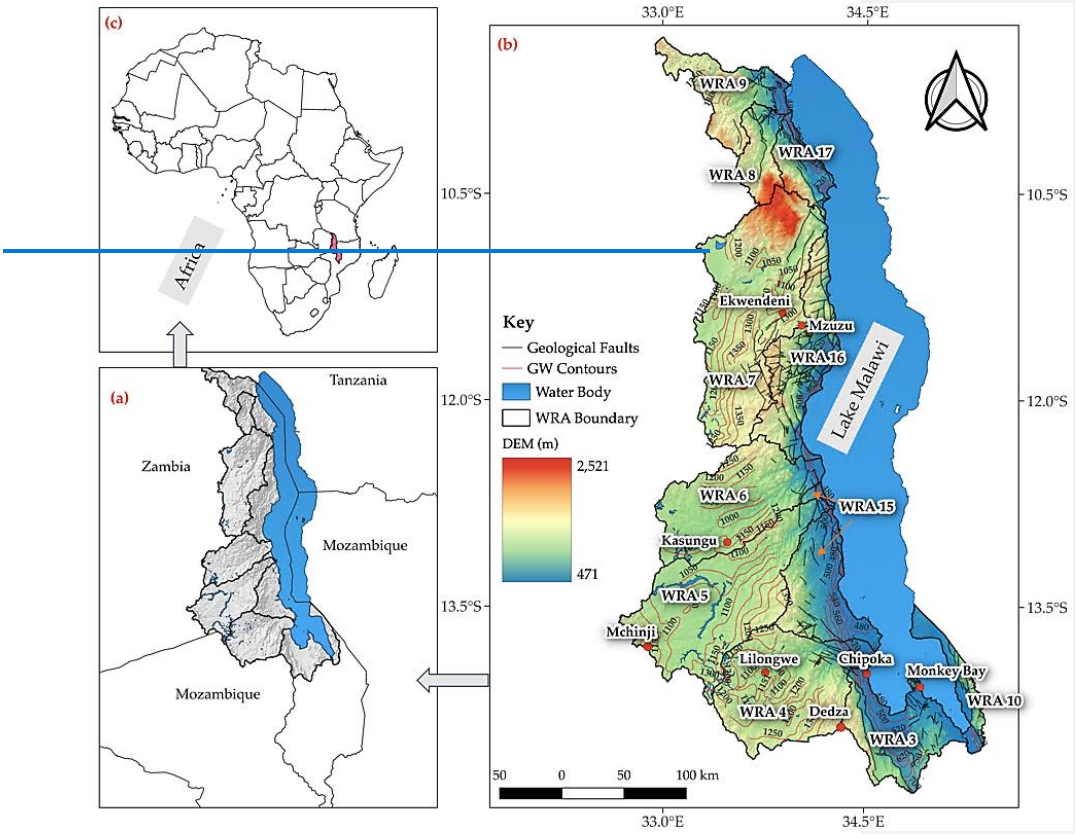

Figure 1 Study area showing (a) study area location in Malawi and its transboundary extent (Malawi, Mozambique, Zambia, and Tanzania), and (b) study area extent with water resources areas (WRAs) (c) Malawi location in Africa.

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2.1. Water Resources

Water resources in the study area consist of surface waters such as rivers, lakes, lagoons, and water reservoirs, as well as groundwater reserves found in aquifers [33]. The surface water and groundwater resources are, in part, shared across borders, requiring a multinational approach for equitable and sustainable management such as the 2004 ZAMCOM agreement. With a total of 49,032 groundwater points (community water supply boreholes and protected shallow wells) distributed across the basin, only approximately 85.8% are functional or partially functional [6]. The majority (63.8%) of these groundwater points consist of community water supply boreholes fitted with hand pumps, followed by protected dug wells [6]. Annual averaged surface runoff contributions to Lake Malawi are around 391 m^3/s (for Malawi), 486 m^3/s (for Tanzania), and 41 m^3/s (for Mozambique), with a mean outflow of 395 m^3/s [6]. ~~The~~ Lake Malawi's stand flu~~a~~ctuates between 471.5 ~~to~~ and 477 masl, with a range of 474 to 475.3 masl ~~rercored~~ recorded in 2022, contributing to an annual recharge input of 35.9 km^3 [6]. The highlands and catchment areas contribute to surface water runoff, which eventually replenishes rivers and streams flowing into Lake Malawi, with 63% of Malawi's surface runoff water

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discharging into ~~the~~ Lake Malawi [~~34~~33]. Key surface water storage reservoirs include Kamuzu ~~dam~~ Dam I and Kamuzu ~~dam~~ Dam II on Lilongwe River, with a combined supply capacity of 125,000 m³/day~~.~~, The Lunyangwa ~~dam~~ Dam on the Lunyangwa River ~~with~~ has a supply capacity of 25,900 m³/day [~~35~~34], and the Bwanje Valley D~~d~~am on the Naminkokwe River ~~with~~ has a supply capacity of 5.6 million m³ [30]. The Kamuzu D~~d~~ams primarily supply water to Malawi's capital, Lilongwe, while the Lunyangwa D~~d~~am serves Mzuzu City, Ekwedeni township, and other surrounding areas. The Bwanje V~~v~~alley D~~d~~am supports the Bwanje V~~v~~alley irrigation scheme, providing a water supply source, hydropower generation potential, and environmental flows. Other water storage reservoirs include the Chitete D~~d~~am in the Kasungu township and the Lusa D~~d~~am in Mchinji, which are mainly used for water supply, irrigation, and supporting small-scale fish farming for rural livelihoods.

2.2. Topography

The Lake Malawi basin has a diverse topography, ranging in altitude from 471 to 2521 m, with a mean of 1102 masl (Figure 2a). It consists of highlands, plateaus, rift valley escarpments, rift valley plains, and rift valley floors (Figure 2b). Notable ~~highland features~~highland features include Dedza mountain, the Dzalanyama range, the Mchinji highlands, the Viphya mountains, and the Nyika highlands, ~~that~~ which vary from 667 to 2521 m, with a mean elevation of 1618 m asl. The plateaus primarily feature gentle slopes, including wetland ecosystems locally known as '*dambos*' that easily flood with no well-defined channels. The *dambos* play a significant role in groundwater storage and subsequent draining within the plateaus. The Kasungu–~~-~~Lilongwe plain is the most extensive plateau, covering *ca* 6000 km² and ranging in altitude from 1000 to 1800 m asl [30]. This area is predominantly agricultural, with few remaining areas of indigenous savannah scrub woodlands and forests. The underlying strata of the plateaus consist mainly of colluvium overlying in ~~-~~situ layers of saprolite (weathered bedrock) [15]. The rift valley escarpment spans from north to south, containing rivers that erode the rift valley scarp as they flow into the rift valley plain, exposing the bedrock [13]. The escarpment varies in altitude from 480 to 2035 m, with a mean of 924 m asl. The western Lake Malawi shoreline is dominated by the rift valley plain, featuring steep sloping land between the Lake and plateaus. The rift valley plain ranges in altitude from 471 to 1550 m, with a mean of 574 m asl. The rift valley floor encompasses the Lake Malawi basin and its surrounding walls, including rocky slopes and escarpments. It also includes a series of terraces that slope from the rift valley walls towards the Lake Malawi shoreline [~~36~~35]. The topography significantly impacts climate, hydrology, groundwater occurrence, and population distribution~~,~~ and influences water supply demands.

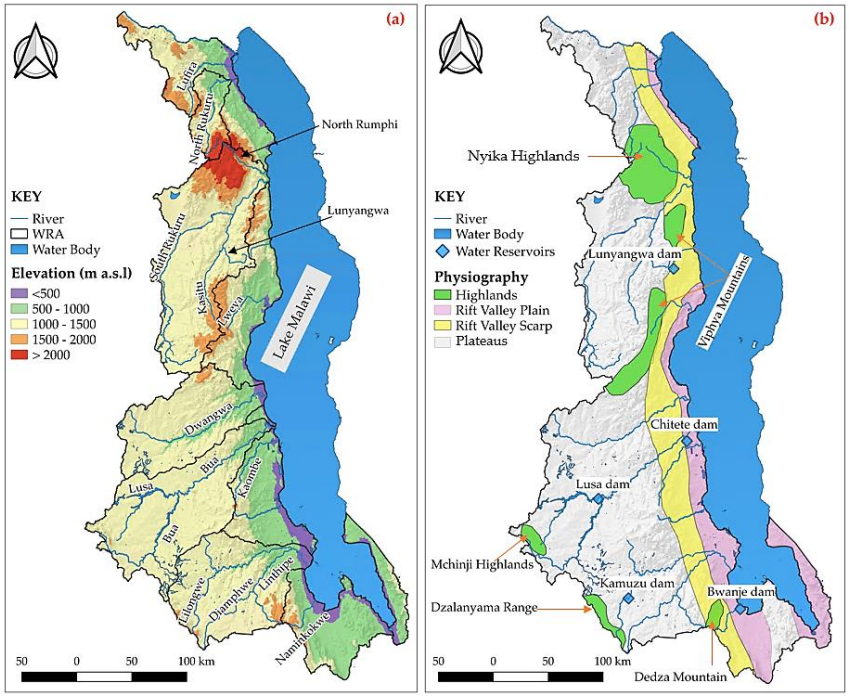

Figure 2. Study area showing (a) topography (SRTM elevation data:USGS) and main drainage systems and (b) physiographic zones and water reservoirs.

2.3. Geological Setting

The Lake Malawi basin is a rift valley basin mostly made up of basement complex rocks, constituting ~~of~~ metamorphic and igneous rocks from the late Precambrian to lower Paleozoic periods [~~37~~36]. The geological successions across the basin include Quaternary Alluvium and Colluvium, Cretaceous to Pleistocene formations, Jurassic Age Chilwa Alkaline Province formations, ~~and~~ Jurassic Age Karoo Stromberg Volcanic formations, the Karoo Sedimentary Series from the Permo-Triassic period, and the Basement Complex formations from the Late Precambrian and Lower Paleozoic periods [~~37~~36]. The basin is characterised by various geological processes such as escarpment formation, faulting, fracturing, erosion, rift valley floor development, and sedimentation [~~38~~37]. There are major faults occurring from north to south and north-northwest to south-southwest, with notable fault lines along Lake Malawi [~~39~~38]. The~~-~~ g~~G~~eological features of the basin exhibit a dynamic environment where geological and geomorphological processes are continuously occurring~~,~~ with a potential influence on its hydrogeology [~~40,41~~33]. The presence of basement-complex rocks, consisting of late Precambrian to lower Paleozoic metamorphic and igneous rocks, forms the basin foundation, resulting in low-yielding aquifers. However, the weathered zones of these aquifers, about 15–30 m thick in plateau areas, serve as important sources of domestic water supplies [~~41~~33]. Uplift and erosion resulting from the rift valley's development have reduced aquifer thickness, especially along escarpment crests and near bedrock outcrops, impacting groundwater availability. Alluvial deposits beneath lakeshore plains, formed by sedimentation from rivers and the lake, create high-yielding aquifers with varied characteristics both vertically and laterally. The

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fracture zones of the rift valley escarpment, formed by faulting and fracturing processes which increase permeability and water flow, create medium-yielding aquifers [~~39~~38]. Ongoing geological processes, such as faulting, fracturing, erosion, and sedimentation, continuously impact aquifer permeability, storage capacity, and water resource availability [~~38~~37]. Thus, an understanding of the geological characteristics and processes is crucial for effectively managing and sustaining the water resources of the basin.

2.4. Hydrogeological Setting

The ~~hydrostratographic~~ hydrostratigraphic units within the aquifer system of the Lake Malawi basin encompass a weathered and fractured basement, as well as consolidated and unconsolidated sedimentary units (Figure 3). These units constitute three primary aquifer groups: c~~C~~onsolidated sedimentary rock, unconsolidated sedimentary units overlying weathered basement, and weathered basement overlying fractured basement [6]. The unconsolidated sedimentary units overlying weathered basement aquifer constitutes intergranular pore spaces that facilitate groundwater transmission. The weathered basement units overlying fractured basement aquifer comprises intergranular pore spaces, fissures, fractures, and joints that enable groundwater flow. The consolidated sedimentary rock largely constitutes sandstone and shale, while the unconsolidated sedimentary units overlying weathered basement aquifer is mostly made up of colluvium and alluvium. The weathered basement overlying fractured basement aquifer mostly constitutes charnockitic gneiss and hornblende-biotite-gneiss. The basement complex is~~,~~ a primary source of groundwater in Malawi, and its mineral content largely influences the groundwater quality in the basin. Key rock minerals include plagioclase, pyroxenes, feldspars, amphiboles, and biotite [~~42~~39]. These are largely natural sources of chemical species like calcium, magnesium, sodium, and potassium. Plagioclase minerals are sources of calcium and sodium during weathering, and the type of plagioclase in Malawi is more calcium-rich than sodium-~~ -~~rich ~~therefore.~~ Therefore, there is more calcium in groundwater as ~~they dissolve~~it dissolves [13]. The dissolution of mafic minerals releases magnesium ions (as well as iron and other ions) in groundwater, some of which bear ~~s~~ fluoride ions [12]. The consolidated sedimentary aquifers are found in the northern part, where ~~it~~ they occur~~s~~ sparsely, while the unconsolidated sedimentary units overlying the weathered basement group largely occur~~s~~ on~~in~~ the western side. The weathered basement units overlying the fractured basement aquifer group ~~is~~ are mostly found ~~in~~ on the eastern side, particularly along the rift scarp zones. Isolated outcrops of basement lithologies occur in the basin, with some folded exposures, especially along the Malawi–~~ ~~~~–~~Zambia border [6]**.** The Lake Malawi shoreline areas within the rift valley plain are ~~characterized~~ characterised by unconsolidated fluvium, colluvium, and alluvium sedimentary units where they overlay weathered basement units. The potential yield of the unconsolidated sedimentary units overlying the weathered basement aquifer is estimated to be around 20 L/s, while water supply boreholes within the weathered basement overlying the fractured basement aquifer have a lower yield of up to 2 L/s [13].

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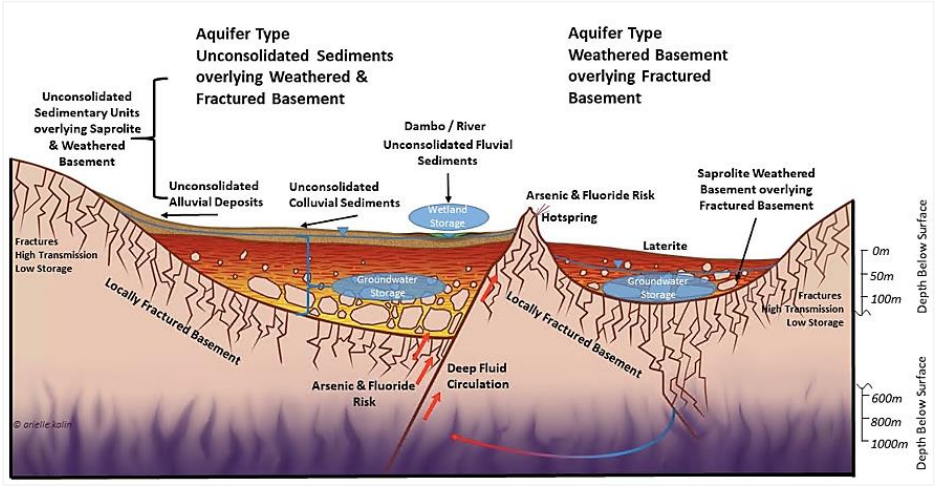

Figure 3. Idealised cross-section hydrostratographic units (aquifers) in the Lake Malawi basin (after [6]).

2.5. Climate

The Lake Malawi basin climate is classified as tropical-continental, influenced by various factors such as altitude, relief, and presence of Lake Malawi [6]. The Köppen–Geiger system categorises the climate as Aw or Savannah, described as "Not (Af) and Pdry < 100 − MAP/25", where Af is rainforest, MAP is mean annual precipitation, and Pdry is the precipitation of the driest month [43,40]. The basin has a dual-season system, with a wet season from November to April and a dry season from May to October. The dry season, driven by south-easterly winds, is mostly cool-dry from May to August and hot-dry from September to October. The wet season is influenced by north-easterly winds; the Intertropical Convergence Zone (ITCZ), the Congo Air Boundary (CAB), and Tropical Cyclones and accounts for ca 90% of annual precipitation [41,45,42]. The majority of rain falls between December and March, with January receiving the highest amounts in most areas of the basin. However, there is a contrasting pattern near the western shoreline of Lake Malawi, where peak precipitation is usually observed in March [46,43].

Annually, precipitation ranges from 623 to 1654 mm, averaging 927 mm. The rift valley plain, bordering Lake Malawi, receives the most rain, with a mean of 1036 mm, which is linked to lake effects [47,44] whereas the western plateaus exhibit more aridity, which is linked to topographic isolation. The basin's diverse relief and proximity to Lake Malawi have a significant impact on the spatial distribution of precipitation [47,44,48,45]. The mMean annual temperature ranges from 12.9 to 24.7 °C, averaging 20.5 °C. The Nyika highlands experience cooler temperatures, averaging 17.6 °C, whereas the rift valley lakeshore plain, with the lowest topographic extremes, experiences hotter temperatures, averaging 23.4 °C. The coldest months in the LMB are June and July, while the hottest months are October and November. The presence of Lake Malawi moderates the surrounding areas, resulting in a mean daytime temperature of 30.3 °C and a night-time temperature of 10.3 °C [49,46].

3. Materials and Methods

3.1. Sampling and Analytical Techniques

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Three groundwater sampling surveys were conducted between 2021 and 2022. The sampling design provided a representative geographical spread and balanced hydrogeological coverage. The sampling timelines captured seasonal and topographic effects on groundwater dynamics. Sampling coverage was constrained by ease of access, more so ~~in~~in the wet season when travel to remote or low-lying flood-prone areas was risky. Water samples were collected from boreholes, dug wells fitted with handpumps, and hot springs that were in constant use for water supply during sampling, and purged ~~where~~ when not in use to ensure the samples were representative.

Isotope hydrology *samples* (*n* = 327 subdivided into 160 wet season samples and 167 dry season samples) were collected in 50 mL high-density polyethylene (HDPE) bottles with inner caps, sealed with waterproof tape, preserved at 4 °C, and kept away from direct sunlight during transportation and at the laboratory. A set of samples ~~was~~ was analys~~z~~ed using a laser spectroscopy-based technique ~~by~~ using the Picarro isotopic water ~~analyzer~~ analyser (Model: L2140-*i*, Picarro Inc., Santa Clara, CA, USA) at the IAEA laboratory in Vienna, Austria. Another set of isotope hydrology samples was analys~~z~~ed using a Picarro isotopic water ~~analyzer~~ analyser (Model: L2110-*i*, Picarro Inc., Santa Clara, CA, USA) at the Central Water Laboratory in Lilongwe, Malawi. The isotope hydrology samples were ~~analyzed~~ analysed in non-consecutive duplicates in high-precision mode with dry synthetic air carrier gas. Each such analysis consisted of six injections. Lake Kyoga and Standard-09 (Greenland Ice) working reference materials (RMs) were enriched and depleted, respectively. The controls were Standard 11 (Monaco Lagoon) and Standard 06 (Heidelberg tap water) for quality assurance and quality control purposes. Data reduction was performed in the Laboratory Information Management System (LIMS) for lasers [~~50~~47] using residual memory correction after ignoring the first three injections. Two reference points were used to ~~normalize~~ normalise the Vienna Standard Mean Ocean Water (VSMOW)-Standard Light Antarctic Precipitation (SLAP) scale. The long-term deviation of control samples demonstrated that the measurements were accurate to within 0.1‰ or better for $\delta^{18}O$ and 0.5‰ or better for $\delta^{2}H$, and the isotope analysis results were reported as ratios compared to V-SMOW standards (Equation (1)).

$$\delta_{s/std} = \left(\frac{R_s - R_{std}}{R_{std}}\right) \times 1000 \quad (1)$$

In Equation (1), Rs is the isotopic ratio of the sample, Rstd is the isotopic ratio of the standard, and δ is the delta notation, where $\delta_{s/std}$ is reported in per mil (‰). The d~~D~~ parameter (d) was calculated from Dansgaard's equation [~~51~~48] ~~relating~~relating to the $\delta^{18}O$ and $\delta^{2}H$ of water, defined as $d = \delta^{2}H - 8\delta^{18}O$ ‰. The process of handling water samples, including onsite measurements, sample collection, transportation, holding, preparation, and analysis, followed the International Standard Procedures (ISP) [~~52~~49]. This adherence ensured the consistency and reliability of the isotopic data generated.

On-site measurements (electrical conductivity (EC), total dissolved solids (TDS), and pH) were conducted using a portable multi-meter (Model: HI-98194, Hannah Instruments, Woonsocket, RI, USA). A pair of water samples ~~was~~ were collected from each site, one acidified and the other non-acidified, using 1L polyethylene bottles rinsed with distilled water. The water quality samples (n = 727) were labelled, preserved at 4 °C during transportation and storage, and filtered through 0.45 μm Whatman filters prior to analysis at the laboratory. Anions (F, Cl, NO_3, and SO_4) were measured using ~~a~~ Metrohm ion chromatography (Model: 850 Professional IC, Metrohm, Switzerland), while cations (Na, K, Mg, Ca, Fe and Mn) were measured using an ~~inductively coupled~~inductively coupled plasma spectrometer (Model: iCAP 6200, Series Thermo-Fisher Scientific, Waltham, MA, USA) at the Environmental Analytical Laboratory of the University of Strathclyde in Glasgow, Scotland. Carbonate and bicarbonate were measured using a titrimetric method, while alkalinity was measured using a photometric ~~analyzer~~ analyser (Model: KONE Aquakem V.7.2.AQ2, Skalar, Netherlands). All field sampling, measurements and laboratory analyses were conducted in line with the ISP [~~53~~50], and the accuracy of the

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hydrochemical analysiis ~~was~~ was validated using the ionic balance method, adhering to an allowable ionic balance error (IBE) of ± 5% (Equation (2)) [5350].

$$\text{IBE\%} = \frac{\sum(\text{Cations} - \text{Anions})}{\sum(\text{Cations} + \text{Anions})} \text{ x } 100 \quad (2)$$

3.2. Computation of Gibbs Diagram, Chloro-Alkaline Indices, and Saturation Index (SI)

Gibbs diagram plots used the anionic weight ratio $Cl^-/(Cl^- + HCO_3^-)$ and cationic weight ratio $Na^+/(Na^+ + Ca^{2+})$ as functions of log-transformed TDS) [5451] and was used to identify ~~controlling~~ geochemical reactions controlling ~~of~~ groundwater chemical evolution in Lake Malawi basin. Schoeller chloro-alkaline indices, defined in Equations (3) and (4), were employed to refine evidence of cation exchange reactions and ascertain the nature and extent of their occurrence in groundwater within the Lake Malawi basin.

$$\text{CAI (I)} = \frac{Cl^- - (Na^+ + K^+)}{(Cl^-)} \quad (3)$$

$$\text{CAI (II)} = \frac{Cl^- - (Na^+ + K^+)}{(HCO_3^- + CO_3^{2-} + SO_4^{2-} + NO_3^-)} \quad (4)$$

In Equations (3) and (4), ~~I~~if the CAI-I and CAI-II are less than zero, the cation exchange is a forward reaction. If the CAI-I and CAI-II are greater than zero, the cation exchange is a reverse reaction [5852]. The s~~S~~aturation index (SI) was used to evaluate the equilibrium state with respect to groundwater and solid mineral phases [5355–5855]. The SI, defined in Equation (5), was calculated using PHREEQC software (version 3.7.3), which calculates the logarithm of the ratio between ion activity product (IAP) and solubility product (Ksp) [5956].

$$\text{SI} = \log\left(\frac{\text{IAP}}{K_{sp}}\right) \quad (5)$$

In Equation (57), IAP = ion activity product, K_{sp} = solubility product, where an SI equal to zero indicates an equilibrium state. If the SI is less than zero, the groundwater is undersaturated with respect to the mineral phase, and there is potential for mineral dissolution. When the SI is greater than zero, the groundwater is oversaturated.

4. Results

4.1. Hydrogeochemical Characteristics

The g~~G~~roundwater pH ranged~~s~~ from acidic to alkaline (pH: 4.5–9.4), with a mean of 6.9~~,~~ and a median of 6.4. The Total dissolved solids (TDS) va~~r~~ried~~,~~ widely from~~:~~ 23 to 2662 mg/L~~)~~, with a mean of 305 mg/L and a median of 210 mg/L (Figure 4, Supplementary Material (SM)~~.~~ ~~—~~Table S1). The d~~D~~ominant cations were~~are~~ calcium, sodium, and magnesium, with considerable variation. The majority of groundwater samples (88%) had TDS below 600 mg/L, which falls within the World Health Organi~~s~~zation (WHO) recommended guidelines for good taste. The remaining 12% ~~have~~ had elevated TDS concentrations~~,~~ exceeding 1000 mg/L [6057]. While most groundwater samples were aligned with the WHO's recommended guidelines, there ~~are~~ were cases where the groundwater may not fully meet the taste and palatability expectations. Bicarbonate, chloride, and sulphate ~~are~~ were the dominant anions, with nitrate~~,~~ and fluoride present at generally low to moderate concentrations.

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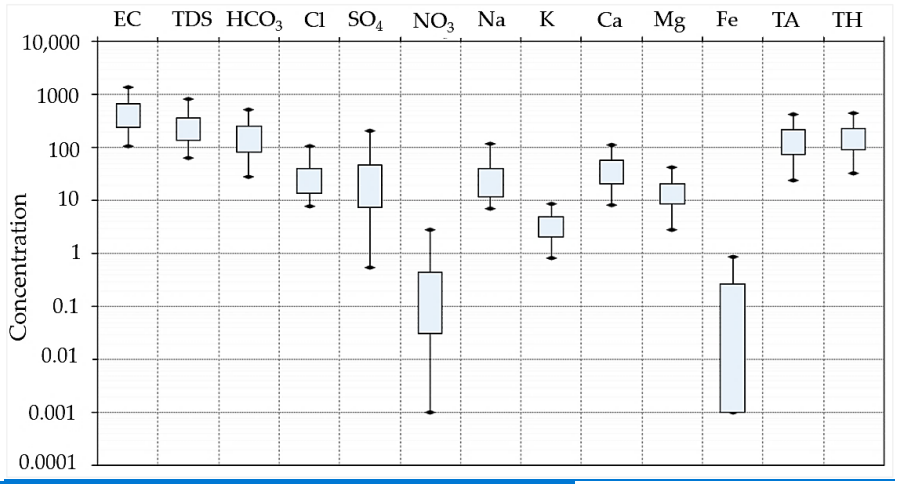

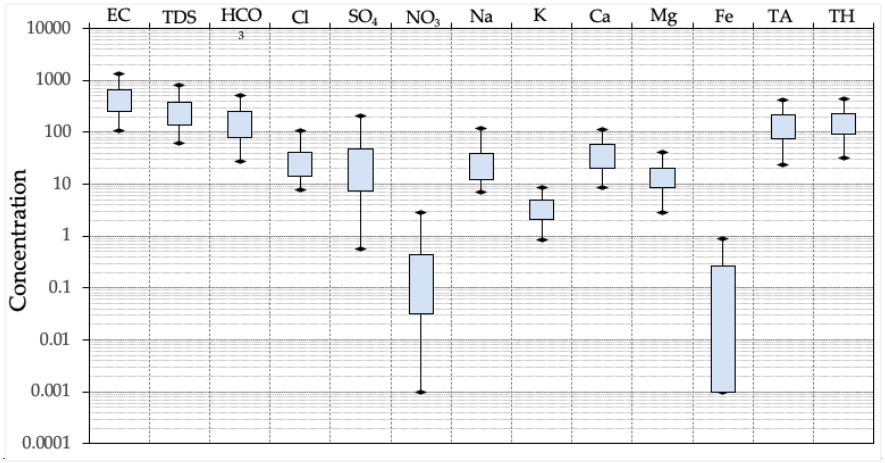

Figure 4. Observed hydrochemical interquartile plot for groundwater in Lake Malawi basin: It shows the distribution of electrical conductivity (EC) (μS/cm), total dissolved solids (TDS) (mg/L), total alkalinity (TA) as $CaCO_3$ (mg/L), total hardness (TH) as $CaCO_3$ (mg/L), and major ions (mg/L) in groundwater.

Previous studies reported arsenic occurrence [11] and widespread risks of fluoride [12] in groundwater. This study ~~has~~ found that nitrate ~~is~~ was ubiquitous in groundwater, detected~~able~~ in most of the groundwater points (93.1%) and varied~~ying~~ widely from <0.001 to 235 mg/L, with isolated outliers recorded in the northern part of the basin (Figure 5a). The nitrate concentrations ~~are~~ were generally consistent with the recommended WHO guidelines for drinking water (Figure 5b). Given there is no natural source of nitrate in Malawi's groundwater, the ubiquitous nature of this contaminant points towards human-induced pollution. This highlights a critical need to model nitrate-related contamination sources across the country, considering a surge in likely sources, including pit latrines,

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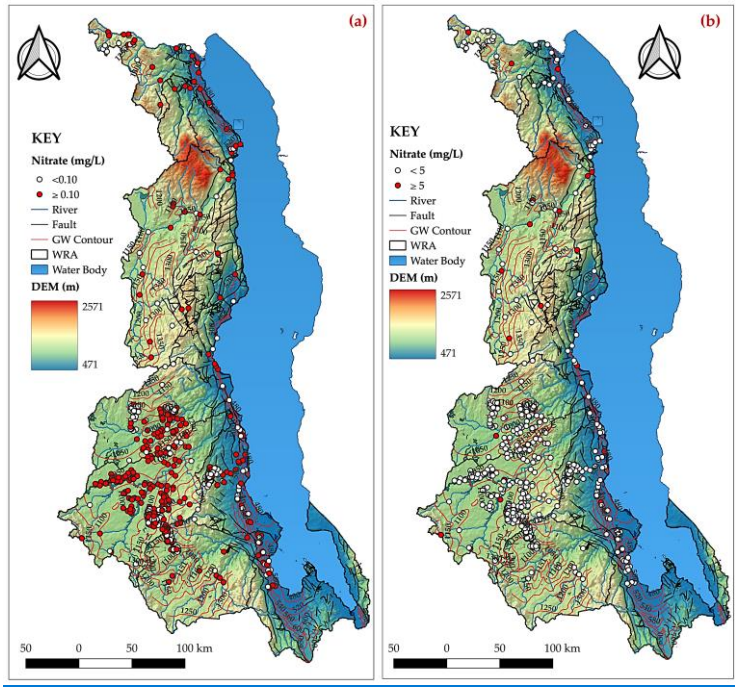
septic systems, and extensive fertiliser use due to SDG 6 drivers and the current population boom.



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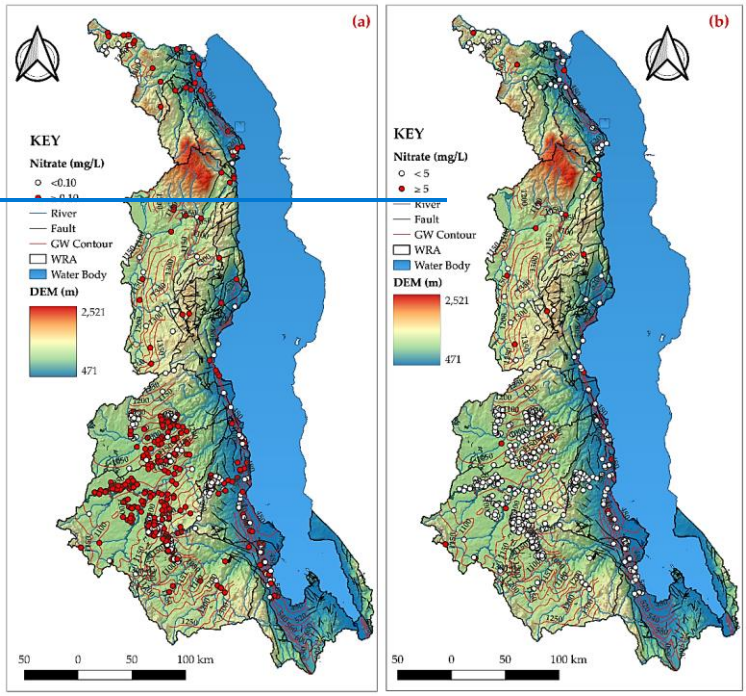

Figure 5. Spatial distribution of nitrate concentrations in groundwater across the LMB.(a) shows general distribution of measurable nitrate and (b) shows measurable nitrate concentration projecting potential impact.

4.2. Hydrogeochemical Facies

A Piper plot was used to examine groundwater hydrogeochemistry, delineating distinct hydrogeochemical facies based on dominant cationic and anionic species [61~~,~~58]. This approach refined the understanding of the hydrogeochemical signatures of Lake Malawi basin groundwater and how minerals in the host rock matrix impact the groundwater along its ~~flow~~flow -path. The c~~C~~lassification of hydrogeochemical facies identified five groundwater types (Figure 6): (1) Ca-Mg-HCO_3, (2) Ca-Mg-SO_4, (3) Na-Cl, (4) Ca-Mg-SO_4-Cl, and Na-HCO_3-Cl (5). The most prevalent groundwater type ~~is~~ was Ca-Mg-HCO_3, comprising 73.9% of the groundwater samples. This dominance suggests groundwater evolves from recharge through geochemical reactions with primary silicates and secondary carbonates and/or high-Mg dolomitic carbonate rock matrices~~x~~. The c~~C~~lose proximity of distinct hydrochemical facies suggests groundwater mixing from multiple sources, supported by the presence of mixed water types (Ca-Mg-SO_4 and Na-HCO_3-Cl). A mixing trend observed in a cation ternary diagram (Figure 6) suggests cation exchange reactions, increasing the dissolved sodium concentration by exchanging ~~for~~ with calcium ~~onto~~ in clays.

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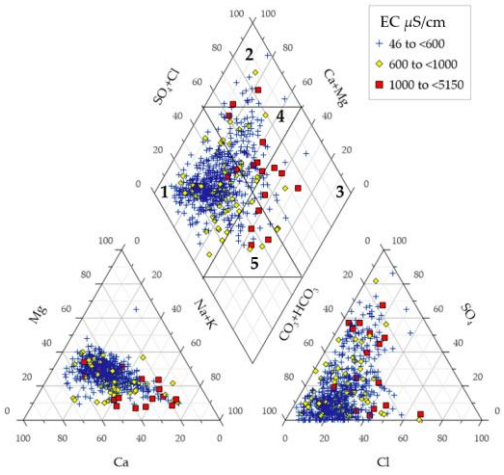

Figure 6. Piper plot for groundwater samples: Various colours show hydrochemical facies based on electrical conductivity (EC), a proxy indicator of total dissolved salts (TDS).

~~Spatial~~ The spatial distribution of the water types aligned~~s~~ with the TDS, exhibiting greater uniformity in highland ~~-~~plateau areas and more inhomogeneity in low-lying areas, especially in the lakeshore and flood plains (Figure 7a,b). This inhomogeneity suggests the influence of various factors, such as the seepage of surface water into groundwater, ~~and~~ the presence of older groundwater with higher calcium or sodium concentrations due to prolonged travel time, and the ~~mineral~~ dissolution of minerals resulting in calcium, sodium, and magnesium in solution.

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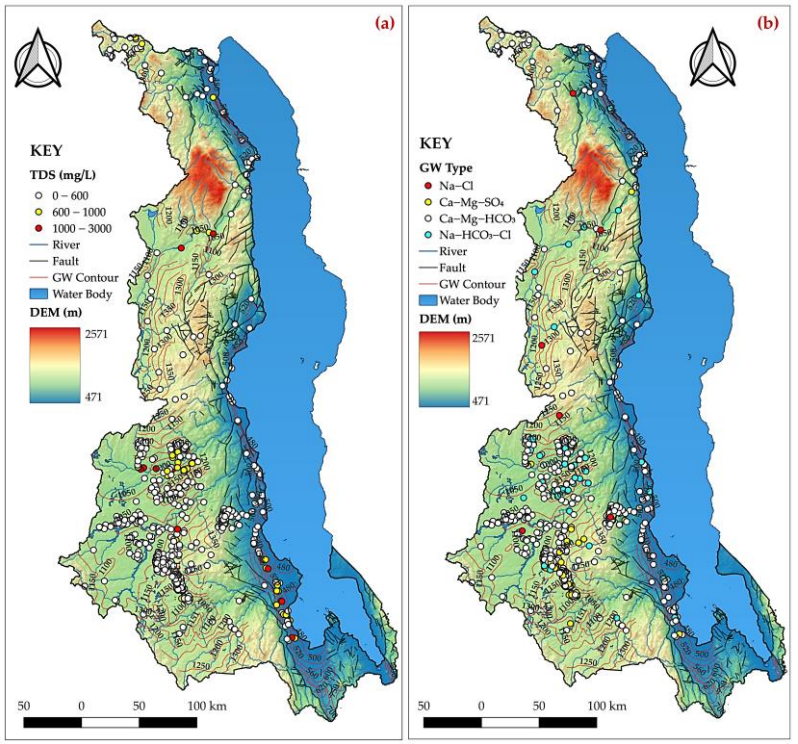
(a)
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TDS (mg/L)
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1000 – 3000
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(b)
KEY
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Na–Cl
Ca–Mg–SO4
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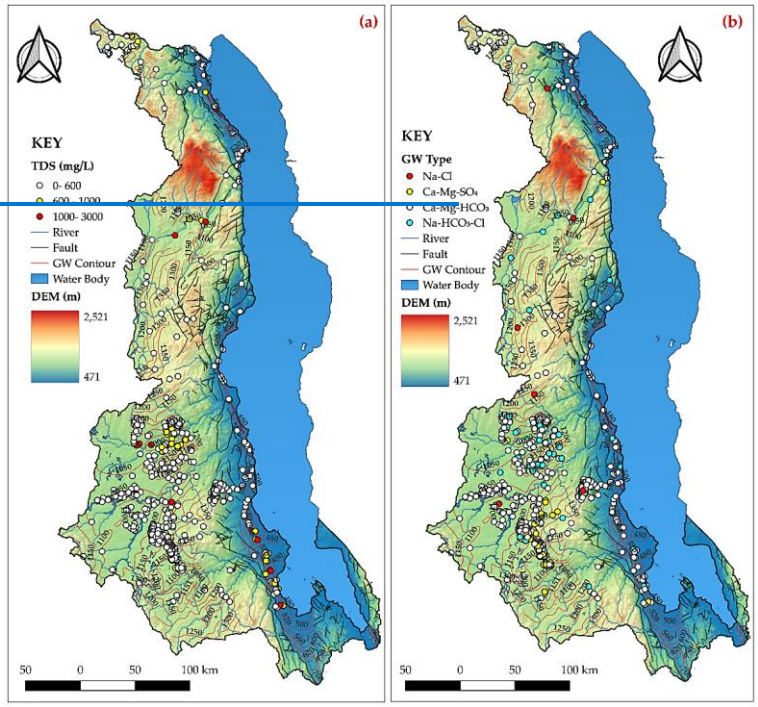

Figure 7. Spatial distribution of (a) TDS and (b) water types in groundwater across LMB.

4.3. Mechanisms Controlling Mineral Enrichment

Groundwater mineral enrichment is influenced by geochemical reactions (e.g., evaoration, precipitation, and mineral weathering) along a flow path [~~62~~29]. The Gibbs diagram (Figure 8) identifies water–rock mineral reactions as the dominant geochemical mechanism controlling groundwater mineral enrichment. It also depicts an increasing cationic weight ratio $Na^+/(Na^+ + Ca^{2+})$ with a corresponding minimal change in the TDS, suggesting cation exchange as another controlling geochemical reaction. Tables 1 and S5 display various rock minerals and their respective interactions with water, resulting in the release of ionic species into groundwater that influence its chemical composition.

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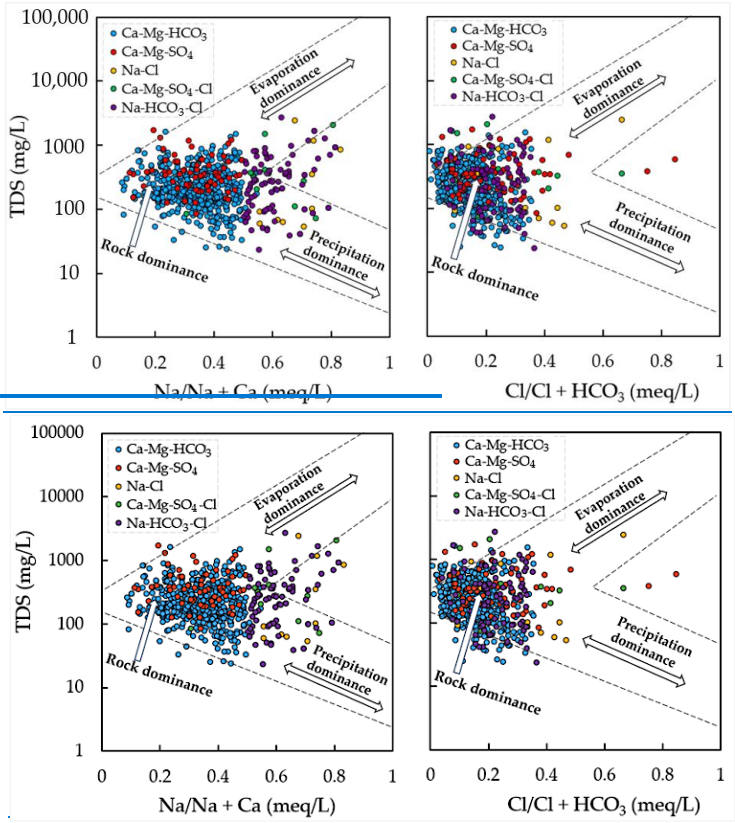

Figure 8. Gibbs diagram showing key mechanisms controlling groundwater chemistry.

Table 1. Natural sources of ionic species in groundwater present in Lake Malawi basin aquifers.

Mineral/Ion Species Source	Chemical Formulae	Ionic Species	Reaction Type
Carbon Dioxide (CO_2)	CO_2 ($+H_2O$)	H^+, HCO_3^-	Congruent
Plagioclase	$(Na,Ca)(Al,Si)_4O_8$	Ca^{2+}, Na^+	Incongruent
Anorthite	$CaAl_2Si_2O_8$	Ca^{2+}, HCO_3^-	Incongruent
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$	K^+, Mg^{2+}, F^-	Incongruent
Calcite	$CaCO_3$	Ca^{2+}, CO_3^-, HCO_3^-	Congruent
Albite	$NaAlSi_3O_8$	Na^+	Incongruent
Muscovite	$KAl_2(AlSi_3O_{10})(F,OH)_2$	K^+, F^-	Incongruent
Olivine	Mg_2SiO_4	Mg^{2+}	Incongruent
Amphiboles	$Ca_2(MgFeAl)_5(AlSi)_8O_{22}$	Mg^{2+}, Ca^{2+}	Incongruent
Fluorapatite	$Ca_5(PO_4)_3F$	Ca^{2+}, F^-, PO_4	Incongruent
Fluorite	CaF_2	Ca^{2+}, F^-	Congruent
Pyrite	FeS_2	SO_4^{2-}	Incongruent

The ~~c~~Calcium vs. bicarbonate (Ca^{2+}/HCO_3^-) weight ratio was used to examine carbonate mineral-related geochemical reactions (e.g., the dissolution of calcite and apparent

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high-Mg dolomitic carbonate controlled by the dissolution of Mg-silicates and plagioclase) controlling Lake Malawi basin groundwater mineral enrichment. The results identifieds high-Mg dolomitic carbonate dissolution as a controlling geochemical reaction, revealed by the clustering of groundwater data within 1:1 and 1:2 HCO_3^-/Ca^{2+} weight ratios (Figure 9a).

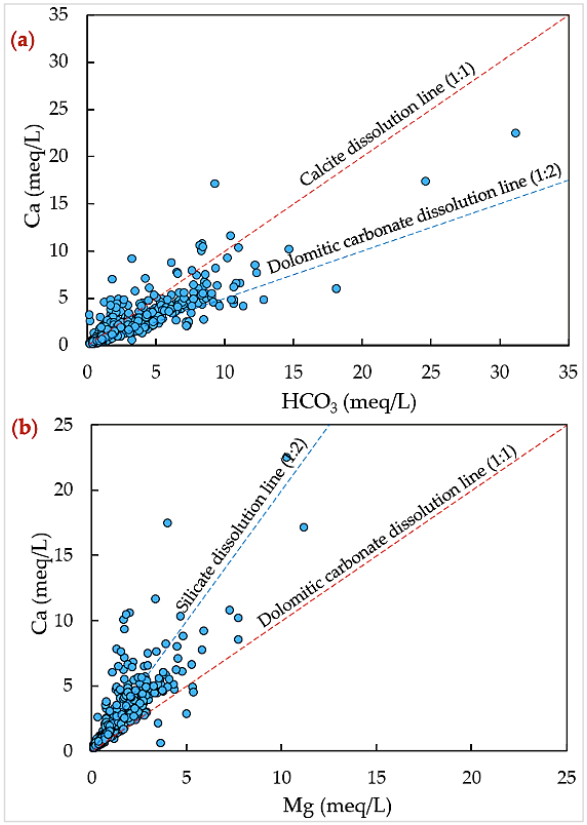

Figure 9. Relationship between major ion concentrations of groundwater samples, (a) Ca^{2+} vs. HCO_3^-, and (b) Ca^{2+} vs. Mg^{2+}.

~~Calcium~~ The calcium vs. magnesium (Ca^{2+}/Mg^{2+}) weight ratio was used to further examine the carbonate and silicate mineral-related geochemical reactions controlling the Lake Malawi basin groundwater mineral enrichment. The results identifieds dolomitic carbonate dissolution and calcium or magnesium silicate dissolution as the controlling geochemical mechanisms of groundwater mineral enrichment (Figure 9b), revealed by a dominant Ca^{2+}/Mg^{2+} weight ratio greater than 1:1, clustering within 1:2 equiline. A groundwater data subset~~,~~ plotteds above the 1:1 equiline for the Ca^{2+}/Mg^{2+} weight ratio~~,~~ suggeststing excess Ca^{2+} derived from other geochemical reactions.

Cation exchange reactions were examined using the linear relationship of adjusted calcium and magnesium concentrations ($Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-}$) vs. sodium and potassium adjusted concentrations ($Na^+ + K^+ - Cl^-$) to refine the cation exchange reaction

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controlling insights. The aforementioned adjustments were made to eliminate any potential influence deriving from silicate weathering, gypsum (unlikely), and halite (unlikely) dissolution reactions. The resulting slope for the linear relationship agrees with the expected ideal slope of −1, suggesting silicate mineral reactions with forward cation exchange ~~reaction~~ reactions (Figure S1a) [~~63~~59]. The Schoeller chloro-alkaline indices (CAI-I; CAI-II) calculated based on Equations (3) and (4) suggest the dominant occurrence of cation exchange forward reaction influencing groundwater mineralisation (Figure S1b).

4.4. Geochemical Modelling

Geochemical modelling identified probable reactions controlling chemical evolution and chemical changes resulting from such reactions [~~64~~29]. The saturation index (SI) calculated based on Equation (5) provided insights into an equilibrium state with respect to groundwater and solid mineral phases [53–55]. The results showed that groundwater from 58% of the samples ~~is~~ was undersaturated ($SI_{calcite}$: −2.8 to 0) with respect to mineral phase calcite ($CaCO_3$), while the remaining 42% ~~is~~ was at equilibrium or oversaturated ($SI_{calcite}$: 0 to 1.9) with respect to mineral phase calcite ($CaCO_3$) (Figure 10a). The negative $SI_{calcite}$ suggests a thermodynamic potential for calcite to dissolve in the groundwater. The positive $SI_{calcite}$ suggests conditions likely to reverse the reaction, resulting in the precipitation of calcite from the solution phase. The $SI_{calcite}$ near zero or remaining as a constant down gradient along the groundwater flow path suggests apparent equilibrium conditions in the groundwater system (where the mass transfer precipitation/dissolution of carbonate minerals continues as silicate weathering occurs). The negative $SI_{calcite}$ is associated with groundwater recharge in highlands, which is characterised by low pH. The positive $SI_{calcite}$ is associated with high groundwater pH, likely influenced by the weathering of silicate minerals, raising carbonate ions (CO_3^{2-}) while reducing hydrogen ions (H^+). It should be noted that the s~~S~~aturation i~~I~~ndex for carbonate species is co-dependent on an accurate field measurement of alkalinity, ~~and~~ pH, ~~and~~ temperature (in -situ), and pCO_2; thus, with uncertainty, the slightly positive values may, in fact, be in equilibrium. Given calcite is generally not kinetically hindered, the results shown in Figure 10a likely, therefore, converge to equilibrium (through the precipitation of carbonate phases or, where highly undersaturated, dissolution).

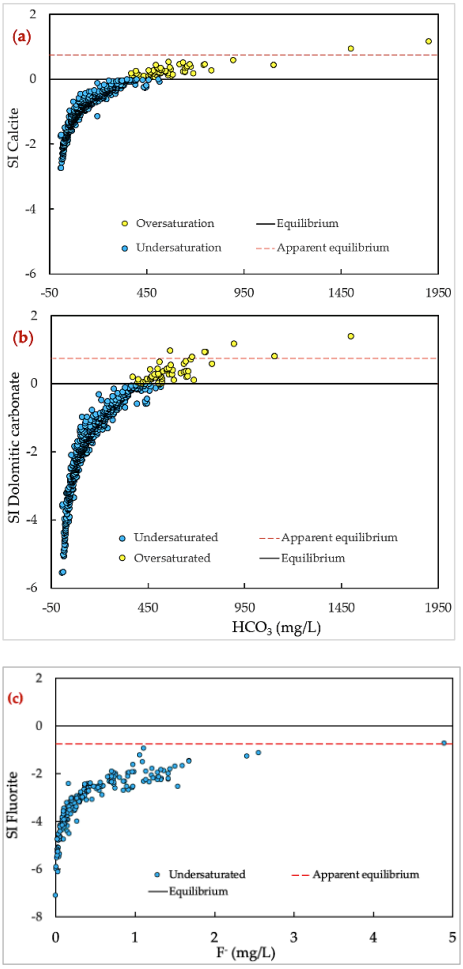

Figure 10. Saturation ~~i~~Indices (SI) for (a) calcite, (b) ~~for~~ dolomitic carbonate, and (c) fluorite from groundwater samples in the Lake Malawi basin.

Groundwater from 61% of the samples exhibited undersaturation conditions ($SI_{dolomitic\ carbonate}$: −5.6 to 0) with respect to mineral phase dolomite ($CaMg(CO_3)_2$), which here is considered the end-member of a high Mg dolomitic carbonate (the source of Mg most likely from the incongruent dissolution of ferromagnesian silicate minerals). The remaining 39% exhibited oversaturation ($SI_{dolomitic\ carbonate}$: 0 to 3.6) with respect to mineral phase dolomite (Figure 10b). The negative $SI_{dolomitic\ carbonate}$ suggests a thermodynamic potential for a high Mg dolomitic carbonate to dissolve in groundwater. The positive $SI_{dolomitic\ carbonate}$ suggests conditions are likely to reverse the reaction, resulting in high Mg carbonate precipitation from the solution phase. The p~~P~~recipitation of dolomite is kinetically hindered, and, therefore, high SI values may be due to slow rates of high Mg carbonate precipitation. These geochemical reactions suggest the presence of carbonate minerals~~,~~ undergoing

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continuous dissolution and precipitation in groundwater. The SI ranges for Gypsum ($CaSO_4.2H_2O$) (SI_{gypsum}: −6.9 to −0.4) indicate this evaporite mineral is not actively involved in geochemical reactions but is able to dissolve in the Lake Malawi basin groundwater should it locally exist (Figure S2). Given there is no current geologic evidence for the occurrence of these minerals, a detailed mineralogic analysis of aquifer materials is needed, and thermodynamic interpretation should be avoided.

It is possible that deep fluid flow (hidden hot springs) is also a source of sulphate and fluoride and requires further investigation [~~65~~60]. The SI of Fluorite (CaF_2) spanned~~s~~ from −8.8 to −0.8, approaching apparent equilibrium. This trend may be a common ion effect with calcite (Figure 10a,c), but given the increasing concentrations of fluoride, there is a need for further substantiating evidence of deep fluid circulation from geothermally active areas, herein the source of fluoride ions in groundwater [~~65~~60].

4.5. Isotope Hydrology Characteristics

4.5.1. Precipitation Stable Isotope Signatures

The isotope hydrology of precipitation in the Lake Malawi basin was ~~measure~~ measured on samples collected at four observatory stations as part of the Malawi Network of Isotopes in Precipitation (MNIP) (Table S2). The precipitation δ^2H signatures (n = 91) ranged from −111.2‰ to +12.4‰, with a mean of −35.6‰, and $\delta^{18}O$ signatures ranged from −14.3‰ to +1.0‰, with a mean of −6.1‰ (Figure 11a,b; Table S3). The p~~P~~recipitation d-parameter ~~is~~ was distributed between −2.2‰ and +19.3‰, with a mean of +13.3‰. The mean d-parameter of +13.3‰ showed~~s~~ that the recycling of atmospheric moisture by large-scale evaporation process off Lake Malawi ~~is~~ was highly likely, a proxy indicator of an isotopic offset of the local air mass from the global air mass (Figure 11a). This isotopic offset ascribed to the d-parameter in precipitation is consistent with the African Great Lakes region isotopic effect.

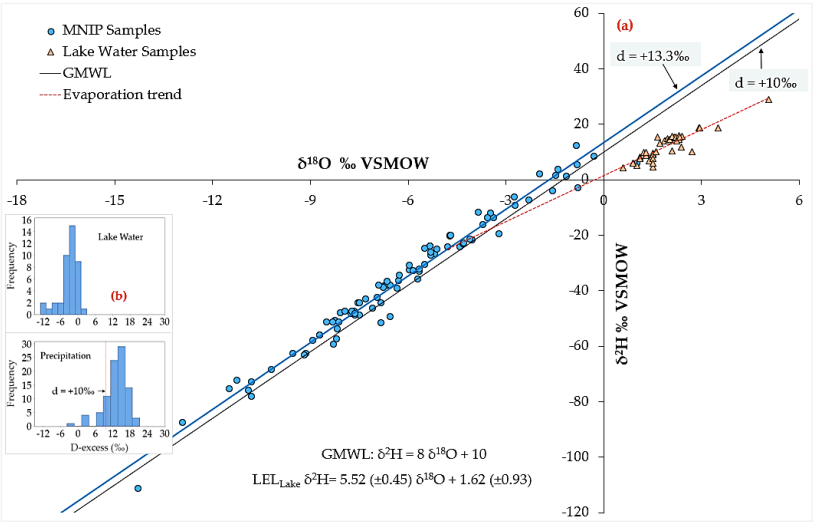

Figure 11. (a) Plot of δ^2H–$\delta^{18}O$ signatures for precipitation samples from MNIP stations and lake sites in the Lake Malawi basin. A blue line (slope of 8; d-parameter of +13.3‰) represents the distribution of the d-parameter for local precipitation, a proxy for an isotopic offset of local air mass from the global air mass represented by the Global Meteoric Water Line (GMWL). The red line represents

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the lake evaporation line (LEL). (b) Histogram providing the distribution of d-parameter for precipitation and lake water samples.

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The wide range of measured isotopes (range: +123‰ for $\delta^{2}H$, +15.3‰ for $\delta^{18}O$) is attributed to controlling factors such as evaporation, different moisture sources, and the influence of Lake Malawi producing spatial and seasonal variations [30,~~45~~42,~~47~~44,~~48~~45].

4.5.2. Groundwater Stable Isotope Signatures

Groundwater $\delta^{2}H$ range from -47.4 ‰ to −15.8 ‰, with a ~~of~~ mean of −34.6‰, and $\delta^{18}O$ ranged from -8.9‰ and −2.5‰, with a ~~of~~ mean of −5.6‰ (Figure 12a; Table S4). The d~~D~~-parameter ranged~~s~~ from −10.5 to +28.6‰, with a ~~of mean~~mean of +10.0‰ (Figure 12b). Most groundwater samples, ~~categorized~~ categorised as Group G1, ~~are~~ were depleted in heavier isotopes and aligned ~~–~~with the Global Meteoric Water Line (GMWL), suggesting groundwater recharge from modern non-evaporated local meteoric waters (Figure 12a). This is ~~refined~~ defined by the mean groundwater signatures corresponding to the mean precipitation signatures. A subset of samples, Group G2, deviated~~s~~ below the GMWL, exhibiting isotopic enrichment, prominent during the 'dry season'~~,~~ in low-lying and near-lake sites, ascribed to secondary evaporative fractionation. The secondary evaporative fractionation prior to groundwater recharge occurs either during the initial runoff preceding infiltration, within the groundwater body itself, or from infiltrating ~~the~~ isotopically enriched surface water (e.g., from irrigation return). The Group G2 could also be influenced by deep-seated hydrothermal waters (Figure 12c). The Group G3 samples plot above the meteoric water line. Precipitation, which comes from moisture in a closed evaporative basin and/or ~~are~~ is initially snow, may have significantly enhanced the d-parameter for this group [~~66~~61,~~67~~62]. Recent studies of $\delta^{17}O$ further elucidate~~s~~ these effects, and future studies~~y~~ of $\delta^{17}O$ in precipitation in the African Great Lakes region ~~is~~ are highly warranted [~~68~~63].

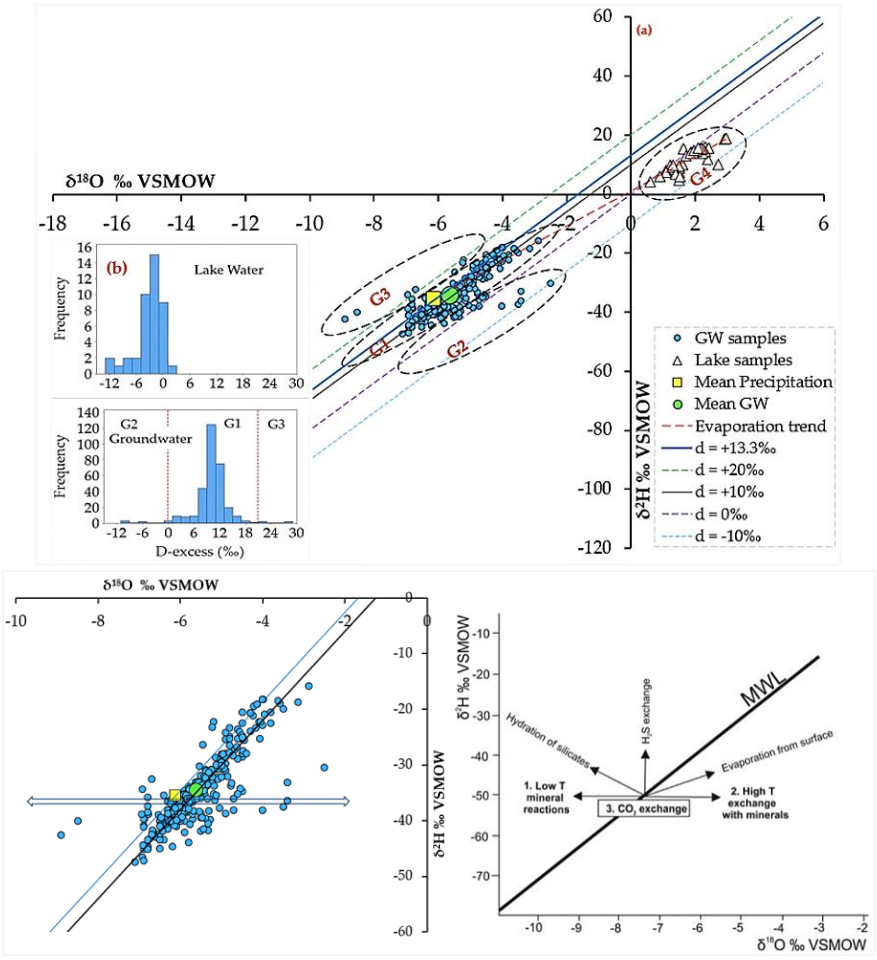

Figure 12. (a) Plot of δ^2H–$\delta^{18}O$ signatures for groundwater and lake samples in Lake Malawi basin. (b) Histogram showing the distribution of the d-parameter for groundwater and lake water samples. (c) Plot of δ^2H–$\delta^{18}O$ signatures for groundwater samples and associated controlling process influencing isotopic signatures in Lake Malawi basin.

Overall, the mean $\delta^{18}O$–δ^2H signatures of groundwater ~~are~~ were consistent with the mean $\delta^{18}O$–δ^2H signatures of modern local precipitation. The evaporation trend in Figure 12a is a proxy indicator of lake water and groundwater mixing, suggesting lake water infiltration to the aquifer and groundwater discharge to the lake water system.

4.5.3. Dynamics: Spatial Distribution and Seasonal Effects

The spatial distribution of δ^2H–$\delta^{18}O$ signatures aligns with geographic expectations, with enriched δ^2H–$\delta^{18}O$ signatures predominant in low-lying and near-lake sites~~,~~ and depleted δ^2H–$\delta^{18}O$ signatures dominant in highland -plateau sites (Figure 13). Nonetheless,

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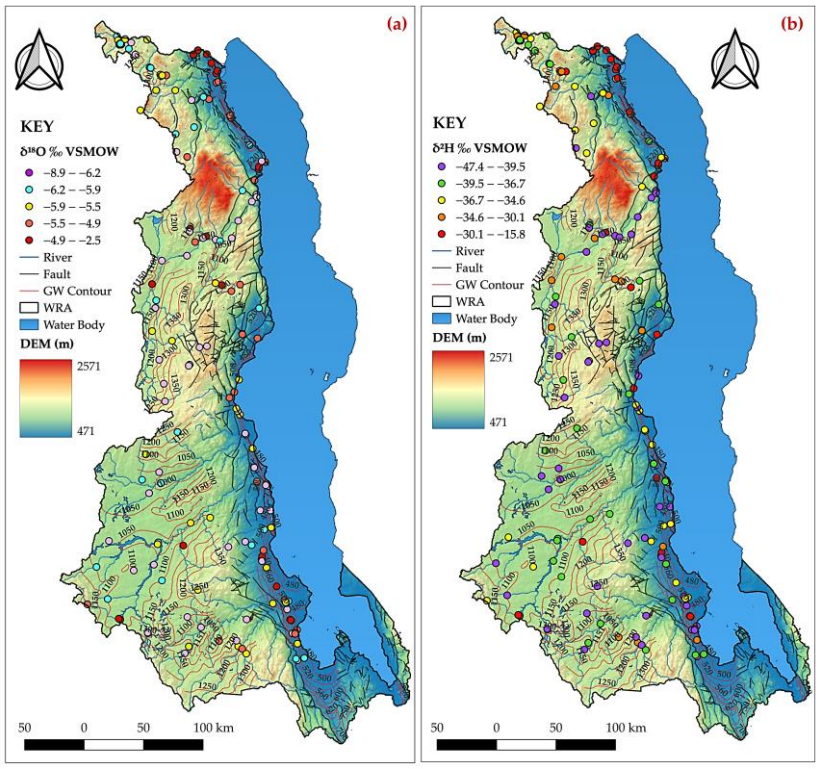
there ~~is~~ was no statistically significant evidence of a distinct elevation effect on isotopic signatures of groundwater (Figure S3). There ~~is~~ was a discernible seasonally variant disparity in the spatial distribution of $\delta^{2}H$–$\delta^{18}O$ signatures, wherein certain upland and lowland sites exhibited enriched and depleted $\delta^{2}H$–$\delta^{18}O$ signatures, respectively (Figure S4). The order of magnitude of the hydraulic head is consistent with progressive groundwater isotopic fractionation, whereby shallow groundwater (susceptible to phreatic evaporation) exhibits less negative $\delta^{2}H$–$\delta^{18}O$ signatures than deep groundwater. Near-geologic fault groundwater sites exhibit ~~a~~ complex isotopic signatures' inhomogeneity ascribed to multi-influential process controls linked to groundwater sample flow ~~-~~path chronicle and/or evaporative effects (Figure 13).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δ18O ‰ VSMOW
−8.9 – −6.2
−6.2 – −5.9
−5.9 – −5.5
−5.5 – −4.9
−4.9 – −2.5
River
Fault
GW Contour
WRA
Water Body
DEM (m)
2571
471
50 0 50 100 km
(b)
KEY
δ2H ‰ VSMOW
−47.4 – −39.5
−39.5 – −36.7
−36.7 – −34.6
−34.6 – −30.1
−30.1 – −15.8
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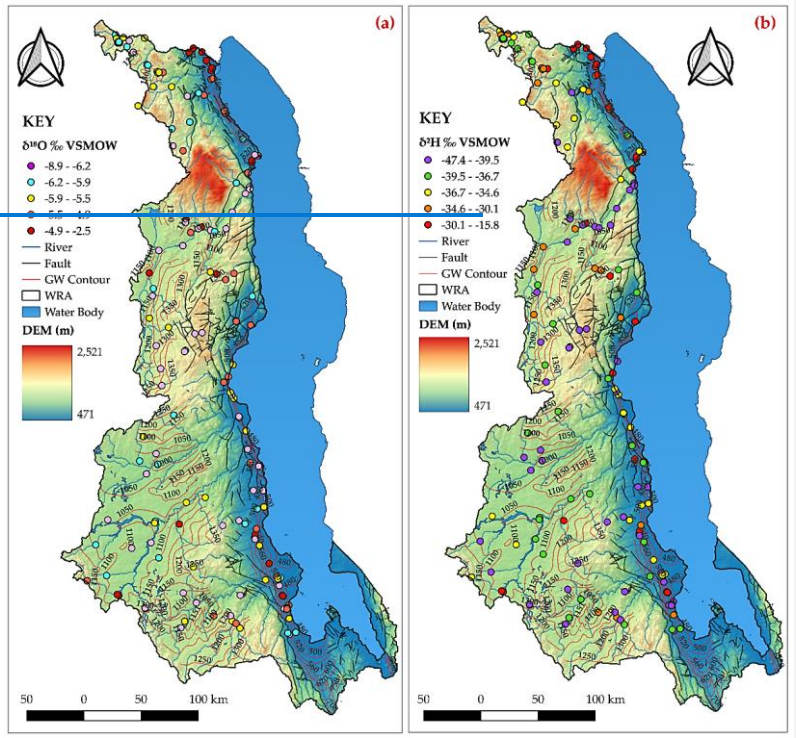

Figure 13. Spatial distribution of groundwater (a) δ18O and (b) δ2H signatures in the Lake Malawi Basin.

Groundwater δ2H–δ18O signatures for wet and dry seasons reveal distinct patterns (Figure 14). Dry season δ2H–δ18O signatures exhibited evaporative influences on groundwater either pre- or post-recharge, and the potential infiltration of enriched lake water. They ~~are~~ were enriched in heavier isotopes than wet season δ2H–δ18O signatures, with a wider intra-seasonal inhomogeneity. However, some anomalies defy seasonal expectations, with enriched δ2H–δ18O signatures in the wet season and depleted δ2H–δ18O signatures in the dry season. These anomalies may be attributed to a combination of factors, including local recharge mechanisms, mixing of water sources, and anthropogenic influences. ~~These~~ This basin's hydrogeological system complexities highlight the intricate interplay of meteoric water input, evaporation effects, recharge processes, deep fluid circulation, and mixing sources within the Lake Malawi basin.

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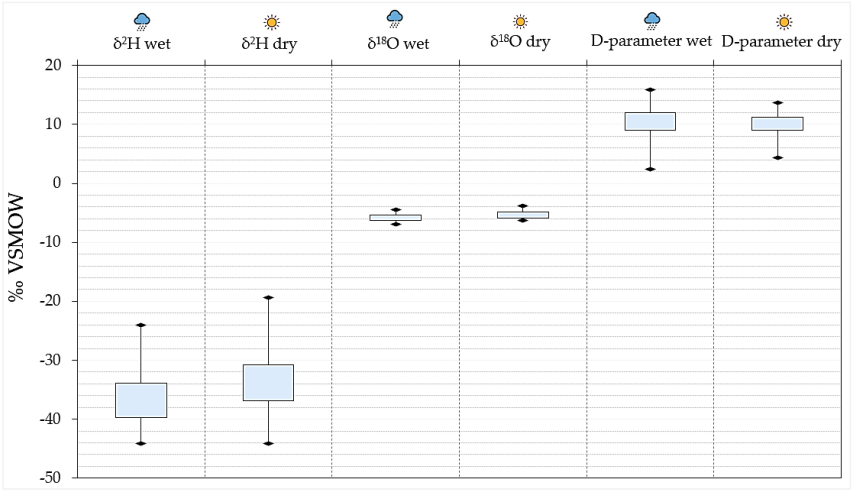

Figure 14. Box plot of groundwater δ^2H–$\delta^{18}O$ signatures and d-parameter for wet and dry ~~season~~ seasons in the Lake Malawi Basin.

4.6. Integrated Isotopic-Hydrogeochemical and Geospatial Insights

Examining δ^2H–$\delta^{18}O$ signatures in conjunction with hydrogeochemical data provides a refined understanding of the groundwater recharge process and evolution. The prevalent Ca-Mg-HCO_3 groundwater type, characteri~~s~~ed by low ~~mineralization~~ mineralisation and alignment with the GMWL, indicates a recent recharge from local precipitation that has not undergone significant evaporation (Figure 15). Another common type, Ca-Mg-SO_4 groundwater with a slightly higher electrical conductivity that plots just below the meteoric water line, suggests evaporative effects either pre- or post-recharge. The mixed groundwater types, Na-HCO_3-Cl and Ca-Mg-SO_4-Cl, plot~~s~~ along the GMWL but with outliers, suggesting the mixing of groundwater from multiple sources. Diverse processes, such as mineral–water reactions and evaporative effects, contribute to these mixed groundwater types. The Na-Cl groundwater type plots along and slightly below the GMWL, suggesting the mixing of older groundwater with newer meteoric water, with the latter dominating isotopically. Given the limited constraints on this observation, additional investigation is necessary to elucidate the findings. The combined isotope hydrology and hydrogeochemistry results point towards a mix of processes impacting groundwater evolution. The complexity of hydrochemical types and isotopic signatures, particularly near the lakeshore area at Lake Malawi, suggest intricate groundwater flow patterns and historical influences converging in this region.

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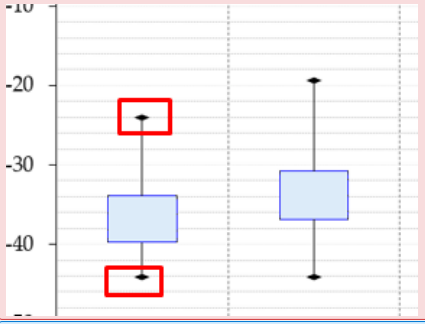

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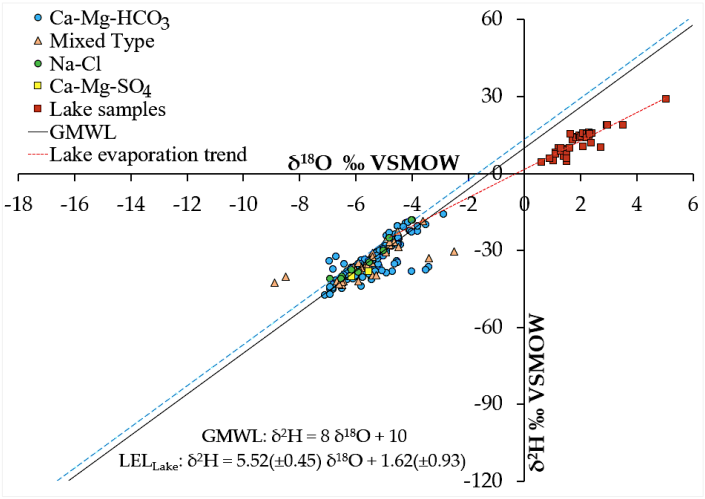

Figure 15. Plot of δ^2H and $\delta^{18}O$ signatures for groundwater samples based on groundwater types and electrical conductivity in Lake Malawi Basin. The mixed water type group comprises Ca-Mg-SO_4-Cl and Na-HCO_3-Cl.

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5. Discussion

5.1. Origin of ~~ionic~~ Ionic Species in Groundwater

Groundwater hydrochemistry exhibits a wide array of cationic and anionic species, dominated by Ca^{2+}, Na^+, HCO_3^-, and Cl^-. These ionic species are attributed to a range of natural and anthropogenic processes. Sodium (Na^+) is mainly obtained through the weathering of silicate rocks like albite ($NaAlSi_3O_8$), a sodium-rich plagioclase feldspar. Other sources of Na^+ include cation exchange reactions that exchange calcium (Ca^{2+}) from sodium-rich groundwater in clay. Highly localis~~z~~ed evaporation and precipitation of trona ($Na_3CO_3{\cdot}NaHCO_3{\cdot}2H_2O$) in thermal spring sites constrained in the northern part of the basin yields sodium bicarbonate ($NaHCO_3$) deposits, which dissolve~~s~~ to release Na^+ in groundwater. Calcium (Ca^{2+}) is primarily derived from anorthite ($CaAl_2Si_2O_8$), a calcium-rich plagioclase, along with other rock minerals like hornblende ($Ca_2(MgFeAl)_5(AlSi)_8O_{22}$) and calcite. Magnesium (Mg^{2+}) sources include the weathering of magnesium-bearing silicate minerals like biotite ($K(Mg,Fe)_3(AlSi_3)_{10}(OH,F)$), olivine ($Mg_2SiO_4$), and amphibole (hornblende ($Ca_2(MgFeAl)_5(AlSi)_8O_{22}$)). Potassium ($K^+$) is likely derived from muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$ and biotite, typically found in sediments. Carbonate species (CO_3^{2-} and HCO_3^-) in groundwater are derived from carbonate mineral reactions, primarily calcite dissolution. The presence of SO_4^{2-} in groundwater suggests the occurrence of oxidation reactions of pyrite rock mineral (FeS_2) or deep fluid migration. The detection of NO_3^- in Malawi's groundwater, where no geogenic source exists, suggests human influence. Identifying and addressing human-driven nitrate contamination sources is crucial for achieving Sustainable Development Goal 6 objectives. Fluoride (F^-) occurrence in groundwater can be attributed to various minerals, including micas, fluorapatite ($Ca_5(PO_4)_3F$), fluorite (CaF_2), and concealed thermal springs [~~65~~60].

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5.2. Groundwater Evolution

Groundwater recharge in the Lake Malawi basin primarily occurs as a result of the infiltration of precipitation, a fundamental process that introduces fresh meteoric water into the subsurface. This influx of water initiates a complex series of geochemical reactions

with rock minerals driven by soil carbon dioxide as an acid source. Plagioclase feldspars, essential components of the rock matrix, undergo incongruent reactions upon interaction with meteoric water, leading to the release of calcium and sodium ions along with insoluble secondary clay minerals from complex smectites to simple kaolite (Table S5). The dissolution of carbonate species contributes to the overall chemical composition of groundwater in the basin. As groundwater flows through the rock matrix, incongruent reactions with silicates continue until saturation with carbonate minerals, predominantly calcite, is reached, after which mass transfer reactions continue at equilibrium, exerting significant control over groundwater chemistry. The weathering of plagioclase feldspar thus maintains an equilibrium with calcite. The presence of substantial carbonate in groundwater leads to the accumulation of calcite over time, especially in fractures and cavities within aquifer rocks. These fractures and cavities serve as crucial sites for the initiation of carbonate crystal formation, further influencing the groundwater system's chemical and isotopic composition. Noteworthy changes in the aquifer's composition and characteristics occur gradually due to the progressive buildup of calcite, and it is strongly advised that future studies include carbon isotope ($\delta^{13}C$) dynamics. Moreover, the formation of secondary calcite, following the initial precipitation, adds diversity to the range of minerals present in the groundwater system. Secondary calcite is widely distributed in fractures, veins, and cavities within granite and aquifer rocks, underscoring its importance across various geological formations. Where geothermal water mixes with meteoric water, fluorite is likely controlling levels of fluoride in groundwater, and further investigation is needed. In essence, the intricate interplay between precipitation, geochemical reactions, mineral dissolution, and carbonate mineral precipitation shapes the groundwater ~~mineralization~~ mineralisation processes in the Lake Malawi basin, highlighting the dynamic nature of hydrogeological systems in this region.

5.3. Implications for Water Resource Management

This~~e~~ study establishes a current baseline for understanding the isotope hydrology and hydrogeochemistry of groundwater in the Lake Malawi basin. This baseline is critical for monitoring future changes in the region's water resources. This~~e~~ study's findings are particularly relevant in water resource areas like WRA 4, WRA 5, WRA 6, WRA 8, and WRA 9 (Figure 1), where the Malawi Government aims to restore catchments and improve water security, agricultural productivity, and rural livelihoods. Insights gained from this research on groundwater recharge, evolution, and hydrogeochemical characteristics are valuable in shaping future policies in this domain as follows ~~as~~:

- Understanding the origins and influences impacting groundwater recharge can guide the development and implementation of sustainable water resource management policies. These policies can focus on safeguarding and maintaining groundwater quality, especially in areas at risk of pollution or contamination, thereby underpinning efforts towards SDG 6 targets related to water and sanitation;
- Utilis~~z~~ing knowledge about different groundwater types and their unique characteristics can shape decisions related to land-use planning. Areas with sensitive groundwater recharge zones may necessitate stricter regulations to preserve water quality and promote responsible usage;
- Policy initiatives should ~~emphasize~~ emphasise the importance of the ongoing monitoring of groundwater quality and quantity. Regulations could be implemented to govern land practices near recharge zones and protected groundwater areas based on identified hydrochemical features and isotopic markers;
- Recogni~~z~~ing the potential impact of evaporation on groundwater quality can spur the development of strategies to mitigate these effects. Policies targeting the reduction of evaporation-related factors, such as managing surface–water interactions or regulating land use activities, may be essential;

- Given the intricate nature of groundwater recharge processes highlighted in thise study, policies promoting collaboration among various stakeholders, including governmental bodies, researchers, and local communities, can be instrumental. This collaborative approach can facilitate a comprehensive strategy for groundwater management and conservation;-
- The nitrate concentration in the groundwater aligns with the recommended guidelines by the World Health Organiszation for safe drinking water, as illustrated in Figure 56. Despite this compliance, there is a pressing necessity to develop a detailed model that specifically addresses groundwater contamination associated with nitrates, particularly in light of the upsurge in fertiliszer use, pit latrines, -and septic systems arising from the rapid population growth. By creating a more comprehensive and focused analysis on of nitrate-related pollution, we can better understand and mitigate the potential risks posed by these sanitation systems to ensure the continued safety of our drinking water sources;-
- Future isotope hydrology studies should include $\delta^{15}N - \delta^{18}O$ (NO_3), $\delta^{13}C$ (dissolved and mineral phases), and $\delta^{34}S - \delta^{18}O$ (SO_4) along with methods to study groundwater ages;-
- In essence, thise study's outcomes provide valuable insights to guide policymakers in crafting regulations and actions that support sustainable groundwater management, ensure water availability, and safeguard water resources for future generations.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Table S1: Descriptive statistical summary of hydrochemical analysis results of groundwater samples from Lake Malawi Basin, Table S2: List of Malawi-Network of Isotopes in Precipitation (MNIP) stations in Lake Malawi Basin, Table S3: Descriptive statistical summary of stable isotopic signatures of precipitation from MNIP stations in Lake Malawi Basin, Table S4: Descriptive statistical summary of stable isotopic signatures of groundwater from Lake Malawi Basin. Table S5: Natural sources of ionic species in groundwater and corresponding geochemical reactions. Figure S1: Cross plot of ion weight ratios on cation exchange in groundwater, Figure S2: Plot of saturation indices for gypsum and halite minerals in groundwater, Figure S3: Relationship between stable isotopes signatures and elevation, Figure S4: Relationship between $\delta^{18}O$ signatures and Elevation in Lake Malawi Basin, Figure S5: Relationship between $\delta^{18}O$ signatures and electrical conductivity in Lake Malawi Basin.

Author Contributions: Conceptualiszation, L.C.B. and R.M.K.; methodology, L.C.B.; validation, L.C.B.; formal analysis, L.C.B. and R.M.K.; investigation, L.C.B.; resources, L.C.B. and R.M.K.; data curation, L.C.B.; writing—original draft preparation, L.C.B.; writing—review and editing, L.C.B., R.M.K. and V.P., visualizationvisualisation, L.C.B. and R.M.K.; supervision, R.M.K. and V.P.; project administration, L.C.B., R.M.K. and V.P.; funding acquisition, L.C.B., R.M.K. and V.P. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The research data provided in this study can be obtained upon reasonable request from the corresponding author.

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Conflicts of Interest: The authors declare no conflicts of interest.

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Date: 19 November 2024 at 21:06
To: Limbikani Chitsundi Banda limbikanicbanda@gmail.com

Your Submission **STOTEN-D-24-44759**

Ms. Ref. No.: **STOTEN-D-24-44759**
Title: Isotopic and Hydrochemical Tracers Reveal Surface Water Dynamics in the Lake Malawi Basin: A Mixed-Proxy Approach for Water Resource Conceptualization
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Dear Mr Limbikani Chitsundi Banda,

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Associate Editor
Science of the Total Environment

Thank you for submitting your manuscript entitled "Isotopic and Hydrochemical Tracers Reveal Surface Water Dynamics in the Lake Malawi Basin: A Mixed-Proxy Approach for Water Resource Conceptualization," to Science of the Total Environment. While the topic is interesting, the manuscript presents some methodological and structural issues that must be addressed before it can be reviewed.
Your study's core focus on isotopic and hydrochemical tracers in the Lake Malawi Basin represents an important research direction, particularly given the region's vulnerability to climate change.
While providing background information, the introduction fails to clearly articulate the research gap and establish a compelling theoretical framework. The connection between previous studies and your research objectives remains unclear. The research objectives on page 4 are overly broad and lack specific, measurable outcomes to advance the field.
The methodology section needs to be revised to add more statistical details. While you describe the sampling procedures, your sampling strategy and sample sizes are insufficiently justified. The statistical treatment of the isotopic and hydrochemical data needs robust error analysis and uncertainty quantification. The quality control measures for sample collection and analysis need more detailed documentation, particularly regarding potential contamination sources and analytical uncertainties.
The results section, while extensive, needs more data visualization and interpretation. Many figures are descriptive rather than analytical, and the statistical relationships between variables must be thoroughly explored. The discussion section needs to engage with the broader implications of your findings critically and adequately address potential limitations of your approach. The conceptual model presented in Figure 10 lacks validation against independent data sets and seems oversimplified, given the complex hydrogeological setting of the Lake Malawi Basin.
The writing style varies considerably throughout the text, suggesting inconsistent editing. The paper is exceptionally long (over 1000 lines) yet needs to maintain focus on its core arguments. Many sections, particularly the discussion, contain redundant information that could be condensed.
The policy implications section appears disconnected from the technical findings and makes broad recommendations without sufficient support from your data. This section needs to be more tightly integrated with your analytical results and should provide more specific, evidence-based recommendations.
The conclusions, while identifying important points, largely restate results without synthesizing them into novel insights that advance the field. The scientific contribution of the work needs to be more clearly articulated and positioned within the current state of knowledge in hydrogeological research.

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11.3 References: Hydrogeological & Groundwater Quality Atlas-Malawi:

The PhD researcher contributed tremendously to development and updating of the new Hydrogeological and Groundwater Quality Atlas for Malawi during the period of the PhD. This work contributed to the professional skills and knowledge development of the PhD researcher. The associated references for the scientific contributions are detailed below.

Hydrogeology and Groundwater Quality Atlas Bulletin

1. Kalin, R.M., Mleta, P., Addison, M.J., Banda, L.C., Butao, Z., Nkhata, M., Rivett, M.O., Mlomba, P., Phiri, O., Mambulu, J, Phiri, O.C., Kambuku, D.D., Manda, J., Gwedeza, A., Hinton, R. (2022) Hydrogeology and Groundwater Quality Atlas of Malawi, Bulletin, Ministry of Water and Sanitation, Government of Malawi, ISBN 978-1-915509-00-0 151pp.

Hydrogeology and Groundwater Quality Atlas WRA Annexes

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2. Kalin, R.M., Mleta, P., Addison, M.J., Banda, L.C., Butao, Z., Nkhata, M., Rivett, M.O., Mlomba, P., Phiri, O., Mambulu, J, Phiri, O.C., Kambuku, D.D., Manda, J., Gwedeza, A., Hinton, R. (2022) Hydrogeology and Groundwater Quality Atlas of Malawi, Shire River Catchment, Water Resource Area 1 Lower Shire, Ministry of Water and Sanitation, Government of Malawi, ISBN 978-1-915509-02-4 129pp.

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National Scale Maps at A0

1. Kalin, R.M., Addison, M.J., Mleta, P., Banda, L.C., Butao, Z., Nkhata, M., Rivett, M.O., Mlomba, P., Phiri, O., Mambulu, J, Phiri, O.C., Kambuku, D.D., Manda, J., Gwedeza, A., (2022) Hydrogeology and Groundwater Quality Atlas of Malawi, Map Aquifer Groups of Malawi, Ministry of Water and Sanitation, Government of Malawi, ISBN 978-1-915509-17-8 1pp A0.

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10.4. Research Data

10.4.1 Stable Isotope Data – Groundwater

GROUNDWATER STABLE ISOTOPE DATA

Sample ID	δ^2D ‰ VSMOW	$\delta^{18}O$ ‰ VSMOW	D-excess ‰		Sample ID	δ^2D ‰ VSMOW	$\delta^{18}O$ ‰ VSMOW	D-excess ‰
StrathGW229	-36.5	-6.3	13.9		GW86	-24.9	-4.8	13.5
StrathGW225	-35.8	-6.8	18.6		GW87	-30.4	-5.0	9.8
StrathGW350	-45.2	-6.8	9.2		GW88	-34.8	-5.8	11.8
StrathGW157	-43.4	-6.4	7.8		GW89	-43.0	-6.6	9.8
StrathGW185	-38.4	-5.8	8.0		GW40	-38.2	-6.0	9.8
StrathGW442	-39.1	-6.1	9.7		GW41	-34.6	-5.9	12.6
StrathGW424	-39.7	-5.7	5.9		GW42	-30.9	-5.4	12.3
StrathGW181	-38.9	-5.7	6.7		GW43	-25.4	-4.9	13.8
GW138	-27.9	-4.8	10.4		GW44	-27.9	-4.9	11.3
GW139	-39.8	-5.3	2.4		GW45	-26.5	-4.8	11.9
GW140	-39.6	-5.4	3.6		GW46	-23.6	-4.6	13.2
GW141	-41.9	-6.7	11.4		GW47	-25.4	-4.5	10.6
GW142	-39.0	-6.2	10.6		GW32	-43.4	-6.5	8.6
GW143	-28.6	-4.5	7.3		GW33	-42.5	-6.7	11.1
GW144	-42.8	-6.7	10.8		GW34	-39.5	-6.1	9.6
GW145	-40.6	-6.4	10.4		GW35	-34.1	-5.6	10.3
GW130	-37.4	-5.9	10.0		GW36	-29.4	-5.0	10.6
GW131	-43.9	-5.8	2.5		GW37	-20.0	-3.5	8.0
GW132	-41.7	-6.7	11.8		GW38	-27.2	-4.7	10.2
GW133	-36.9	-6.1	11.9		GW39	-30.7	-5.0	9.3
GW134	-38.8	-6.2	10.5		GW56	-35.7	-5.8	10.7
GW135	-36.1	-5.7	9.7		GW57	-38.1	-6.3	12.3
GW136	-23.3	-4.2	10.0		GW58	-37.3	-6.1	11.7
GW137	-41.7	-5.3	0.9		GW59	-35.5	-5.9	11.6
GW154	-36.8	-6.1	12.3		GW60	-34.3	-5.8	12.1
GW155	-39.5	-6.4	11.3		GW61	-36.7	-6.1	11.7
GW156	-34.0	-5.7	11.5		GW62	-37.4	-6.8	17.0
StrathGW413	-28.9	-4.6	7.9		GW63	-38.7	-4.9	0.5
StrathGW605	-36.0	-4.7	1.6		GW48	-23.9	-4.3	10.5
StrathGW625	-39.5	-6.5	12.4		GW49	-20.6	-4.5	15.4
StrathGW20	-37.3	-5.9	9.5		GW50	-25.3	-4.8	13.1
StrathGW395	-38.6	-5.5	5.4		GW51	-24.2	-4.9	15.0
GW146	-38.2	-5.7	7.3		GW52	-23.3	-4.8	15.1
GW147	-39.5	-6.1	8.9		GW53	-32.2	-5.1	8.6
GW148	-39.5	-5.5	4.3		GW54	-36.4	-5.9	10.8

GW149	-37.3	-5.9	9.5		GW55	-40.1	-6.5	11.9
GW150	-40.9	-6.4	10.5		GW8	-37.6	-5.9	9.3
GW151	-36.2	-6.0	11.6		GW9	-28.5	-4.9	10.7
GW152	-36.3	-5.8	10.1		GW10	-31.0	-4.9	8.2
GW153	-39.5	-6.5	12.4		GW11	-36.4	-6.1	12.4
GW106	-39.7	-6.9	15.3		GW12	-47.4	-7.1	9.4
GW107	-35.1	-6.0	12.7		GW13	-41.5	-6.3	8.9
GW108	-36.1	-6.0	11.6		GW14	-46.6	-6.9	8.8
GW109	-35.6	-5.8	10.6		GW15	-35.2	-5.9	12.0
GW110	-35.4	-5.9	11.8		GW193	-34.7	-5.7	11.2
GW111	-22.3	-5.2	19.3		GW1	-35.0	-5.5	9.0
GW112	-33.2	-5.6	11.9		GW2	-43.5	-6.8	10.9
GW113	-35.8	-5.9	11.4		GW3	-34.9	-5.5	9.4
GW98	-41.2	-6.5	10.4		GW4	-37.8	-5.1	2.6
GW99	-36.4	-5.9	10.7		GW5	-29.8	-4.9	9.4
GW100	-38.9	-6.8	15.3		GW6	-39.5	-5.5	4.5
GW101	-38.5	-6.8	15.9		GW7	-29.5	-5.0	10.5
GW102	-26.4	-5.5	17.3		GW24	-33.9	-5.8	12.5
GW103	-28.7	-5.1	12.5		GW25	-40.4	-6.4	10.8
GW104	-36.5	-6.3	13.9		GW26	-38.5	-6.1	10.3
GW105	-35.3	-5.4	8.0		GW27	-33.1	-3.4	-5.9
GW122	-31.9	-5.5	12.1		GW28	-34.3	-6.9	21.2
GW123	-41.0	-6.9	14.3		GW29	-42.6	-8.9	28.6
GW124	-38.9	-6.5	13.4		GW30	-38.1	-4.0	-6.1
GW125	-36.9	-6.0	10.8		GW31	-45.1	-6.9	10.1
GW126	-41.9	-5.5	2.1		GW16	-42.4	-6.5	9.6
GW127	-40.2	-6.4	10.6		GW17	-47.2	-6.9	8.0
GW128	-41.5	-5.4	2.0		GW18	-45.0	-6.5	7.0
GW129	-40.5	-5.3	2.1		GW19	-44.7	-6.8	9.7
GW114	-35.2	-5.9	11.9		GW20	-45.2	-6.8	9.2
GW115	-38.3	-6.1	10.7		GW21	-38.3	-6.2	11.3
GW116	-23.2	-5.2	18.6		GW22	-41.2	-6.9	14.0
GW117	-40.3	-6.2	9.5		GW23	-36.7	-5.8	9.7
GW118	-30.2	-5.5	14.0		GW169	-38.3	-5.5	6.0
GW119	-33.4	-5.3	9.2		GW170	-31.8	-5.3	10.7
GW120	-37.1	-5.9	10.4		GW171	-37.5	-5.9	9.8
GW121	-36.2	-6.2	13.6		GW172	-33.7	-5.7	11.6

GW72	-40.0	-6.0	8.0		GW173	-33.0	-5.6	11.7
GW73	-35.9	-5.8	10.6		GW174	-34.5	-5.7	10.9
GW74	-38.4	-6.1	10.4		GW175	-34.8	-5.7	10.8
GW75	-39.0	-6.3	11.4		GW176	-31.1	-5.4	11.9
GW76	-36.7	-5.7	8.9		GW161	-37.9	-6.0	9.7
GW77	-40.1	-5.9	7.1		GW162	-39.5	-5.5	4.3
GW78	-39.6	-6.4	11.6		GW163	-40.6	-6.4	10.4
GW79	-39.4	-6.1	9.7		GW164	-38.2	-5.7	7.3
GW64	-38.7	-5.9	8.5		GW165	-39.5	-6.1	8.9
GW65	-40.2	-6.1	8.6		GW166	-36.3	-5.2	5.0
GW66	-29.0	-5.0	11.3		GW167	-40.1	-6.3	10.4
GW67	-24.8	-4.5	11.2		GW168	-40.2	-6.1	8.9
GW68	-27.9	-4.5	8.1		GW185	-34.0	-5.6	10.5
GW69	-41.0	-6.1	7.8		GW186	-33.8	-4.8	4.4
GW70	-35.2	-5.2	6.4		GW187	-31.4	-5.3	10.9
GW71	-40.1	-6.0	7.9		GW188	-30.1	-5.1	10.8
GW90	-42.1	-5.9	5.1		GW189	-35.4	-5.8	11.3
GW91	-37.6	-6.2	12.0		GW190	-21.2	-4.2	12.7
GW92	-36.9	-6.0	11.3		GW191	-25.3	-4.1	7.3
GW93	-35.4	-6.4	15.8		GW192	-34.9	-5.7	10.6
GW94	-35.9	-5.5	8.1		GW177	-36.9	-5.9	9.9
GW95	-39.7	-6.9	15.4		GW178	-34.8	-5.8	11.4
GW96	-38.9	-6.9	16.6		GW179	-35.8	-5.8	10.4
GW97	-35.0	-5.9	12.2		GW180	-37.0	-6.0	11.3
GW80	-38.4	-5.9	8.8		GW181	-36.2	-6.0	12.1
GW81	-39.7	-6.0	8.5		GW182	-34.0	-5.5	9.8
GW82	-44.6	-6.8	9.8		GW183	-33.1	-5.3	9.2
GW85	-25.1	-4.8	13.3		GW184	-35.3	-5.9	12.1
GW85	-25.1	-4.8	13.3		GW106	-38.5	-6.1	10.6
GW86	-24.9	-4.8	13.5		GW107	-30.9	-5.2	10.7
GW87	-30.4	-5.0	9.8		GW108	-34.3	-5.6	10.7
GW88	-34.8	-5.8	11.8		GW109	-33.8	-5.5	10.5
GW89	-43.0	-6.6	9.8		GW110	-33.1	-5.4	10.3
GW40	-38.2	-6.0	9.8		GW111	-18.7	-3.1	6.4
GW41	-34.6	-5.9	12.6		GW112	-32.1	-5.4	11.3
GW42	-30.9	-5.4	12.3		GW113	-34.7	-5.7	11.0
GW43	-25.4	-4.9	13.8		GW98	-39.4	-6.5	12.4

10.4.2. Stable Isotope Data – Surface Water

SURFACE WATER STABLE ISOTOPE DATA

Sample ID	Source Type	δ^2D ‰ VSMOW	$\delta^{18}O$ ‰ VSMOW	D-excess ‰		Sample ID	Source Type	δ^2D ‰ VSMOW	$\delta^{18}O$ ‰ VSMOW	D-excess ‰
Iso-SW01	River	-32	-4.2	1.6		Iso-SW141	River	-28.9	-5.70	16.7
Iso-SW02	River	-30.2	-4.3	4.2		Iso-SW142	River	-43.6	-6.90	11.6
Iso-SW03	River	-34.6	-4.59	2.12		Iso-SW143	River	-35.5	-6.20	14.1
Iso-SW04	River	-35.7	-5.68	9.74		Iso-SW144	River	-36.4	-5.90	10.8
Iso-SW05	River	-31.2	-4.92	8.16		Iso-SW145	River	-35.2	-6.20	14.4
Iso-SW06	River	-6.6	-0.38	-3.56		Iso-SW146	River	-38.8	-6.10	10
Iso-SW07	River	-23.3	-3.49	4.62		Iso-SW147	River	-35.7	-5.80	10.7
Iso-SW08	River	-28.4	-3.8	2		Iso-SW148	River	-37.1	-5.90	10.1
Iso-SW09	River	2.2	1.91	-13.08		Iso-SW149	River	-44.3	-6.90	10.9
Iso-SW10	River	-38	-6.04	10.32		Iso-SW150	River	-45.8	-7.00	10.2
Iso-SW11	River	-3.3	1.19	-12.82		Iso-SW151	River	-46.7	-7.30	11.73
Iso-SW12	River	-23	-3.04	1.32		Iso-SW152	River	-36.6	-5.90	10.6
Iso-SW13	River	-29.9	-4.6	6.9		Iso-SW153	River	-34.8	-5.90	12.4
Iso-SW14	River	-30.3	-4.86	8.58		Iso-SW154	River	-39.9	-5.80	6.5
Iso-SW15	River	-35.7	-5.35	7.1		Iso-SW155	River	-40.2	-5.90	7
Iso-SW16	River	-25.1	-3.38	1.94		Iso-SW156	River	-37.3	-5.10	3.48
Iso-SW17	River	-20.7	-3.35	6.1		Iso-SW157	River	-42.5	-6.60	10.3
Iso-SW18	River	-20.6	-2.89	2.52		Iso-SW158	River	-40.0	-5.70	5.6
Iso-SW19	River	-25.1	-4.08	7.54		Iso-SW159	River	-40.5	-6.30	9.9
Iso-SW20	River	-32.7	-5.34	10.02		Iso-SW160	River	-30.1	-4.60	6.7
Iso-SW21	River	-34.2	-5.56	10.28		Iso-SW161	River	-35.8	-5.20	5.8
Iso-SW22	River	-26.8	-3.64	2.32		Iso-SW162	River	-23.9	-3.40	3.3
Iso-SW23	River	-30.7	-5.50	13.3		Iso-SW163	River	-30.1	-4.50	5.9
Iso-SW24	River	-29.5	-5.45	14.1		Iso-SW164	River	-4.6	-1.90	10.6
Iso-SW25	River	-26.4	-4.90	12.8		Iso-SW165	River	-39.1	-6.50	12.9
Iso-SW26	River	-16.4	-3.47	11.36		Iso-SW166	River	-37.6	-6.10	11.2
Iso-SW27	River	-14.2	-2.03	2.04		Iso-SW167	River	-39.5	-6.40	11.7
Iso-SW28	River	-30.7	-4.58	5.94		Iso-SW168	River	-40.2	-6.20	9.4
Iso-SW29	River	-22.3	-3.41	4.98		Iso-SW169	River	-37.3	-6.20	12.3
Iso-SW30	River	-15.9	-3.46	11.78		Iso-SW170	River	-29.5	-5.20	12.1
Iso-SW31	River	-32.3	-5.70	13.3		Iso-SW171	River	-27.2	-4.90	12
Iso-SW32	River	-30.4	-5.46	13.28		Iso-SW172	River	-29.8	-4.87	9.16
Iso-SW33	River	-30.3	-5.06	10.18		Iso-SW173	River	-33.4	-5.60	11.4

Iso-SW34	River	-30.3	-5.05	10.1		Iso-SW174	River	-29.6	-5.20	12
Iso-SW35	River	-34.1	-5.10	6.7		Iso-SW175	River	-30.5	-5.80	15.9
Iso-SW36	River	-29.9	-5.00	10.1		Iso-SW176	River	-31.6	-5.40	11.6
Iso-SW37	River	-39.2	-6.49	12.72		Iso-SW177	River	-24.5	-4.00	7.5
Iso-SW38	River	-39.2	-6.04	9.12		Iso-SW178	River	-37.0	-5.80	9.4
Iso-SW39	River	-37.6	-5.78	8.64		Iso-SW179	River	-40.5	-6.20	9.1
Iso-SW40	River	-38.2	-6.41	13.08		Iso-SW180	River	-27.6	-4.00	4.4
Iso-SW41	River	-35.1	-4.60	1.7		Iso-SW181	River	-29.3	-5.10	11.5
Iso-SW42	River	-30.8	-4.10	2		Iso-SW182	River	-24.5	-4.30	9.9
Iso-SW43	River	-36.2	-4.80	2.2		Iso-SW183	River	-28.7	-5.10	12.1
Iso-SW44	River	-18.5	-2.80	3.9		Iso-SW184	River	-28.9	-4.9	10.3
Iso-SW45	River	-30.2	-4.44	5.32		Iso-SW185	River	-27.4	-4.90	11.8
Iso-SW46	River	-35.8	-5.33	6.84		Iso-SW186	River	-35.9	-6.00	12.1
Iso-SW47	River	-31.7	-4.40	3.5		Iso-SW187	River	-40.5	-6.03	7.74
Iso-SW48	River	-31.6	-4.88	7.44		Iso-SW188	River	-45.3	-6.90	9.9
Iso-SW49	River	-25.6	-3.75	4.4		Iso-SW189	River	-39.4	-6.05	9
Iso-SW50	River	-26.1	-4.02	6.06		Iso-SW190	River	-28.8	-4.30	5.6
Iso-SW51	River	-19.0	-2.36	-0.12		Iso-SW191	River	-34.5	-5.80	11.9
Iso-SW52	River	-20.5	-2.10	-3.7		Iso-SW192	River	-19.5	-3.90	11.7
Iso-SW53	River	8.90	2.54	-11.42		Iso-SW193	River	-32.6	-5.20	9
Iso-SW54	River	-8.90	-0.73	-3.06		Iso-SW194	River	-17.9	-3.00	6.1
Iso-SW55	River	-11.6	-1.80	2.8		Iso-SW195	River	-29.4	-4.90	9.8
Iso-SW56	River	-33.1	-5.86	13.78		Iso-SW196	River	-35.1	-6.00	12.9
Iso-SW57	River	-34.9	-5.60	9.9		Iso-SW197	Stream	-36.3	-4.90	2.9
Iso-SW58	River	-30.4	-4.86	8.48		Iso-SW198	River	-33.6	-5.40	9.6
Iso-SW59	River	-21.9	-3.61	6.98		Iso-SW199	River	-20.1	-4.40	15.1
Iso-SW60	River	-23.7	-4.26	10.38		Iso-SW200	River	-28.6	-4.20	5
Iso-SW61	River	-29.1	-4.45	6.5		Iso-SW201	River	-30.1	-5.40	13.1
Iso-SW62	River	-31.1	-4.93	8.34		Iso-SW202	River	-28.3	-4.5	7.7
Iso-SW63	River	-22.7	-3.06	1.78		Iso-SW203	River	-27.9	-5.1	12.9
Iso-SW64	River	-24.0	-4.60	12.8		Iso-SW204	River	-24.3	-4.23	9.54
Iso-SW65	River	-19.1	-3.31	7.38		Iso-SW205	River	-26.8	-4.7	10.8
Iso-SW66	River	-15.9	-2.83	6.74		Iso-SW206	River	-26.9	-4.80	11.5
Iso-SW67	River	-27.9	-4.79	10.42		Iso-SW207	River	-25.0	-4.28	9.24
Iso-SW68	River	-30.8	-5.11	10.08		Iso-SW208	River	10.8	1.05	2.4
Iso-SW69	River	-20.5	-2.96	3.18		Iso-SW209	River	-31.8	-5.25	10.2

Iso-SW70	River	-19.8	-3.75	10.2		Iso-SW210	River	-24.9	-4.50	11.1
Iso-SW71	River	-16.1	-3.11	8.78		Iso-SW211	River	-31.6	-5.20	10
Iso-SW72	River	-23.4	-4.34	11.32		Iso-SW212	River	-29.2	-4.45	6.4
Iso-SW73	River	-21.4	-3.95	10.2		Iso-SW213	River	-30.8	-5.80	15.6
Iso-SW74	River	-18.9	-3.79	11.42		Iso-SW214	River	-19.5	-4.18	13.94
Iso-SW75	River	-33.9	-5.74	12.02		Iso-SW215	River	-23.8	-3.90	7.4
Iso-SW76	River	-24.8	-4.23	9.04		Iso-SW216	River	-25	-3.9	6.2
Iso-SW77	River	-30.0	-4.96	9.68		Iso-SW217	River	-22.9	-4.00	9.1
Iso-SW78	River	-31.4	-5.25	10.6		Iso-SW218	River	-23.8	-4.10	9
Iso-SW79	River	-18.0	-2.39	1.12		Iso-SW219	River	-22.8	-4.5	13.2
Iso-SW80	River	-25.6	-4.60	11.2		Iso-SW220	River	-24.4	-4.50	11.6
Iso-SW81	River	-11.7	-1.73	2.14		Iso-SW221	Lake	9.80	1.23	-0.04
Iso-SW82	River	-27.5	-4.55	8.9		Iso-SW222	Lake	14.1	1.88	-0.94
Iso-SW83	River	-11.9	-1.54	0.42		Iso-SW223	Lake	13.1	1.72	-0.66
Iso-SW84	River	-20.3	-3.48	7.54		Iso-SW224	Lake	14.1	1.88	-0.94
Iso-SW85	River	-26.9	-4.82	11.66		Iso-SW225	Lake	13.9	1.93	-1.54
Iso-SW86	Stream	-26.3	-2.80	-3.9		Iso-SW226	Lake	14.0	1.86	-0.88
Iso-SW87	River	-16.8	-1.20	-7.2		Iso-SW227	Lake	14.7	1.95	-0.9
Iso-SW88	River	-11.3	-1.50	0.7		Iso-SW228	Lake	14.0	1.97	-1.76
Iso-SW89	River	-18.4	-1.90	-3.2		Iso-SW229	Lake	10.40	2.10	-6.4
Iso-SW90	River	-28.8	-4.70	8.8		Iso-SW230	Lake	15.0	2.15	-2.2
Iso-SW91	River	-27.4	-3.83	3.24		Iso-SW231	Lake	28.9	5.05	-11.5
Iso-SW92	River	-27.5	-4.94	12.02		Iso-SW232	Lake	14.6	2.03	-1.64
Iso-SW93	River	-22.6	-3.44	4.92		Iso-SW233	Lake	15.5	2.17	-1.86
Iso-SW94	River	-26.4	-4.49	9.52		Iso-SW234	Lake	15.6	2.09	-1.12
Iso-SW95	River	-26.2	-4.58	10.44		Iso-SW235	Lake	14.4	2.31	-4.08
Iso-SW96	River	-25.0	-4.28	9.24		Iso-SW236	Lake	15.3	2.22	-2.46
Iso-SW97	River	14.4	2.31	-4.08		Iso-SW237	Lake	16.0	2.30	-2.4
Iso-SW98	River	-31.0	-5.12	9.96		Iso-SW238	Lake	15.5	1.64	2.38
Iso-SW99	River	-24.0	-3.98	7.84		Iso-SW239	Lake	14.0	2.23	-3.84
Iso-SW100	River	-31.3	-5.08	9.34		Iso-SW240	Lake	15.7	2.41	-3.58
Iso-SW101	River	15.7	2.41	-3.58		Iso-SW241	Lake	15.3	2.33	-3.34
Iso-SW102	River	-29.2	-4.45	6.4		Iso-SW242	Lake	4.7	1.50	-7.3
Iso-SW103	River	-31.8	-5.49	12.12		Iso-SW243	Lake	8.1	1.10	-0.7
Iso-SW104	River	-19.5	-4.18	13.94		Iso-SW244	Lake	7.5	1.10	-1.28
Iso-SW105	River	-23.3	-3.72	6.46		Iso-SW245	Lake	9.2	1.30	-1.2

Iso-SW106	River	-21.8	-4.2	11.8		Iso-SW246	Lake	5.9	0.89	-1.25
Iso-SW107	River	-22.6	-3.52	5.56		Iso-SW247	Lake	9.5	1.50	-2.5
Iso-SW108	River	-23.6	-3.86	7.28		Iso-SW248	Lake	6.7	1.40	-4.5
Iso-SW109	River	-22.13	-4.58	14.51		Iso-SW249	Lake	8.9	1.50	-3.1
Iso-SW110	River	-20.8	-3.98	11.04		Iso-SW250	Lake	5.0	1.02	-3.16
Iso-SW111	River	-22.4	-3.56	6.08		Iso-SW251	Lake	8.6	1.30	-1.8
Iso-SW112	River	-36.3	-5.24	5.62		Iso-SW252	Lake	18.7	3.50	-9.3
Iso-SW113	River	-37.3	-5.53	6.94		Iso-SW253	Lake	7.5	1.50	-4.5
Iso-SW114	River	-37.1	-5.60	7.7		Iso-SW254	Lake	5.9	0.90	-1.3
Iso-SW115	River	-35.9	-6.1	12.9		Iso-SW255	Lake	9.8	1.30	-0.6
Iso-SW116	River	-32.6	-5.80	13.8		Iso-SW256	Lake	5.9	1.52	-6.26
Iso-SW117	River	-9.7	-1.90	5.5		Iso-SW257	Lake	18.7	2.92	-4.66
Iso-SW118	River	-26.4	-4.40	8.8		Iso-SW258	Lake	4.3	0.60	-0.5
Iso-SW119	River	-35.0	-5.50	9		Iso-SW259	Lake	18.8	2.95	-4.8
Iso-SW120	River	-7.6	-1.50	4.4		Iso-SW260	Lake	10.0	1.60	-2.8
Iso-SW121	River	-45.0	-6.70	8.6		Iso-SW261	Lake	10.1	2.71	-11.58
Iso-SW122	River	-5.2	-1.50	6.8		Iso-SW262	Lake	11.8	2.39	-7.32
Iso-SW123	River	-27.1	-4.50	8.9		Iso-SW263	Reservoir	-37.9	-6.07	10.66
Iso-SW124	River	-36.8	-5.30	5.6		Iso-SW264	Reservoir	-19.4	-3.80	11
Iso-SW125	River	-39.0	-6.20	10.6		Iso-SW265	Reservoir	-19.3	-3.78	10.94
Iso-SW126	River	-40.0	-6.00	8		Iso-SW266	Reservoir	-26.9	-4.96	12.78
Iso-SW127	River	-30.2	-4.90	9		Iso-SW267	Reservoir	-8.70	-0.79	-2.38
Iso-SW128	River	-25.0	-4.40	10.2		Iso-SW268	lagoon	2.90	0.18	1.46
Iso-SW129	River	-25.6	-4.40	9.6		Iso-SW269	Reservoir	-20.9	-3.38	6.14
Iso-SW130	River	-27.1	-5.40	16.1		Iso-SW270	Reservoir	-25.0	-4.28	9.24
Iso-SW131	River	-45.2	-6.90	10		Iso-SW271	Reservoir	-26.4	-4.49	9.52
Iso-SW132	River	-37.0	-5.90	10.2		Iso-SW272	Reservoir	-26.2	-4.58	10.44
Iso-SW133	River	-35.0	-5.50	9		Iso-SW273	Reservoir	-40.7	-6.25	9.3
Iso-SW134	River	-35.3	-6.31	15.18		Iso-SW274	Reservoir	-40.6	-6.26	9.48
Iso-SW135	River	-35.3	-5.90	11.9		Iso-SW275	Reservoir	-45.0	-7.00	11
Iso-SW136	River	-38.7	-6.30	11.7		Iso-SW276	Reservoir	-22.8	-4.30	11.6
Iso-SW137	River	-20.10	-3.90	11.1		Iso-SW277	Reservoir	-27.3	-4.70	10.3
Iso-SW138	River	-19.40	-3.90	11.8		Iso-SW278	Reservoir	-35.8	-6.10	13
Iso-SW139	River	-42.0	-6.23	7.84		Iso-SW279	Reservoir	-15.5	-3.40	11.7
Iso-SW140	River	-38.9	-5.80	7.5		Iso-SW280	Lagoon	-1.5	-0.50	2.5

10.4.3 Hydrochemical Data – Groundwater

GROUNDWATER HYDROCHEMICAL DATA

Sample ID	pH	EC μS/cm	TDS mgL^{-1}	CO_3 mgL^{-1}	HCO_3 mgL^{-1}	Cl mgL^{-1}	SO_4 mgL^{-1}	NO_3 mgL^{-1}	F mgL^{-1}	Na mgL^{-1}	K mgL^{-1}	Ca mgL^{-1}	Mg mgL^{-1}	Fe mgL^{-1}	Mn mgL^{-1}
Strath_GW01	5.84	397	203	0	175	18.90	20.50	0.760	0.405	15.4	5.9	30.9	18.9	0.020	0.020
Strath_GW02	5.95	466	238	0	205	30.58	20.36	0.010	0.166	27.1	39.2	28.2	17.5	0.022	0.009
Strath_GW03	6.5	313	160	0	135	17.00	8.29	14.390	0.090	13.5	0.5	25.2	15.4	0.021	0.003
Strath_GW04	6.12	72	37	0	28	8.80	0.33	0.020	0.190	5.4	0.9	6.1	2.0	0.020	0.001
Strath_GW05	6.46	146	75	0	43	10.10	20.00	0.030	1.367	8.9	1.5	10.3	6.3	0.021	0.384
Strath_GW06	6.12	147	75	0	25	9.10	18.50	24.727	0.308	8.5	1.4	11.0	6.5	0.030	0.040
Strath_GW07	6.8	459	234	0	213	23.62	18.81	0.010	0.090	21.0	3.6	38.8	19.8	0.020	0.090
Strath_GW08	6.11	71	36	0	26	6.20	1.68	4.370	0.030	5.0	1.2	5.0	2.6	0.071	0.006
Strath_GW09	6.78	316	161	0	170	13.20	0.23	0.010	0.010	8.1	2.5	28.0	16.9	0.250	0.130
Strath_GW10	7.34	798	410	0	350	31.00	44.61	10.000	0.210	29.3	6.4	79.4	28.9	0.020	0.010
Strath_GW11	5.8	120	61	0	37	9.10	10.03	11.080	0.140	7.2	1.7	9.1	5.9	0.018	0.020
Strath_GW12	6.71	94	49	0	35	8.41	4.01	0.720	0.050	6.7	1.4	9.1	2.1	0.110	0.030
Strath_GW13	7.01	2620	1349	15	895	237.00	208.00	1.600	0.320	197.0	6.7	204.0	94.0	0.020	0.590
Strath_GW14	7.01	72	37	2	27	6.10	1.70	0.010	0.060	5.1	1.0	6.1	2.1	0.410	0.020
Strath_GW15	5.78	48	25	0	21	2.70	0.14	2.900	0.047	2.4	0.3	3.5	1.7	1.480	0.050
Strath_GW16	5.86	113	59	0	20	15.00	6.10	0.010	4.900	13.1	1.4	9.1	1.3	0.021	0.064
Strath_GW17	6.75	609	315	0	245	60.90	16.40	0.010	0.003	45.0	2.7	57.0	14.7	0.020	0.070
Strath_GW18	7.03	1128	561	2	500	35.00	88.00	5.960	0.550	19.8	2.8	98.0	65.0	0.025	0.010
Strath_GW19	6.78	2360	1223	0	745	199.00	286.00	29.170	0.589	196.7	2.5	171.0	94.0	0.021	0.487
Strath_GW20	6.36	671	347	0	230	54.50	60.64	26.420	0.016	50.7	4.2	49.7	23.6	0.000	0.004
Strath_GW21	7.21	1629	843	12	290	390.00	0.74	0.010	0.090	240.0	3.6	41.9	42.6	0.030	0.030
Strath_GW22	9.42	579	300	80	104	40.30	11.20	0.010	0.390	39.0	2.2	49.0	18.5	0.250	0.009
Strath_GW23	6.62	396	205	0	150	27.00	30.00	0.030	0.153	20.0	0.9	40.0	12.0	0.018	0.010
Strath_GW24	7.1	395	204	10	151	15.40	32.00	0.010	0.310	13.5	3.0	43.2	13.0	0.070	0.670
Strath_GW25	6.09	125	65	0	35	17.40	8.70	5.330	0.220	15.2	1.9	8.5	2.1	0.021	0.001
Strath_GW26	5.79	73	39	0	18	10.40	5.80	0.032	0.000	8.9	1.1	4.0	1.3	0.021	0.001
Strath_GW27	6.89	734	380	0	285	70.05	36.50	0.120	0.027	56.4	3.6	66.0	18.0	0.021	0.507
Strath_GW28	6.625	125	86	0	43	7.90	10.20	1.200	0.022	6.9	2.2	10.8	3.8	0.021	0.001
Strath_GW29	6.54	920	633	0	350	95.00	9.20	0.090	0.083	65.3	2.9	88.0	21.5	1.057	0.079
Strath_GW30	6.11	260	174	0	85	30.36	7.30	0.010	0.020	21.7	4.0	19.8	5.3	0.021	0.068
Strath_GW31	6.59	668	346	0	235	67.00	6.32	35.210	0.130	57.7	5.6	60.0	11.3	0.076	0.043
Strath_GW32	6.52	248	128	0	82	17.70	24.50	0.120	0.110	15.6	2.9	22.7	5.9	0.840	0.160
Strath_GW33	6.81	586	304	0	228	44.00	43.00	0.330	0.240	32.3	1.9	72.4	9.9	0.060	0.238
Strath_GW34	5.53	66	33	0	15	7.30	2.17	2.970	2.560	5.4	2.2	4.8	1.7	0.083	0.006
Strath_GW35	5.84	397	203	0	175	18.90	20.50	0.760	0.405	15.4	5.9	30.9	18.9	0.020	0.020
Strath_GW35	6.66	280	145	0	120	15.30	16.70	0.020	0.730	11.7	2.9	29.5	8.1	0.054	0.002
Strath_GW36	6.82	337	174	0	122	24.40	32.00	0.050	0.040	20.8	2.9	26.0	13.0	0.035	0.024
Strath_GW37	5.29	63	33	0	29	3.71	1.80	0.000	0.220	2.5	1.6	6.0	2.5	0.040	0.035

Sample ID	pH	EC μS/cm	TDS mgL^{-1}	CO_3 mgL^{-1}	HCO_3 mgL^{-1}	Cl mgL^{-1}	SO_4 mgL^{-1}	NO_3 mgL^{-1}	F mgL^{-1}	Na mgL^{-1}	K mgL^{-1}	Ca mgL^{-1}	Mg mgL^{-1}	Fe mgL^{-1}	Mn mgL^{-1}
Strath_GW38	5.04	46	23.1	0	13	5.80	2.90	1.500	0.030	4.0	1.7	2.8	1.1	0.080	0.040
Strath_GW39	6.28	150.7	77.9	0	48	9.02	13.00	11.130	0.100	8.7	3.6	12.5	4.8	0.062	0.003
Strath_GW40	5.56	77.7	40.3	0	25	4.36	7.30	2.320	0.060	3.2	3.6	4.2	3.4	0.094	0.011
Strath_GW41	7.52	2250	1163	20	784	263.00	58.00	0.050	0.360	295.0	21.8	98.0	49.0	0.160	0.040
Strath_GW42	6.54	172	89	0	65	9.10	13.40	4.000	0.400	6.8	2.3	15.4	6.1	0.661	0.438
Strath_GW43	6.4	356	183	0	165	11.76	9.30	18.000	0.040	9.6	1.5	37.0	14.3	0.046	0.011
Strath_GW44	6.6	434	225	0	90	19.10	103.10	11.040	0.990	11.7	3.9	52.8	12.7	0.791	0.708
Strath_GW45	6.43	434	225	0	205	8.50	33.00	0.180	0.090	7.0	1.7	56.9	14.3	0.021	0.148
Strath_GW46	6.73	687	356	0	264	75.90	13.72	0.040	1.060	69.0	17.1	42.0	17.1	0.190	0.000
Strath_GW47	5.17	46	24	0	16	5.39	1.40	0.530	0.100	3.1	0.3	3.4	1.8	0.200	0.080
Strath_GW48	6.54	206	107	0	56	19.77	17.90	10.630	0.420	13.8	3.0	16.9	7.2	0.119	0.019
Strath_GW49	6.54	360	187	0	175	15.30	18.00	0.010	0.150	13.6	3.1	29.9	18.8	0.171	0.014
Strath_GW50	6.8	434	224	0	174	39.00	12.40	0.740	0.160	33.2	5.1	32.5	12.6	0.050	0.010
Strath_GW51	6.15	182	94	5	60	12.00	8.60	6.700	0.090	11.1	2.1	13.5	6.3	0.050	0.010
Strath_GW52	5.88	192	100	0	45	38.00	2.50	0.010	0.190	26.2	2.3	8.2	3.1	0.067	0.005
Strath_GW53	6.29	220	114	0	64	28.00	18.00	0.020	0.210	23.0	2.8	13.3	6.8	0.063	0.002
Strath_GW54	6.41	330	171	0	145	23.00	12.00	0.480	0.320	19.7	3.7	28.5	12.3	0.043	0.134
Strath_GW55	6.38	438	227	0	188	27.60	16.90	6.880	0.320	24.4	4.9	38.9	14.3	0.035	0.057
Strath_GW56	6.58	780	377	0	295	56.62	38.00	0.020	0.440	43.2	6.1	69.8	19.4	0.186	0.034
Strath_GW57	6.68	1064	550	0	400	115.00	28.00	0.010	0.190	97.2	8.7	82.1	25.8	0.012	0.029
Strath_GW58	6.55	313	162	0	125	25.00	15.30	0.010	0.530	17.0	2.7	22.8	15.0	0.035	0.015
Strath_GW59	6.8	5150	2662	0	1500	702.00	145.82	235.46	1.680	682.2	16.3	349.0	49.1	0.021	0.124
Strath_GW60	6.7	902	467	0	380	75.00	13.59	6.490	0.310	63.0	4.0	73.0	31.6	0.020	0.010
Strath_GW61	6.72	1086	562	0	520	104.00	84.20	0.380	0.220	94.8	3.9	136.3	26.5	0.006	0.026
Strath_GW62	6.73	1888	978	0	560	219.00	97.40	1.320	0.870	208.0	3.3	91.8	45.3	0.230	1.875
Strath_GW63	6.91	1820	941	0	570	196.15	101.49	0.030	0.750	123.5	11.8	164.1	47.5	1.397	0.724
Strath_GW64	7.04	2280	1177	2	580	359.00	89.86	51.180	2.410	295.0	5.3	89.4	65.5	0.021	0.438
Strath_GW65	6.02	201	104	0	65	19.20	20.10	0.010	0.040	15.6	2.9	17.0	5.3	0.045	0.014
Strath_GW66	6.63	425	220	0	182	26.70	15.00	0.020	0.050	18.7	2.4	50.0	9.5	0.021	0.040
Strath_GW67	6.55	237	123	0	122	9.20	5.70	0.000	0.160	10.2	1.5	22.0	6.6	10.780	0.260
Strath_GW68	6.41	187	97	0	82	10.90	7.70	0.700	0.120	9.9	1.4	17.5	6.2	0.045	0.047
Strath_GW69	6.78	247	128	0	76	20.30	22.00	0.370	0.050	15.6	0.5	17.5	9.8	0.125	0.065
Strath_GW70	6.91	566	293	0	132	52.13	80.50	0.920	0.030	39.0	2.4	46.0	12.5	1.380	0.100
Strath_GW71	7.09	1363	706	5	516	141.00	10.64	0.040	1.600	130.0	3.9	56.0	60.8	0.021	0.012
Strath_GW72	7.26	2110	1249	12	690	310.00	26.60	0.020	0.760	340.0	10.4	84.0	22.3	0.021	0.061
Strath_GW73	7.02	527	273	2	172	69.00	13.80	0.510	0.400	50.0	3.7	29.8	15.4	3.790	0.160
Strath_GW74	6.38	149	77	0	40	13.60	8.49	27.090	0.410	8.1	2.5	10.1	6.7	4.150	0.470
Strath_GW75	6.45	179	92	0	63	18.40	7.80	0.100	0.150	15.8	0.4	12.7	4.7	1.460	0.070
Strath_GW76	6.44	390	202	0	165	21.20	27.00	0.010	0.240	18.8	3.3	50.8	4.3	0.020	0.160
Strath_GW77	6.63	150	78	0	42	10.40	17.90	7.400	0.170	9.8	0.3	12.0	4.5	0.025	0.005

Sample ID	pH	EC μS/cm	TDS mgL^{-1}	CO_3 mgL^{-1}	HCO_3 mgL^{-1}	Cl mgL^{-1}	SO_4 mgL^{-1}	NO_3 mgL^{-1}	F mgL^{-1}	Na mgL^{-1}	K mgL^{-1}	Ca mgL^{-1}	Mg mgL^{-1}	Fe mgL^{-1}	Mn mgL^{-1}
Strath_GW78	6.41	227	117	0	89	22.58	5.20	0.500	0.140	14.2	2.9	21.6	5.4	0.631	0.106
Strath_GW79	6.11	166	86	0	68	12.40	5.20	0.130	0.060	9.4	1.5	12.8	6.8	0.067	0.002
Strath_GW80	6.6	306	158	0	135	11.50	23.10	0.990	0.270	9.5	3.7	35.1	8.9	0.050	0.299
Strath_GW47	5.17	46	24	0	16	5.39	1.40	0.530	0.100	3.1	0.3	3.4	1.8	0.200	0.080
Strath_GW48	6.54	206	107	0	56	19.77	17.90	10.630	0.420	13.8	3.0	16.9	7.2	0.119	0.019
Strath_GW49	6.54	360	187	0	175	15.30	18.00	0.010	0.150	13.6	3.1	29.9	18.8	0.171	0.014
Strath_GW50	6.8	434	224	0	174	39.00	12.40	0.740	0.160	33.2	5.1	32.5	12.6	0.050	0.010
Strath_GW51	6.15	182	94	5	60	12.00	8.60	6.700	0.090	11.1	2.1	13.5	6.3	0.050	0.010
Strath_GW52	5.88	192	100	0	45	38.00	2.50	0.010	0.190	26.2	2.3	8.2	3.1	0.067	0.005
Strath_GW53	6.29	220	114	0	64	28.00	18.00	0.020	0.210	23.0	2.8	13.3	6.8	0.063	0.002
Strath_GW54	6.41	330	171	0	145	23.00	12.00	0.480	0.320	19.7	3.7	28.5	12.3	0.043	0.134
Strath_GW55	6.38	438	227	0	188	27.60	16.90	6.880	0.320	24.4	4.9	38.9	14.3	0.035	0.057
Strath_GW56	6.58	780	377	0	295	56.62	38.00	0.020	0.440	43.2	6.1	69.8	19.4	0.186	0.034
Strath_GW57	6.68	1064	550	0	400	115.00	28.00	0.010	0.190	97.2	8.7	82.1	25.8	0.012	0.029
Strath_GW58	6.55	313	162	0	125	25.00	15.30	0.010	0.530	17.0	2.7	22.8	15.0	0.035	0.015
Strath_GW59	6.8	5150	2662	0	1500	702.00	145.82	235.46	1.680	682.2	16.3	349.0	49.1	0.021	0.124
Strath_GW60	6.7	902	467	0	380	75.00	13.59	6.490	0.310	63.0	4.0	73.0	31.6	0.020	0.010
Strath_GW61	6.72	1086	562	0	520	104.00	84.20	0.380	0.220	94.8	3.9	136.3	26.5	0.006	0.026
Strath_GW62	6.73	1888	978	0	560	219.00	97.40	1.320	0.870	208.0	3.3	91.8	45.3	0.230	1.875
Strath_GW63	6.91	1820	941	0	570	196.15	101.49	0.030	0.750	123.5	11.8	164.1	47.5	1.397	0.724
Strath_GW64	7.04	2280	1177	2	580	359.00	89.86	51.180	2.410	295.0	5.3	89.4	65.5	0.021	0.438
Strath_GW65	6.02	201	104	0	65	19.20	20.10	0.010	0.040	15.6	2.9	17.0	5.3	0.045	0.014
Strath_GW66	6.63	425	220	0	182	26.70	15.00	0.020	0.050	18.7	2.4	50.0	9.5	0.021	0.040
Strath_GW67	6.55	237	123	0	122	9.20	5.70	0.000	0.160	10.2	1.5	22.0	6.6	10.780	0.260
Strath_GW68	6.41	187	97	0	82	10.90	7.70	0.700	0.120	9.9	1.4	17.5	6.2	0.045	0.047
Strath_GW69	6.78	247	128	0	76	20.30	22.00	0.370	0.050	15.6	0.5	17.5	9.8	0.125	0.065
Strath_GW70	6.91	566	293	0	132	52.13	80.50	0.920	0.030	39.0	2.4	46.0	12.5	1.380	0.100
Strath_GW71	7.09	1363	706	5	516	141.00	10.64	0.040	1.600	130.0	3.9	56.0	60.8	0.021	0.012
Strath_GW72	7.26	2110	1249	12	690	310.00	26.60	0.020	0.760	340.0	10.4	84.0	22.3	0.021	0.061
Strath_GW73	7.02	527	273	2	172	69.00	13.80	0.510	0.400	50.0	3.7	29.8	15.4	3.790	0.160
Strath_GW74	6.38	149	77	0	40	13.60	8.49	27.090	0.410	8.1	2.5	10.1	6.7	4.150	0.470
Strath_GW75	6.45	179	92	0	63	18.40	7.80	0.100	0.150	15.8	0.4	12.7	4.7	1.460	0.070
Strath_GW76	6.44	390	202	0	165	21.20	27.00	0.010	0.240	18.8	3.3	50.8	4.3	0.020	0.160
Strath_GW77	6.63	150	78	0	42	10.40	17.90	7.400	0.170	9.8	0.3	12.0	4.5	0.025	0.005
Strath_GW78	6.41	227	117	0	89	22.58	5.20	0.500	0.140	14.2	2.9	21.6	5.4	0.631	0.106
Strath_GW79	6.11	166	86	0	68	12.40	5.20	0.130	0.060	9.4	1.5	12.8	6.8	0.067	0.002
Strath_GW80	6.6	306	158	0	135	11.50	23.10	0.990	0.270	9.5	3.7	35.1	8.9	0.050	0.299
Strath_GW81	6.36	79	43	0	19	6.23	1.12	17.280	0.020	5.6	3.4	5.8	1.9	0.203	0.011
Strath_GW82	6.06	51	26	0	18	5.40	1.61	0.930	0.160	3.1	0.9	3.7	2.0	0.004	0.012
Strath_GW83	6.73	881	455	0	340	83.00	20.00	4.960	0.140	70.9	2.6	79.8	18.8	3.129	0.157

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Strath_GW84	6.8	1073	557	0	550	11.28	47.00	1.230	1.210	21.0	3.0	108.7	44.0	0.021	0.022
Strath_GW85	7.26	666	345	6	160	109.00	11.02	1.760	0.050	83.0	2.6	26.1	9.9	0.132	0.045
Strath_GW86	6.81	1100	569	0	508	91.35	29.48	0.250	1.680	83.9	5.2	87.8	42.4	0.021	0.101
Strath_GW87	6.48	294	152	0	48.2	5.14	2.90	7.300	0.030	4.3	0.2	9.5	4.7	0.103	0.004
Strath_GW88	5.84	194	100	0	80	14.35	5.00	5.300	0.020	10.5	2.1	14.6	7.8	0.050	0.030
Strath_GW89	6.92	623	323	0	202	49.11	58.00	0.150	0.300	33.1	2.6	51.3	19.6	0.021	0.546
Strath_GW90	6.47	364	188	0	165	21.68	9.93	8.540	0.910	18.9	3.5	27.0	16.9	0.021	0.077
Strath_GW91	6.51	313	162	0	118	31.02	7.50	0.010	0.260	24.2	1.4	23.2	9.6	0.193	0.104
Strath_GW92	6.53	275	142	0	109	25.13	6.20	0.010	0.120	18.2	1.9	21.7	9.2	0.026	0.408
Strath_GW93	5.44	102	53	0	48	4.57	1.80	7.200	0.030	2.8	1.3	9.9	4.9	0.021	0.010
Strath_GW94	7.03	847	509	0	390	40.90	43.60	0.290		34.0	2.8	77.5	36.8	0.548	
Strath_GW95	5.27	249	150	0	80	14.60	36.40	0.140		8.0	5.2	20.4	11.8	0.571	
Strath_GW96	6.37	311	188	0	71	9.83	80.30	0.380		16.0	4.5	24.9	12.6	0.576	
Strath_GW97	6.66	308	183	0	123	23.20	18.80	0.120		11.0	1.1	29.3	13.1	0.763	
Strath_GW98	6.97	512	308	0	250	19.10	22.70	0.220		17.0	0.9	48.3	23.2	0.553	
Strath_GW99	6.95	1359	747	0	513	46.00	183.00	0.056	1.280	126.0	2.2	124.0	20.4		
Strath_GW100	6.95	1359	747	0	678	33.80	59.90	0.385		30.0	2.2	132.0	64.2	0.894	
Strath_GW101	6.92	2150	1183	0	505	166.00	408.00	0.140	0.980	196.0	18.9	201.0	20.4		
Strath_GW102	6.6	512	307	0	251	14.30	28.70	0.510		22.0	0.7	42.9	24.2	0.596	
Strath_GW103	6.69	495	297	0	205	13.40	57.90	0.080		33.0	3.3	36.8	18.9	0.875	
Strath_GW104	6.86	450	270	0	234	11.60	16.20	0.290		14.0	0.9	42.9	20.8	0.560	
Strath_GW105	6.8	389	233	0	174	17.00	25.50	1.950		22.0	1.0	31.9	15.8	0.551	
Strath_GW106	6.97	578	346	0	248	20.60	52.30	0.530		18.0	1.2	53.7	26.8	0.562	
Strath_GW107	6.77	641	384	0	166	43.50	115.00	2.010		38.0	2.3	49.1	26.8	0.587	
Strath_GW108	7.06	1281	768	0	492	18.70	202.00	0.720		100.0	4.0	90.9	46.3	0.613	
Strath_GW109	6.28	240	144	0	99	18.40	11.60	0.300		12.0	1.2	19.3	10.4	0.566	
Strath_GW110	7.04	1815	1090	0	430	49.10	468.00	0.120		200.0	3.2	101.0	52.8	0.550	
Strath_GW111	7.08	1021	562	0	517	12.00	63.80	0.005	1.340	89.0	1.6	98.0	16.5		
Strath_GW112	6.96	1119	615	0	525	23.10	91.20	0.048	1.540	92.0	0.6	101.0	23.3		
Strath_GW113	7.4	913	501	0	394	46.80	62.10	0.013	1.180	117.0	1.2	54.0	14.6		
Strath_GW114	7.06	791	435	0	393	41.90	11.80	0.936		32.0	1.5	90.3	23.5	0.777	
Strath_GW115	7.38	1035	621	0	353	61.60	136.00	0.080		58.0	17.0	91.9	38.6	0.569	
Strath_GW116	7.06	791	435	0	419	27.00	9.90	0.936	1.110	53.0	1.5	79.0	19.4		
Strath_GW117	7.19	864	512	0	260	22.30	180.00	0.080		71.0	5.5	58.9	29.9	0.615	
Strath_GW118	7.01	1193	656	0	649	27.00	20.60	1.730	1.420	124.0	1.3	89.0	23.3		
Strath_GW119	7.53	1278	703	0	658	23.80	59.90	0.385	1.330	108.0	1.7	129.0	17.5		
Strath_GW120	6.9	825	454	0	659	18.00	26.70	0.029	1.290	74.0	1.8	132.0	23.3		
Strath_GW121	7.03	1106	608	0	493	43.00	60.00	0.038	1.140	76.0	2.1	120.0	13.6		
Strath_GW122	6.78	829	498	0	224	80.10	112.00	0.210		77.0	2.3	52.2	27.5	0.590	
Strath_GW123	6.92	1155	694	0	332	64.30	204.00	0.100		62.0	1.8	99.7	44.9	0.831	

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Strath_GW124	7.07	2680	1474	0	512	164.00	657.00	0.035	1.420	326.0	4.4	209.0	22.4		
Strath_GW125	6.42	449	269	0	153	42.00	38.40	0.610		32.0	1.5	33.2	16.9	0.570	
Strath_GW126	6.82	669	368	0	232	55.80	59.40	0.040	1.300	17.0	1.8	89.0	17.4	0.000	
Strath_GW127	7.03	1240	682	0	524	25.30	145.00	0.032	1.420	116.0	1.6	110.0	21.4		
Strath_GW128	6.57	1608	884	0	499	186.00	121.00	0.034	1.230	66.0	3.1	212.0	24.3		
Strath_GW129	6.81	1761	969	0	621	168.00	125.00	0.285	1.440	140.0	5.0	186.0	21.4		
Strath_GW130	8.31	220	132	3	89	12.40	14.10	0.042		10.0	5.4	22.4	6.2	0.050	
Strath_GW131	6.86	1156	636	0	398	109.00	90.00	0.531	1.510	50.0	5.0	156.0	16.5		
Strath_GW132	5.89	99	54	0	42	7.50	2.95	0.387	0.460	5.4	0.8	8.5	3.6	0.081	0.001
Strath_GW133	6.4	119	65	0	48	10.20	3.80	0.047	0.750	9.4	0.9	9.8	3.3	0.069	0.001
Strath_GW134	6.49	85	47	0	25	10.30	5.49	0.024	0.001	8.1	0.3	6.3	1.9	0.127	0.001
Strath_GW135	7.8	487	292	8	200	37.40	11.80	0.074	0.000	35.0	3.1	42.1	14.2	0.019	0.001
Strath_GW136	7.41	138	83	4	20	12.00	30.00	0.010	0.000	7.0	1.1	11.8	5.5	0.189	0.001
Strath_GW137	7.4	336	202	5	165	12.90	6.94	0.108	0.000	11.4	2.1	33.3	13.5	0.048	0.001
Strath_GW138	7.13	160	96	0	46	17.10	17.30	0.763	0.000	13.0	0.2	11.8	5.8	0.221	0.001
Strath_GW139	7.01	176	97	0	55	13.90	21.20	0.716	0.000	11.0	0.2	16.2	5.3	0.940	0.001
Strath_GW140	7.11	105	63	0	40	8.20	8.05	0.158	0.000	7.0	0.2	9.1	3.1	0.310	0.883
Strath_GW141	7.48	95	57	5	25	10.20	5.09	0.739	0.000	7.0	1.3	7.5	2.5	0.146	3.020
Strath_GW142	7.51	240	144	2	80	17.30	29.60	0.080	0.000	13.0	1.2	22.6	8.6	0.798	0.792
Strath_GW143	7.3	253	152	2	95	17.40	20.10	0.771	0.000	16.0	1.4	18.5	8.5	4.610	0.230
Strath_GW144	6.26	100	50	0	30	8.50	12.00	0.126	0.000	6.0	0.1	7.5	3.6	0.480	1.001
Strath_GW145	7.43	132	79	4	45	9.10	9.91	0.743	0.000	7.0	0.1	12.3	5.2	0.643	0.120
Strath_GW146	6.9	95	52	0	21	9.10	16.20	0.650	0.000	8.0	0.5	7.9	2.1	0.976	0.000
Strath_GW147	6.8	127	70	0	32	14.30	17.20	0.058	0.000	10.0	1.2	10.8	3.1	0.881	0.000
Strath_GW148	6.58	209	105	0	65	13.50	30.40	0.288	0.000	11.0	1.4	18.4	6.9	0.817	1.962
Strath_GW149	7.49	92	55	3	21	10.20	9.43	0.742	0.000	7.0	0.0	7.3	2.1	1.270	1.280
Strath_GW150	7.52	164	99	3	58	13.50	10.60	0.734	0.000	11.0	0.3	15.2	4.6	0.555	0.200
Strath_GW151	6.89	113	68	0	45	10.20	4.00	0.309	0.000	8.0	0.2	9.1	3.3	0.398	0.861
Strath_GW152	6.49	108	65	0	39	8.20	9.10	0.100	0.000	7.0	0.2	9.6	2.8	0.811	1.013
Strath_GW153	7.27	178	107	2	63	9.60	17.70	0.765	0.000	8.5	2.1	14.7	6.7	0.956	0.230
Strath_GW154	7.47	146	88	5	50	7.60	11.70	0.745	0.000	7.0	1.9	12.0	5.8	0.434	0.610
Strath_GW155	6.32	109	55	0	27	8.90	17.60	0.104	0.000	8.0	0.8	8.6	2.8	0.401	1.051
Strath_GW156	7.18	116	69	0	37	10.20	10.30	0.694	0.000	8.0	0.4	8.6	4.1	0.110	0.030
Strath_GW157	7.74	108	65	15	17	9.10	1.45	0.157	0.000	7.0	0.5	9.3	3.2	0.341	0.841
Strath_GW158	6.84	123	74	0	36	13.10	14.00	0.757	0.000	10.0	0.6	9.6	4.0	0.404	0.120
Strath_GW159	6.26	158	96.9	0	95	15.70	0.41	0.010	0.060	13.7	2.5	18.6	4.1	1.955	0.151
Strath_GW160	6.35	185	113.5	5	85	9.40	0.41	0.950	0.270	8.3	0.3	10.0	5.8	14.193	0.296
Strath_GW161	7.44	430	263.8	10	205	16.30	4.39	0.010	1.100	14.2	7.7	35.0	21.0	0.631	0.261
Strath_GW162	6.36	201	123.3	0	103	11.60	0.41	0.010	0.110	10.5	1.1	17.5	7.9	0.922	0.470
Strath_GW163	7.57	1755	1060	5	256	131.00	312.50	0.001	0.000	134.0	5.6	143.2	21.4	0.001	0.000

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Strath_GW164	6.44	2486	1505	0	637	322.16	266.60	0.001	0.000	242.0	13.1	232.6	40.9	0.001	0.000
Strath_GW165	7.66	1001	602	15	399	72.60	36.20	0.012	0.000	54.0	3.6	88.6	38.0	0.001	0.000
Strath_GW166	6.56	3925	2389	0	672	896.00	63.40	0.250	0.000	498.0	6.5	207.0	57.0	0.001	0.000
Strath_GW167	7.63	1563	943	3	470	191.06	74.30	0.001	0.000	116.0	10.5	129.0	34.2	0.001	0.000
Strath_GW168	7.58	364	219	2	110	50.10	12.60	0.227	0.000	28.0	7.0	25.3	10.2	0.001	0.000
Strath_GW169	6.55	1036	624	0	412	94.60	26.90	0.029	0.000	76.0	8.8	88.9	28.9	0.001	0.000
Strath_GW170	6.26	346	208	0	132	44.50	2.10	0.001	0.000	25.0	3.8	25.2	12.5	0.001	0.000
Strath_GW171	7.59	334	201	2	132	29.10	15.30	0.008	0.000	23.0	5.2	29.2	9.2	0.001	0.000
Strath_GW172	6.3	1159	698	0	470	116.00	14.30	0.001	0.000	84.0	4.2	98.2	34.6	0.001	0.000
Strath_GW173	7.55	1117	673	3	440	104.00	46.90	0.034	0.000	80.0	4.2	96.0	33.4	0.001	0.000
Strath_GW174	7.67	1094	659	4	408	117.00	38.90	0.154	0.000	90.0	8.4	96.2	23.6	0.001	0.000
Strath_GW175	6.37	935	563	0	475	56.40	4.20	0.001	0.000	40.0	4.1	110.0	28.2	0.001	0.000
Strath_GW176	7.59	845	509	0	416	86.40	4.20	0.001	0.000	54.0	4.5	88.6	29.9	0.001	0.000
Strath_GW177	7.58	674	405	0	298	55.90	12.70	0.001	0.000	38.0	4.2	69.0	18.4	0.001	9.000
Strath_GW178	5.93	351	211	0	162	30.10	0.09	0.013	0.000	15.0	2.4	33.9	13.7	0.001	0.000
Strath_GW179	6.33	233	140	0	116	14.80	0.09	0.001	0.000	11.5	1.5	20.3	10.4	0.001	0.000
Strath_GW180	6.86	415	249	0	164	38.70	4.12	0.001	0.000	25.0	4.5	30.9	12.5	0.001	0.000
Strath_GW181	6.43	440	261	0	212	32.80	0.09	0.192	0.000	18.0	5.1	38.9	18.9	0.001	0.000
Strath_GW182	6.38	642	386	0	241	76.20	15.00	0.001	0.000	46.0	5.1	56.3	19.4	0.001	0.000
Strath_GW183	6.61	600	303	0	287	47.20	4.99	0.075	0.430	42.0	7.0	53.0	18.0	0.447	0.000
Strath_GW184	6.92	210	126	0	79	16.40	11.70	0.457	0.000	12.0	3.1	15.5	7.6	0.001	0.000
Strath_GW185	8.25	763	459	37	319	27.30	16.29	0.414	0.000	18.0	5.2	86.3	27.5	0.001	0.000
Strath_GW186	7.45	564	339	2	261	35.00	20.15	0.478	0.000	34.0	5.0	53.6	15.6	0.001	0.000
Strath_GW187	8.57	618	372	33	219	43.70	14.79	0.498	0.000	40.0	6.1	48.2	21.5	0.001	0.000
Strath_GW188	8.46	531	319	30	171	34.60	18.19	0.458	0.000	24.0	6.0	47.4	20.6	0.001	0.000
Strath_GW189	7.48	407	245	5	155	35.50	16.22	0.527	0.000	35.0	6.5	27.3	11.7	0.001	0.000
Strath_GW190	7.47	582	350	4	252	41.90	23.49	0.983	0.000	26.0	3.6	58.5	21.7	0.001	0.000
Strath_GW191	7.3	651	391	2	230	82.00	18.48	0.393	0.000	80.0	1.5	36.4	15.6	0.078	0.000
Strath_GW192	8.46	1072	646	18	436	65.50	19.91	0.441	0.000	85.0	8.5	94.0	18.5	0.085	0.000
Strath_GW193	7.48	1346	811	2	575	117.50	32.00	0.411	0.000	108.0	6.2	128.0	26.4	0.001	0.000
Strath_GW194	6.81	363	201	0	135	51.10	0.69	0.051	0.000	40.0	4.0	22.3	8.2	0.048	0.000
Strath_GW195	7.26	478	264	1	220	39.70	0.56	0.059	0.000	40.2	5.4	39.4	11.3	0.050	0.000
Strath_GW196	7.6	766	421	3	259	112.00	0.56	0.063	0.000	81.0	6.2	60.0	12.0	0.040	0.000
Strath_GW197	6.71	237	130	0	109	20.00	0.58	0.036	0.000	18.9	3.0	15.2	8.1	0.040	0.000
Strath_GW198	6.63	365	183	0	161	33.80	1.09	0.405	0.000	30.0	2.7	27.4	9.0	0.000	0.000
Strath_GW199	7.78	247	124	13	92	18.30	0.10	0.120	0.000	17.0	1.5	22.5	7.0	0.000	0.000
Strath_GW200	7.56	812	407	5	269	122.00	4.05	0.016	0.000	116.0	2.9	35.0	13.4	0.000	0.000

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Strath_GW201	6.43	423	254	0	165	49.10	2.63	0.049	0.100	42.0	7.3	27.0	10.6	0.023	0.000
Strath_GW202	6.42	447	268	0	172	56.00	0.91	0.290	0.100	49.0	5.3	26.0	11.0	0.065	0.000
Strath_GW203	6.68	353	212	0	150	34.60	4.16	0.112	0.140	40.0	8.1	20.1	7.1	0.047	0.000
Strath_GW204	6.77	567	340	0	243	60.30	0.82	0.059	0.110	77.0	4.7	27.3	10.6	0.030	0.000
Strath_GW205	6.7	575	345	0	228	67.50	5.31	0.053	0.100	69.0	6.2	31.4	12.5	0.034	0.000
Strath_GW206	6.52	142	86	0	46	21.30	6.90	0.133	0.110	20.0	6.0	6.2	2.1	0.007	0.000
Strath_GW207	6.71	172	103	0	43	21.30	20.80	0.029	0.020	24.0	9.6	5.5	2.1	0.072	0.000
Strath_GW208	6.95	1046	628	0	429	95.50	46.70	2.000	0.060	88.0	7.1	87.0	28.2	0.066	0.000
Strath_GW209	7.04	1202	721	0	465	133.00	44.10	0.143	0.210	130.0	8.0	83.2	25.3	0.057	0.000
Strath_GW210	6.88	1520	912	0	440	96.00	256.00	0.123	0.370	252.0	11.1	50.0	20.0	0.057	0.000
Strath_GW211	6.82	1342	805	0	648	56.40	67.20	0.033	0.300	133.0	5.7	97.0	35.0	0.001	0.000
Strath_GW212	6.83	2754	1653	0	1105	146.00	254.00	3.520	0.270	402.0	10.9	120.0	46.0	0.076	0.000
Strath_GW213	6.88	1520	912	0	448	96.00	256.00	0.123	0.370	252.0	11.1	50.0	20.0	0.057	0.000
Strath_GW214	6.82	1342	805	0	648	56.40	67.20	0.033	0.300	133.0	5.7	97.0	35.0	0.001	0.000
Strath_GW215	6.83	2754	1653	0	1105	146.00	254.00	3.520	0.270	402.0	10.9	120.0	46.0	0.076	0.000
Strath_GW216	6.59	1161	697	0	443	98.00	91.70	0.128	0.210	189.0	8.6	42.0	17.2	0.064	0.000
Strath_GW217	5.9	80	41	0	25	12.00	2.21	0.019	0.270	10.0	2.4	3.8	1.5	0.005	0.000
Strath_GW218	6.63	533	320	0	218	56.00	7.96	0.069	0.370	66.0	2.6	30.0	11.0	0.054	0.000
Strath_GW219	7.05	669	401	0	293	67.80	3.31	0.031	0.040	71.0	6.0	43.0	17.1	0.026	0.000
Strath_GW220	6.97	599	359	0	257	59.00	5.94	0.089	0.110	62.0	2.0	38.7	16.0	0.047	0.000
Strath_GW221	6.73	332	199	0	136	33.60	7.38	0.399	0.110	37.0	5.5	20.0	7.2	0.047	0.000
Strath_GW222	6.56	309	185	0	135	28.90	2.53	0.843	0.090	33.0	4.6	19.4	7.0	0.032	0.000
Strath_GW223	5.91	176	98	0	68	21.60	1.91	0.003	0.090	24.0	3.2	8.5	2.6	0.037	0.000
Strath_GW224	6.7	463	278	0	239	25.40	2.43	0.281	0.110	27.0	6.8	43.0	14.6	0.036	0.000
Strath_GW225	8.06	334	183	15	106	23.00	21.80	0.392	0.000	14.0	3.7	30.2	13.2	0.493	0.000
Strath_GW226	6.7	463	278	0	239	25.40	2.43	0.281	0.110	27.0	6.8	43.0	14.6	0.036	0.000
Strath_GW227	7.63	475	240	14	129	70.90	6.31	0.431	0.000	60.0	2.3	22.0	10.6	0.000	0.000
Strath_GW228	7.3	620	373	0	333	12.80	22.90	2.570	0.000	41.0	5.1	57.0	19.4	0.676	0.000
Strath_GW229	8.51	254	153	10	73	15.50	16.10	0.215	0.000	14.0	5.0	17.0	8.5	0.006	0.000
Strath_GW230	7.3	1029	620	0	461	47.30	59.90	3.000	0.000	110.0	4.7	68.6	22.1	0.894	0.000
Strath_GW231	8.06	280	154	7	103	19.50	16.70	0.271	0.000	17.0	4.4	21.0	10.6	0.522	0.000
Strath_GW232	6.71	172	103	0	43	21.30	20.80	0.029	0.020	24.0	9.6	5.5	2.1	0.072	0.000
Strath_GW233	7.9	704	423	0	304	53.80	22.30	2.380	0.000	41.0	9.5	58.8	24.9	0.683	0.000
Strath_GW234	7.4	830	500	0	356	47.30	44.40	2.330	0.000	42.0	5.2	75.0	29.2	0.789	0.000
Strath_GW235	8.25	292	161	14	87	26.60	12.60	0.268	0.000	17.0	3.8	28.1	9.1	0.190	0.000
Strath_GW236	7.4	738	444	0	338	39.80	27.80	3.030	0.000	35.0	6.8	79.5	19.5	0.698	0.000
Strath_GW237	7.92	320	180	0	137	23.60	22.30	0.357	0.000	17.0	1.7	30.2	13.5	0.443	0.000
Strath_GW238	7.4	551	331	0	278	16.30	25.40	2.830	0.000	44.0	2.7	47.0	15.0	0.771	0.000
Strath_GW239	8.22	380	209	21	126	21.30	19.20	0.273	0.000	18.0	6.6	32.6	15.1	0.225	0.000
Strath_GW240	7.4	462	278	0	263	3.60	16.40	2.380	0.000	20.0	5.4	44.0	19.4	0.813	0.000

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Strath_GW241	7.4	1376	830	0	374	207.40	24.70	2.340	0.000	110.0	3.9	108.0	27.2	0.753	0.000
Strath_GW242	6.88	1520	912	0	448	262.00	25.60	0.123	0.370	252.0	11.1	50.0	20.0	0.057	0.000
Strath_GW243	7.43	1604	888	0	430	120.00	262.00	0.109	0.000	174.0	7.6	112.0	32.0	0.000	0.000
Strath_GW244	7.04	1202	721	0	586	56.40	44.10	0.143	0.210	130.0	8.0	83.2	25.3	0.057	0.000
Strath_GW245	7.36	1060	585	5	450	54.20	69.13	0.253	0.000	67.0	6.0	89.6	36.8	0.000	0.000
Strath_GW246	8.28	320	176	11	83	36.10	22.40	0.287	0.000	16.0	1.9	28.4	13.8	0.254	0.000
Strath_GW247	7.63	464	246	11	190	36.00	6.89	0.608	0.000	28.0	3.8	41.7	14.2	0.000	0.000
Strath_GW248	6.84	850	468	0	365	26.60	84.90	0.283	0.000	23.0	5.3	87.3	38.0	0.169	0.000
Strath_GW249	7.8	712	428	9	225	45.90	89.20	2.990	0.000	49.0	5.7	58.4	23.1	0.777	0.000
Strath_GW250	7.39	183	101	0	45	26.60	16.10	0.246	0.000	18.2	1.8	11.2	5.4	0.424	0.000
Strath_GW251	8.27	450	248	12	156	42.50	16.40	0.393	0.000	32.0	2.6	36.0	17.3	0.263	0.000
Strath_GW252	6.42	447	268	0	192	46.20	0.91	0.290	0.100	45.0	5.3	26.0	12.0	0.065	0.000
Strath_GW253	7.2	169	99	2	60	14.00	8.75	0.001	0.000	12.0	2.6	10.7	6.2	0.000	0.000
Strath_GW254	6.77	567	340	0	243	60.30	0.82	0.059	0.110	77.0	4.7	27.3	10.6	0.030	0.000
Strath_GW255	6.81	575	317	0	229	59.90	14.39	0.034	0.000	40.8	3.3	47.0	18.9	0.000	0.000
Strath_GW256	7.4	1445	872	10	486	106.00	147.00	3.390	0.000	95.0	9.0	149.0	36.0	0.588	0.000
Strath_GW257	7.29	182	100	3	61	20.70	5.75	0.001	0.000	16.5	2.6	10.0	6.4	0.000	0.000
Strath_GW258	7.3	600	390	5	250	40.00	28.30	1.100	0.000	36.0	4.9	49.1	23.5	0.188	0.000
Strath_GW259	7.92	340	187	8	120	29.00	22.40	0.366	0.000	12.0	3.5	32.2	15.1	0.385	0.000
Strath_GW260	5.91	176	98	0	68	21.60	1.91	0.003	0.090	24.0	3.2	8.5	2.6	0.037	0.000
Strath_GW261	7.08	531	293	0	228	36.50	26.00	0.361	0.000	30.0	1.8	42.5	22.3	0.000	0.000
Strath_GW262	7.2	638	384	0	302	37.20	28.20	2.340	0.000	36.0	6.3	59.0	20.3	0.771	0.000
Strath_GW263	6.5	230	138	0	69	19.10	21.80	0.507	0.000	15.0	3.1	16.1	7.0	0.439	0.000
Strath_GW264	6.86	590	325	0	266	26.60	37.10	0.461	0.000	18.0	6.1	51.2	29.4	0.192	0.000
Strath_GW265	8.47	410	220	21	121	38.30	15.80	0.280	0.000	29.0	3.6	35.8	13.4	0.220	0.000
Strath_GW266	7.3	237	142	3	80	18.10	20.60	2.320	0.000	17.0	4.4	16.9	7.8	1.030	0.000
Strath_GW267	8.28	210	116	14	72	17.20	25.70	0.270	0.000	15.0	2.4	22.2	10.9	0.337	0.000
Strath_GW268	7.4	464	279	2	185	46.00	20.50	2.300	0.000	44.0	5.0	32.0	12.4	0.711	0.000
Strath_GW269	7.2	548	329	0	215	52.80	16.70	2.480	0.000	37.0	7.4	39.1	19.8	0.784	0.000
Strath_GW270	6.68	353	212	0	150	34.60	4.16	0.112	0.140	40.0	8.1	20.1	7.1	0.047	0.000
Strath_GW271	7.76	340	187	0	173	24.80	16.80	0.287	0.000	23.0	4.5	31.4	16.7	0.387	0.000
Strath_GW272	7.43	272	163	7	85	21.70	15.30	0.227	0.000	16.0	4.4	20.1	9.2	1.080	0.000
Strath_GW273	8.56	500	301	23	179	21.70	16.80	0.230	0.000	22.0	4.7	46.9	15.0	0.011	0.000
Strath_GW274	8.28	316	174	13	88	28.30	23.20	0.253	0.000	25.0	1.8	18.1	14.4	0.237	0.000
Strath_GW275	6.56	309	185	0	135	28.90	2.53	0.843	0.090	33.0	4.6	19.4	7.0	0.032	0.000
Strath_GW276	7.48	566	340	3	268	28.20	18.90	0.249	0.000	25.0	6.4	52.0	22.3	0.320	0.000
Strath_GW277	8.19	350	192	11	114	30.80	19.80	0.317	0.000	26.0	5.2	28.0	10.5	0.540	0.000
Strath_GW278	8.32	250	138	20	46	24.80	21.00	0.277	0.000	12.0	1.9	23.4	10.6	0.645	0.000
Strath_GW279	7	710	461	0	316	58.00	19.90	0.001	0.000	48.0	3.7	61.7	24.6	0.291	0.000
Strath_GW280	7.8	632	380	0	300	32.80	21.40	2.310	0.000	25.6	5.1	61.4	23.9	0.870	0.000

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Strath_GW281	7.41	400	220	2	154	39.20	15.80	0.322	0.000	20.0	5.5	33.2	16.4	0.219	0.000
Strath_GW282	6.92	590	345	0	290	39.00	3.39	0.925	0.210	38.0	5.7	51.0	19.0	0.026	0.000
Strath_GW283	6.52	142	86	0	46	21.30	6.90	0.133	0.110	20.0	6.0	6.2	2.1	0.007	0.000
Strath_GW284	8.18	170	90	8	34	26.60	19.20	0.278	0.000	18.0	1.9	12.4	6.9	0.302	0.000
Strath_GW285	6.97	599	359	0	253	59.00	5.94	0.089	0.110	62.0	2.0	38.7	16.0	0.047	0.000
Strath_GW286	7.1	580	319	0	219	62.10	19.30	0.428	0.000	40.0	5.1	47.2	18.4	0.169	0.000
Strath_GW287	8.02	329	181	28	112	12.20	19.80	0.320	0.000	8.0	1.4	35.2	15.6	0.473	0.000
Strath_GW288	6.5	370	222	0	148	29.00	25.90	0.466	0.000	22.0	2.1	31.2	13.5	0.865	0.000
Strath_GW289	8.21	229	126	9	69	28.40	17.10	0.423	0.000	14.0	3.1	20.8	9.4	0.264	0.000
Strath_GW290	7.18	330	170	0	138	24.80	15.80	0.301	0.000	15.0	4.3	30.3	13.9	0.175	0.000
Strath_GW291	7.54	235	129	10	85	13.10	12.80	0.323	0.000	7.0	4.4	22.0	10.9	0.191	0.000
Strath_GW292	7.4	1254	756	7	354	121.00	145.00	2.660	0.000	100.0	3.9	97.1	38.0	0.752	0.000
Strath_GW293	7.06	1500	825	0	750	39.50	91.10	0.634	0.000	30.0	6.2	154.0	71.1	0.146	0.000
Strath_GW294	8.39	310	171	16	119	13.00	11.90	0.246	0.000	11.0	4.8	33.2	10.2	0.190	0.000
Strath_GW295	7.74	280	160	7	114	13.00	18.50	0.246	0.000	11.0	7.3	23.4	11.7	0.662	0.000
Strath_GW296	7.41	1177	650	0	488	81.20	65.10	0.018	0.000	78.0	5.2	109.0	33.4	0.000	0.000
Strath_GW297	6.82	1342	805	0	638	56.40	67.20	0.033	0.300	129.0	5.7	97.0	35.0	0.001	0.000
Strath_GW298	8.37	390	215	10	159	21.30	14.40	0.330	0.000	18.0	2.7	40.8	12.7	0.253	0.000
Strath_GW299	8.25	240	133	11	93	19.80	14.90	0.267	0.000	14.0	4.8	21.1	11.2	0.319	0.000
Strath_GW300	7.1	1110	613	0	436	78.80	79.90	1.625	0.000	90.0	5.2	84.0	35.1	0.000	0.000
Strath_GW301	7.41	1061	586	2	462	58.60	59.00	0.862	0.000	60.0	6.2	94.3	37.6	0.000	0.000
Strath_GW302	6.86	1010	606	0	438	88.40	43.40	0.689	0.200	150.0	8.8	42.0	18.6	0.046	0.000
Strath_GW303	6.95	1046	628	0	455	75.50	46.70	2.000	0.060	85.0	7.1	87.0	28.2	0.066	0.000
Strath_GW304	5.9	80	41	0	25	12.00	2.21	0.019	0.270	10.0	2.4	3.8	1.5	0.005	0.000
Strath_GW305	7.9	1065	641	6	265	124.00	124.00	2.810	0.000	110.0	9.9	64.9	27.8	0.800	0.000
Strath_GW306	7.4	579	348	4	245	34.00	33.30	2.420	0.000	28.0	5.7	54.4	20.6	0.673	0.000
Strath_GW307	7.4	330	198	3	150	19.50	15.40	2.540	0.000	18.0	5.6	25.2	14.2	0.695	0.000
Strath_GW308	7.93	330	182	5	151	17.70	12.80	0.361	0.000	19.0	4.3	27.8	13.9	0.202	0.000
Strath_GW309	8.64	300	165	14	107	19.50	17.80	0.427	0.000	17.0	7.2	29.2	10.1	0.342	0.000
Strath_GW310	7.4	678	408	2	202	78.00	53.50	2.610	0.000	80.0	1.6	41.1	13.7	0.889	0.000
Strath_GW311	7.35	410	210	0	185	26.60	15.70	0.216	0.000	25.0	1.9	35.7	14.5	0.161	0.000
Strath_GW312	8.04	150	83	11	41	8.10	12.90	0.416	0.000	5.0	3.6	13.2	6.7	0.625	0.000
Strath_GW313	7.4	102	61	3	23	8.50	12.40	2.540	0.000	6.0	0.3	10.0	3.0	0.828	0.000
Strath_GW314	8.44	460	253	17	188	26.00	14.10	0.317	0.000	24.0	4.7	38.3	19.4	0.191	0.000
Strath_GW315	6.7	575	345	0	228	67.50	5.31	0.053	0.100	65.0	6.2	31.4	12.5	0.034	0.000
Strath_GW316	7.42	720	397	14	259	60.40	26.40	0.333	0.000	48.0	5.5	60.0	24.0	0.000	0.000
Strath_GW317	7.7	829	499	7	300	49.80	82.60	2.380	0.000	45.0	5.8	78.8	26.9	0.847	0.000
Strath_GW318	6.02	274	143	0	104	21.90	19.10	1.407	0.000	19.0	1.2	21.6	11.0	0.392	0.000
Strath_GW319	7.3	682	410	2	137	69.00	128.00	2.290	0.000	67.0	2.4	43.3	19.2	0.863	0.000
Strath_GW320	8.02	244	134	0	79	26.60	23.20	0.303	0.000	13.0	3.8	21.8	9.5	0.416	0.000

Sample ID	pH	EC μS/cm	TDS mgL^{-1}	CO_3 mgL^{-1}	HCO_3 mgL^{-1}	Cl mgL^{-1}	SO_4 mgL^{-1}	NO_3 mgL^{-1}	F mgL^{-1}	Na mgL^{-1}	K mgL^{-1}	Ca mgL^{-1}	Mg mgL^{-1}	Fe mgL^{-1}	Mn mgL^{-1}
Strath_GW321	7.4	331	199	2	141	19.00	20.80	2.360	0.000	14.0	3.5	34.0	10.7	0.773	0.000
Strath_GW322	8.53	284	171	13	83	11.90	21.60	0.223	0.000	14.0	3.7	20.1	10.5	0.581	0.000
Strath_GW323	7.4	540	325	3	219	49.00	21.00	2.350	0.000	35.0	5.7	47.0	18.2	0.841	0.000
Strath_GW324	7.9	1390	838	10	530	153.00	19.70	2.540	0.000	98.0	5.2	131.0	36.3	0.500	0.000
Strath_GW325	7.19	290	150	0	120	18.40	20.90	0.261	0.000	15.0	3.0	24.4	11.9	0.323	0.000
Strath_GW326	6.6	340	244	0	140	18.20	23.80	1.210	0.000	23.0	3.7	21.9	13.5	0.351	0.000
Strath_GW327	7.45	510	281	3	235	28.40	16.60	0.417	0.000	26.0	6.5	42.8	20.2	0.161	0.000
Strath_GW328	7.04	572	315	0	234	56.00	8.20	0.242	0.000	42.0	6.0	48.8	15.4	0.000	0.000
Strath_GW329	6.43	423	254	0	188	39.10	2.63	0.049	0.100	42.0	7.3	27.0	10.6	0.023	0.000
Strath_GW330	7.58	153	85	4	31	21.90	14.40	0.327	0.000	7.0	2.8	13.8	5.8	0.398	0.000
Strath_GW331	7.05	669	401	0	293	67.80	3.31	0.031	0.040	71.0	6.0	43.0	17.1	0.026	0.000
Strath_GW332	7.19	737	405	0	330	47.20	26.50	0.020	0.000	41.0	4.1	62.0	28.9	0.000	0.000
Strath_GW333	8.3	370	208	39	65	26.60	21.80	0.281	0.000	11.0	4.2	33.2	16.4	0.338	0.000
Strath_GW334	6.2	100	60	0	41	9.50	6.44	0.392	0.000	7.0	2.1	8.5	3.1	0.744	0.000
Strath_GW335	7.4	972	585	4	396	72.10	55.60	2.530	0.000	78.0	4.3	75.0	29.1	0.883	0.000
Strath_GW336	7.38	593	357	2	242	40.10	30.60	2.350	0.000	45.0	4.0	44.1	18.6	0.911	0.000
Strath_GW337	8.21	229	126	13	48	26.60	15.60	0.292	0.000	15.0	3.7	18.4	7.8	0.305	0.000
Strath_GW338	7.52	270	149	2	119	14.20	15.30	0.254	0.000	12.0	3.3	23.6	11.6	0.161	0.000
Strath_GW339	7.97	440	242	15	192	30.10	16.60	0.348	0.000	25.0	5.7	40.8	18.1	0.504	0.000
Strath_GW340	8.26	219	120	19	39	16.20	20.80	0.338	0.000	12.0	3.2	19.1	7.2	0.669	0.000
Strath_GW341	7.4	717	431	3	304	52.80	29.30	2.990	0.000	49.0	4.7	58.2	24.3	0.772	0.000
Strath_GW342	7.74	366	180	10	122	30.70	16.10	0.250	0.000	22.0	4.6	29.8	11.1	0.300	0.000
Strath_GW343	7.2	749	376	2	300	84.30	4.50	1.590	0.090	76.2	2.9	53.0	16.0	2.391	0.946
Strath_GW344	7.16	760	382	2	328	75.00	0.41	0.010	0.120	65.5	3.1	55.7	19.3	0.128	0.024
Strath_GW345	7.6	350	176	5	185	9.50	1.66	0.010	0.670	8.4	4.9	37.0	15.0	0.412	0.293
Strath_GW346	7.4	273	162	3	130	15.80	3.73	0.069	0.000	11.0	2.9	27.0	10.1	0.115	0.000
Strath_GW347	6.6	259	156	0	125	15.30	7.13	0.030	0.000	13.0	2.6	24.5	9.0	0.071	0.000
Strath_GW348	6.9	509	306	0	229	25.60	29.90	0.064	0.000	21.0	5.3	52.0	17.4	0.496	0.000
Strath_GW349	6.2	238	148	0	70.8	21.90	29.00	0.071	0.000	19.0	3.5	17.0	7.4	0.434	0.000
Strath_GW350	6	106	63	0	27	12.60	12.60	0.001	0.000	8.0	1.0	8.8	3.0	0.063	0.000
Strath_GW351	6.2	204	123	0	69	14.60	24.10	0.017	0.000	14.0	2.6	16.2	6.8	0.023	0.000
Strath_GW352	6.3	150	90	0	45	16.50	14.60	0.001	0.000	12.0	3.5	11.0	4.0	0.370	0.000
Strath_GW353	6.5	416	246	0	165	16.50	47.90	0.110	0.000	15.7	3.7	40.9	15.6	0.089	0.000
Strath_GW354	5.2	185	112	0	44	15.80	32.60	0.271	0.000	11.0	5.9	14.5	6.1	0.054	0.000
Strath_GW355	6.4	936	549	0	242	18.30	234.00	0.001	0.000	38.0	7.8	90.5	36.0	0.945	0.000
Strath_GW356	6.4	409	252	0	149	22.90	48.70	0.004	0.000	16.0	4.6	40.0	15.6	0.143	0.000
Strath_GW357	6.6	515	302	0	191	18.30	72.30	0.001	0.000	14.0	4.8	57.9	18.4	0.520	0.000
Strath_GW358	6.4	239	143	0	103	21.00	5.79	0.001	0.000	14.0	3.5	21.0	8.0	0.115	0.000
Strath_GW359	6.6	269	157	0	124	20.10	3.83	0.979	0.000	12.0	2.4	26.0	9.9	0.001	0.000
Strath_GW360	6.5	243	146	0	104	22.00	4.72	0.249	0.000	12.0	1.6	24.0	8.6	0.001	0.000

Sample ID	pH	EC μS/cm	TDS mgL^{-1}	CO_3 mgL^{-1}	HCO_3 mgL^{-1}	Cl mgL^{-1}	SO_4 mgL^{-1}	NO_3 mgL^{-1}	F mgL^{-1}	Na mgL^{-1}	K mgL^{-1}	Ca mgL^{-1}	Mg mgL^{-1}	Fe mgL^{-1}	Mn mgL^{-1}
Strath_GW361	6.2	106	63	0	27	19.20	3.42	0.041	0.000	12.0	1.8	6.0	2.4	0.053	0.000
Strath_GW362	6.1	286	174	0	136	19.20	4.89	0.002	0.000	12.0	3.2	28.9	10.0	0.003	0.000
Strath_GW363	6.2	381	223	0	185	22.00	7.72	0.070	0.000	14.0	4.2	37.9	14.6	0.113	0.000
Strath_GW364	6.3	416	252	0	205	22.00	6.93	0.978	0.000	15.0	3.1	42.0	16.2	0.153	0.000
Strath_GW365	6.4	303	177	0	146	17.40	7.23	0.049	0.000	13.0	2.9	28.4	12.2	0.105	0.000
Strath_GW366	6.6	484	296	0	254	14.00	13.40	0.156	0.000	11.0	4.1	52.4	20.0	0.072	0.000
Strath_GW367	6.7	324	190	0	148	19.10	13.00	0.440	0.000	16.0	3.9	29.6	11.8	0.001	0.000
Strath_GW368	6.6	544	321	0	201	29.10	63.70	0.009	0.000	26.0	5.5	51.0	19.6	0.490	0.000
Strath_GW369	6.5	234	139	0	106	17.40	5.64	0.097	0.000	16.0	3.1	20.0	7.0	0.001	0.000
Strath_GW370	6.7	600	363	0	320	19.20	10.80	0.052	0.000	18.0	5.8	62.0	24.0	0.162	0.000
Strath_GW371	6.9	346	204	0	168	19.20	8.35	0.131	0.000	11.0	7.2	34.6	13.0	0.154	0.000
Strath_GW372	6.2	171	103	0	65	11.00	16.60	0.032	0.000	9.0	4.2	14.6	5.9	0.008	0.000
Strath_GW373	5.7	118	68	0	29	17.40	10.60	0.024	0.000	13.0	1.6	7.0	2.8	0.115	0.000
Strath_GW374	6.54	259	129	0	99	23.50	6.88	0.039	0.860	18.0	1.6	20.0	9.0	0.014	0.001
Strath_GW375	7.72	341	166	14	144	8.80	7.14	0.060	0.970	7.9	0.8	41.0	11.5	0.001	0.001
Strath_GW376	7.7	661	325	27	243	27.00	45.30	0.054	0.910	25.0	3.3	54.0	33.9	0.542	0.001
Strath_GW377	6.03	146	74	0	41	14.80	16.00	0.065	0.760	12.3	3.2	10.0	4.5	0.009	0.001
Strath_GW378	6.02	161	97	0	60	16.60	6.33	0.340	0.520	13.0	1.9	11.9	5.0	0.002	0.000
Strath_GW379	6.25	378	227	0	129	30.60	36.70	0.075	0.860	22.0	0.8	37.2	11.6	0.012	0.000
Strath_GW380	6.08	224	134	0	83	28.00	2.20	0.051	0.740	18.0	3.1	16.5	6.7	0.211	0.000
Strath_GW381	6.74	613	368	0	198	17.40	112.00	0.459	1.110	15.4	29.0	11.2	44.5	13.900	0.000
Strath_GW382	6.14	206	124	0	83	17.30	7.46	0.002	0.710	14.0	3.6	13.0	8.6	0.211	0.000
Strath_GW383	7.35	112	67	3	28	11.70	10.50	0.742	0.000	9.1	1.2	8.1	3.1	1.190	0.220
Strath_GW384	7.4	84	50	2	21	9.50	6.76	0.685	0.000	7.8	0.9	5.2	2.1	1.370	0.140
Strath_GW385	6.4	237	142	0	100	22.00	2.73	0.128	0.920	17.0	0.6	18.6	8.9	0.057	0.000
Strath_GW386	6.9	201	111	0	61	16.20	26.40	0.446	0.000	14.0	1.9	17.8	5.4	0.750	0.000
Strath_GW387	6.37	93	49	0	23	10.90	11.20	0.298	0.000	9.0	1.4	5.6	2.0	0.486	1.066
Strath_GW388	7.2	136	75	1	32	14.50	18.30	0.631	0.000	12.0	1.8	10.3	3.1	0.872	0.000
Strath_GW389	7.55	108	54	4	39	7.30	5.40	0.126	0.000	7.0	1.6	7.2	3.8	0.578	1.088
Strath_GW390	6.72	212	127	0	90	15.40	8.90	0.095	0.980	14.0	0.7	17.3	7.8	0.047	0.000
Strath_GW391	6.59	332	199	0	115	20.00	39.80	0.018	0.900	15.0	1.0	35.2	10.0	1.970	0.000
Strath_GW392	6.12	89	53	0	20	13.50	6.89	0.016	0.250	12.0	1.0	4.3	1.4	0.024	0.000
Strath_GW393	6.29	339	203	0	82	17.20	68.10	0.032	0.680	32.0	2.9	23.0	8.6	0.220	0.000
Strath_GW394	6.69	120	72	0	8	16.00	29.10	0.035	0.330	17.0	2.0	5.0	2.0	0.054	0.000
Strath_GW395	7.68	587	295	6	250	42.00	1.17	0.010	0.170	35.5	4.4	45.0	18.9	0.229	0.521
Strath_GW396	7.06	229	115	0	105	11.00	14.80	0.010	0.110	7.8	2.5	23.5	8.4	0.032	0.385
Strath_GW397	6.7	243	146	0	133	8.70	0.41	0.010	0.060	7.3	2.7	24.9	9.4	0.076	0.297
Strath_GW398	7.32	643	331	5	270	55.00	12.80	0.437	0.000	49.0	2.9	55.9	19.1	0.492	0.000
Strath_GW399	7.58	754	367	18	210	105.00	15.40	0.817	0.000	85.0	2.5	40.4	19.1	0.001	0.000
Strath_GW400	7.46	491	244	4	229	29.80	8.81	0.593	0.000	25.0	2.8	41.2	21.0	0.065	0.000

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Strath_GW401	7.57	800	403	10	350	50.00	24.20	1.180	0.000	48.0	2.4	81.0	22.0	0.014	0.000
Strath_GW402	7.53	764	379	5	400	31.90	0.91	0.842	0.000	25.0	3.5	86.3	27.2	0.001	0.000
Strath_GW403	6.96	232	139	0	110	12.60	6.76	0.474	0.000	8.0	5.2	19.9	10.2	0.001	0.000
Strath_GW404	6.87	295	177	0	127	18.90	15.50	0.801	0.000	13.0	5.1	24.6	12.4	0.096	0.000
Strath_GW405	7.6	360	216	10	146	22.00	12.20	0.785	0.000	19.0	5.4	35.0	11.4	0.105	0.000
Strath_GW406	7.54	123	74	3	47	8.90	5.71	0.421	0.000	6.0	4.7	12.2	3.1	0.001	0.000
Strath_GW407	7.86	818	432	12	270	68.00	72.00	1.760	0.000	50.0	1.9	68.9	30.6	0.102	0.000
Strath_GW408	7.57	423	215	6	135	38.20	31.80	0.930	0.000	36.0	3.8	35.0	10.9	0.001	0.000
Strath_GW409	6.62	429	258	0	142	30.20	52.60	0.849	0.000	27.0	2.5	32.4	16.9	0.253	0.000
Strath_GW410	6.38	138	71	0	35	14.00	18.50	0.814	0.000	10.0	1.2	11.0	4.6	0.001	0.000
Strath_GW411	6.74	730	364	0	270	64.30	49.70	0.905	0.000	55.0	2.9	61.9	20.5	0.001	0.000
Strath_GW412	7.76	953	574	12	250	110.00	91.00	1.690	0.000	90.0	3.8	80.0	18.7	0.053	0.000
Strath_GW413	6.74	4009	1592	0	1900	175.00	195.00	0.832	0.000	160.0	14.0	450.0	125.0	2.290	0.000
Strath_GW414	8.26	955	575	6	12	67.30	204.00	1.920	0.000	59.0	1.7	52.1	18.9	0.001	0.000
Strath_GW415	7.28	292	149	2	50	24.60	64.90	0.474	0.000	22.0	3.9	24.1	8.2	0.401	0.000
Strath_GW416	8.3	1276	769	24	470	3.77	168.00	0.776	0.000	77.0	8.4	113.0	34.6	2.020	0.000
Strath_GW417	8.43	789	475	19	103	3.64	206.00	0.481	0.000	38.0	4.5	63.7	21.5	0.067	0.000
Strath_GW418	7.94	327	195	7	115	34.60	8.71	1.040	0.000	25.0	3.3	23.0	11.2	0.001	0.000
Strath_GW419	7.52	315	162	0	125	18.40	24.60	0.549	0.000	15.0	3.0	27.3	11.2	0.088	0.000
Strath_GW420	6.47	716	371	0	121	32.80	160.00	0.898	0.000	41.0	4.5	50.0	22.7	0.065	0.000
Strath_GW421	6.5	284	171	0	105	18.20	28.30	0.439	0.000	17.0	3.3	25.0	10.3	0.100	0.000
Strath_GW422	6.85	177	106	0	72	7.38	15.00	0.906	0.000	6.1	0.5	20.0	5.4	0.001	0.000
Strath_GW423	6.39	251	151	0	65	18.60	35.60	0.551	0.000	14.0	0.7	21.0	9.1	0.001	0.000
Strath_GW424	6.9	570	343	0	89	14.70	147.00	0.829	0.000	44.0	7.9	33.4	14.0	0.387	0.000
Strath_GW425	6.73	312	188	0	139	16.30	14.90	0.602	0.000	11.0	2.6	33.1	10.6	0.800	0.000
Strath_GW426	6.51	241	121	0	82	17.80	28.50	0.462	0.000	13.0	7.3	16.0	6.1	13.300	0.000
Strath_GW427	8.76	721	367	28	150	45.40	121.00	0.957	0.000	39.0	6.4	72.0	22.0	0.056	0.000
Strath_GW428	7.11	605	364	0	124	42.80	144.00	0.494	0.000	44.0	6.9	55.7	18.8	0.001	0.000
Strath_GW429	7.9	543	269	12	185	47.80	29.80	0.475	0.000	44.0	3.8	33.0	20.5	0.056	0.000
Strath_GW430	6.35	721	396	0	181	16.40	182.00	0.045	0.000	23.0	8.3	85.2	21.2	0.153	0.000
Strath_GW431	5.52	546	299	0	288	10.50	19.60	0.213	0.000	9.0	4.2	68.1	19.0	0.046	0.000
Strath_GW432	6.29	144	79	0	68.1	6.92	6.11	0.058	0.000	5.0	2.4	14.5	5.3	0.122	0.000
Strath_GW433	6.23	229	128	0	114	12.40	3.43	0.058	0.000	7.0	3.1	22.8	9.3	0.146	0.000
Strath_GW434	6.05	80	44	0	21.4	8.10	10.60	0.038	0.000	4.0	1.0	8.5	2.1	0.149	0.000
Strath_GW435	6.35	362	199	0	189	14.80	4.64	0.060	0.000	10.0	2.4	36.1	16.1	0.140	0.000
Strath_GW436	6.31	272	149	0	97	8.64	42.20	0.189	0.000	8.0	2.5	28.4	10.7	0.186	0.000
Strath_GW437	6.74	838	459	0	325	41.10	90.60	0.215	0.000	30.0	3.9	92.8	28.6	0.099	0.000
Strath_GW438	6.07	334	181	0	138	15.40	30.80	0.375	0.000	12.0	2.8	30.8	14.6	0.260	0.000
Strath_GW439	6.73	336	185	0	173	13.90	6.23	0.118	0.000	9.0	3.1	36.1	13.2	0.128	0.000
Sample ID	**pH**	**EC**	**TDS**	**CO_3**	**HCO_3**	**Cl**	**SO_4**	**NO_3**	**F**	**Na**	**K**	**Ca**	**Mg**	**Fe**	**Mn**

		μS/cm	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
Strath_GW440	6.43	430	236	0	210	26.80	4.92	0.056	0.000	17.0	3.2	42.1	16.7	0.128	0.000
Strath_GW441	6.78	543	300	0	276	26.90	7.28	0.001	0.000	17.0	3.4	56.2	21.8	0.118	0.000
Strath_GW442	5.53	419	231	0	189	36.40	3.17	0.173	0.000	21.0	4.5	41.5	13.2	0.201	0.000
Strath_GW443	6.76	1014	556	0	270	24.50	241.00	0.001	0.000	42.0	13.0	95.8	38.9	0.089	0.000
Strath_GW444	6.58	309	186	0	114	22.40	20.70	0.573	0.000	12.0	2.7	28.0	11.6	0.001	0.000
Strath_GW445	6.3	543	333	0	112	16.50	150.00	0.020	0.000	37.0	3.2	46.0	17.0	1.230	0.000
Strath_GW446	6.3	532	314	0	120	22.90	130.00	0.036	0.000	34.0	9.4	41.6	17.8	1.720	0.000
Strath_GW447	6.4	125	77	0	42	9.10	14.90	0.169	0.000	4.0	3.0	12.0	4.8	0.294	0.000
Strath_GW448	6.1	355	207	0	95	17.40	72.10	0.041	0.000	20.0	9.3	30.9	10.9	0.177	0.000
Strath_GW449	6.1	227	128	0	74	18.30	26.00	0.160	0.000	14.0	1.7	19.0	8.0	0.239	0.000
Strath_GW450	6.2	186	108	0	62	15.60	19.50	0.028	0.000	9.0	1.4	17.0	7.1	0.088	0.000
Strath_GW451	6.3	368	223	0	105	14.60	74.50	0.046	0.000	23.0	4.3	31.0	12.3	0.046	0.000
Strath_GW452	6	310	183	0	70	25.00	60.00	0.052	0.000	23.0	5.3	24.4	9.0	0.408	0.000
Strath_GW453	6	432	264	0	68	21.00	126.00	0.007	0.000	17.0	4.4	42.1	16.0	1.520	0.000
Strath_GW454	5.7	2130	1290	0	510	27.40	584.00	0.011	0.000	69.0	8.8	216.0	88.4	0.738	0.000
Strath_GW455	5.2	745	428	0	110	32.00	230.00	0.028	0.000	53.0	6.9	60.0	24.0	0.528	0.000
Strath_GW456	6	434	264	0	90	20.10	110.00	0.111	0.000	28.0	2.2	38.3	14.0	0.162	0.000
Strath_GW457	6	230	134	0	32	15.00	65.50	0.057	0.000	11.0	1.2	22.0	8.4	0.073	0.000
Strath_GW458	5.8	105	63	0	25	12.30	14.40	0.011	0.000	9.0	1.3	7.6	3.0	0.056	0.000
Strath_GW459	4	651	375	0	88	27.40	167.00	0.003	0.000	23.0	4.9	50.0	24.5	0.163	0.000
Strath_GW460	5.8	200	120	0	82	18.30	6.75	0.068	0.000	11.0	3.0	17.0	7.3	0.072	0.000
Strath_GW461	6.2	366	216	0	179	21.20	6.03	0.059	0.000	14.0	2.6	36.8	13.9	0.036	0.000
Strath_GW462	6.2	223	134	0	88	24.70	4.26	0.130	0.000	12.0	3.2	20.0	7.6	0.126	0.000
Strath_GW463	6.6	488	292	0	245	29.20	11.30	0.135	0.000	20.0	4.5	46.8	19.0	0.030	0.000
Strath_GW464	6.7	339	205	0	155	26.60	4.76	0.127	0.000	15.0	2.5	32.2	12.9	0.091	0.000
Strath_GW465	6.6	272	160	0	120	24.50	2.66	0.325	0.000	15.0	3.3	23.2	10.0	0.110	0.000
Strath_GW466	6.7	423	260	0	207	26.10	4.60	0.089	0.000	15.0	4.1	38.9	18.6	0.047	0.000
Strath_GW467	6.8	326	190	0	150	23.30	6.87	0.117	0.000	14.0	3.8	30.4	12.6	0.051	0.000
Strath_GW468	6.7	818	498	0	389	59.30	6.19	0.114	0.000	38.0	5.2	72.9	33.5	0.010	0.000
Strath_GW469	6.8	334	192	0	152	24.20	7.85	0.153	0.000	16.0	4.1	29.6	12.9	0.001	0.000
Strath_GW470	6.8	203	121	0	89	17.20	4.04	0.182	0.000	11.0	2.6	16.5	8.0	0.170	0.000
Strath_GW471	6.4	188	112	0	60	20.10	15.90	0.100	0.000	12.0	3.8	16.0	5.6	0.089	0.000
Strath_GW472	6.6	242	147	0	112	16.20	6.20	0.001	0.000	13.0	3.5	22.3	8.0	0.264	0.000
Strath_GW473	6.5	475	280	0	236	26.50	6.40	0.082	0.000	16.0	5.3	46.8	19.2	0.034	0.000
Strath_GW474	6.6	375	228	0	180	23.80	6.27	0.076	0.000	15.0	4.2	36.0	14.2	0.189	0.000
Strath_GW475	6.6	198	119	0	80	20.30	4.62	0.074	0.000	16.0	4.5	15.7	4.5	0.108	0.000
Strath_GW476	7.03	376	207	0	280	16.38	32.20	0.181	0.000	17.0	1.9	56.0	26.5	0.001	0.000
Strath_GW477	6.79	257	141	0	157	16.38	0.10	0.132	0.000	10.0	2.9	32.0	11.7	0.001	0.000
Strath_GW478	6.43	149	82	0	186	23.66	0.10	0.375	0.000	5.0	1.9	43.0	16.5	0.001	0.000
Strath_GW479	6.8	261	142	0	235	14.56	0.10	0.128	0.000	9.0	3.2	52.4	14.6	0.001	0.000
Sample ID	**pH**	**EC**	**TDS**	**CO_3**	**HCO_3**	**Cl**	**SO_4**	**NO_3**	**F**	**Na**	**K**	**Ca**	**Mg**	**Fe**	**Mn**

		μS/cm	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
Strath_GW480	6.71	141	78	0	58.6	20.02	0.10	0.001	0.000	8.0	2.6	12.8	5.8	0.001	0.000
Strath_GW481	6.8	154	85	0	66	16.50	0.10	0.338	0.000	15.0	2.5	12.5	3.2	0.001	0.000
Strath_GW482	6.85	226	124	0	103	21.84	0.10	0.076	0.000	12.0	1.8	22.0	8.7	0.001	0.000
Strath_GW483	6.98	362	199	0	203	21.84	38.90	0.156	0.000	6.0	3.9	51.2	23.6	0.001	0.000
Strath_GW484	6.69	230	127	0	30	12.00	80.00	0.080	0.000	10.0	1.2	27.6	7.7	0.001	0.000
Strath_GW485	6.73	425	234	0	147	21.00	60.73	0.128	0.000	20.0	2.8	41.2	13.6	1.017	0.000
Strath_GW486	7.08	319	175	0	140	21.00	20.67	0.060	0.000	19.0	3.4	25.6	12.7	0.001	0.000
Strath_GW487	6.83	458	153	0	115	10.90	106.00	0.089	0.000	10.0	2.5	60.8	11.7	0.587	0.000
Strath_GW488	6.73	425	234	0	145	21.00	60.73	0.128	0.000	20.0	2.8	41.2	13.6	1.017	0.000
Strath_GW489	7.08	319	175	0	134	22.00	20.67	0.060	0.000	19.0	3.4	25.6	12.7	0.001	0.000
Strath_GW490	6.83	578	153	0	185	10.90	106.00	0.089	0.000	10.0	2.5	60.8	21.7	0.587	0.000
Strath_GW491	6.98	738	240	0	170	21.84	203.00	0.079	0.000	32.0	3.5	59.6	35.6	0.001	0.000
Strath_GW492	5.37	568	312	0	86	34.00	143.00	0.116	0.000	27.0	6.2	46.0	19.0	0.462	0.000
Strath_GW493	6.8	527	289	0	147	58.00	58.96	0.039	0.000	51.0	7.3	38.0	11.6	0.226	0.000
Strath_GW494	6.84	649	247	0	317	21.84	41.64	0.071	0.000	20.0	3.7	78.4	20.4	0.084	0.000
Strath_GW495	6.93	304	167	0	150	19.50	0.10	0.041	0.000	18.0	2.2	25.0	11.2	0.302	0.000
Strath_GW496	6.89	116	64	0	107	29.11	0.10	0.114	0.000	11.0	2.5	20.8	11.7	0.001	0.000
Strath_GW497	6.91	373	205	0	282	23.66	0.10	0.027	0.000	20.0	6.0	48.0	21.7	0.001	0.000
Strath_GW498	7.09	277	152	0	146	16.38	0.10	0.016	0.000	15.0	2.2	25.6	10.7	0.001	0.000
Strath_GW499	7.04	247	134	0	114	22.00	0.10	0.160	0.000	17.0	3.5	23.0	7.1	0.001	0.000
Strath_GW500	7.08	350	136	0	200	12.74	0.10	0.001	0.000	12.0	2.4	38.4	14.6	0.001	0.000
Strath_GW501	6.96	351	193	0	64	25.60	82.00	0.089	0.000	20.0	5.6	28.0	13.8	0.001	0.000
Strath_GW502	7.06	641	353	0	102	59.00	146.00	0.038	0.000	43.0	4.3	65.0	14.7	0.652	0.000
Strath_GW503	6.92	681	375	0	107	29.00	203.00	0.001	0.000	22.0	4.5	58.0	35.0	0.001	0.000
Strath_GW504	6.86	1153	634	0	550	68.00	19.92	0.191	0.000	56.0	7.2	102.0	43.0	0.001	0.000
Strath_GW505	7.31	265	146	2	85	10.92	43.72	0.001	0.000	12.0	2.1	29.8	7.2	0.001	0.000
Strath_GW506	6.95	249	137	0	86	14.40	28.55	0.236	0.000	13.0	2.0	20.1	10.6	0.001	0.000
Strath_GW507	7.04	163	90	0	59	10.92	17.90	0.097	0.000	15.0	1.8	9.8	5.6	0.001	0.000
Strath_GW508	6.92	616	339	0	270	42.80	25.40	0.117	0.000	31.0	2.6	56.0	23.7	0.001	0.000
Strath_GW509	7.01	892	491	0	418	56.40	24.00	0.079	0.000	51.0	5.6	89.6	24.1	0.001	0.000
Strath_GW510	7.23	332	128	2	165	12.90	8.20	0.148	0.000	11.0	3.9	30.0	15.5	0.001	0.000
Strath_GW511	7.23	315	173	3	130	26.00	10.00	0.001	0.000	21.0	2.4	28.5	10.0	0.001	0.000
Strath_GW512	7.16	274	151	0	105	28.00	8.00	0.120	0.000	16.0	1.8	24.0	10.0	0.093	0.000
Strath_GW513	7.3	624	343	4	319	19.20	11.00	0.001	0.000	17.0	2.5	56.8	30.1	0.001	0.000
Strath_GW514	7.33	619	340	3	285	40.50	10.60	0.112	0.000	38.0	1.3	56.0	20.7	0.001	0.000
Strath_GW515	6.92	280	154	0	145	14.56	5.00	0.010	0.000	10.0	0.5	34.0	10.3	0.001	0.000
Strath_GW516	7	191	105	0	78	13.20	8.60	0.121	0.000	11.5	1.3	12.6	8.3	0.306	0.000
Strath_GW517	6.94	319	175	0	150	19.20	7.60	0.001	0.000	16.0	4.1	28.0	11.6	0.001	0.000
Strath_GW518	7.33	471	259	0	224	34.00	7.30	0.107	0.000	26.0	4.6	48.8	13.5	0.001	0.000
Strath_GW519	6.81	357	196	0	94	19.20	78.27	0.001	0.000	29.0	2.1	28.0	11.4	0.151	0.000
Sample ID	**pH**	**EC**	**TDS**	**CO_3**	**HCO_3**	**Cl**	**SO_4**	**NO_3**	**F**	**Na**	**K**	**Ca**	**Mg**	**Fe**	**Mn**

		μS/cm	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
Strath_GW520	6.52	388	233	0	115	18.60	65.70	0.101	0.480	16.0	3.8	38.4	14.3	0.101	0.000
Strath_GW521	7.23	232	128	3	106	12.30	8.50	0.148	0.000	10.0	1.9	25.0	7.5	0.001	0.000
Strath_GW522	7.29	450	275	2	195	33.40	14.60	0.001	0.000	22.0	5.8	42.0	15.8	0.081	0.000
Strath_GW523	7.3	624	343	0	318	38.80	0.10	0.001	0.000	40.0	2.5	46.8	28.6	0.001	0.000
Strath_GW524	6.92	681	375	0	73	24.00	240.00	0.001	0.000	22.0	1.5	93.0	15.9	0.001	0.000
Strath_GW525	6.35	362	199	0	189	14.80	4.64	0.060	0.000	10.0	2.4	36.1	16.1	0.140	0.000
Strath_GW526	7.09	277	152	0	146	16.40	0.00	0.016	0.000	15.0	2.2	25.6	10.7	0.001	0.000
Strath_GW527	6.6	272	160	0	120	24.50	2.66	0.325	0.000	15.0	3.3	23.2	10.0	0.110	0.000
Strath_GW528	7.18	337	207	0	153	22.60	10.70	0.001	0.000	18.0	4.9	31.7	10.7	0.127	0.000
Strath_GW529	6.22	554	332	0	118	12.60	155.00	0.024	0.660	43.0	5.8	41.0	18.0	0.024	0.000
Strath_GW530	6.51	1950	1178	0	199	108.00	625.00	0.025	0.000	97.0	6.4	184.0	72.0	0.267	0.000
Strath_GW531	6.43	430	236	0	210	26.80	4.92	0.056	0.000	17.0	3.2	42.1	16.7	0.128	0.000
Strath_GW532	7.06	641	353	0	102	19.00	206.00	0.038	0.000	13.0	1.3	77.6	24.7	0.652	0.000
Strath_GW533	6.92	616	339	0	275	42.00	25.40	0.117	0.000	31.0	2.6	56.0	25.0	0.001	0.000
Strath_GW534	7.04	247	134	0	115	12.70	12.00	0.160	0.000	8.6	1.3	23.7	11.7	0.001	0.000
Strath_GW535	6.07	334	181	0	138	15.40	30.80	0.375	0.000	12.0	2.8	30.8	14.6	0.260	0.000
Strath_GW536	3.38	1280	766	0	400	16.20	300.00	0.191	0.930	56.0	7.9	152.0	41.8	0.191	0.000
Strath_GW537	4	651	375	0	9	27.40	277.00	0.003	0.000	23.0	4.9	66.0	26.4	0.163	0.000
Strath_GW538	6.73	336	185	0	173	13.90	6.23	0.118	0.000	9.0	3.1	36.1	13.2	0.128	0.000
Strath_GW539	6.8	326	190	0	150	22.10	6.87	0.117	0.000	14.0	3.8	30.4	12.6	0.051	0.000
Strath_GW540	6.92	280	154	0	255	14.60	0.10	0.010	0.000	10.0	5.0	44.0	25.3	0.001	0.000
Strath_GW541	6.31	272	149	0	97	8.60	42.20	0.159	0.000	8.0	2.5	28.4	10.7	0.186	0.000
Strath_GW542	6.57	348	209	0	54	14.40	104.00	0.025	0.420	15.0	3.3	34.0	12.8	0.025	0.000
Strath_GW543	6.9	144	79	0	68	6.90	6.11	0.058	0.000	5.0	2.4	14.5	5.3	0.122	0.000
Strath_GW544	6.93	668	367	0	156	14.20	179.00	0.355	0.000	13.0	1.5	88.0	20.4	0.001	0.000
Strath_GW545	7.03	421	138	0	225	18.20	0.10	0.029	0.029	25.0	1.9	42.5	12.6	0.001	0.000
Strath_GW546	6.7	1376	872	0	111	24.40	540.00	0.033	0.000	48.0	3.2	141.0	55.4	0.683	0.000
Strath_GW547	6.2	366	216	0	179	21.20	6.03	0.059	0.000	14.0	2.6	36.8	13.9	0.036	0.000
Strath_GW548	6.52	77	46	0	23	9.80	5.58	0.005	0.260	8.0	1.2	5.0	2.0	0.151	0.000
Strath_GW549	7.36	398	239	0	121	26.80	57.70	0.140	0.700	40.0	2.6	26.8	10.1	0.071	0.000
Strath_GW550	6.2	223	134	0	88	24.70	4.26	0.130	0.000	12.0	3.2	20.0	7.6	0.126	0.000
Strath_GW551	6.7	423	260	0	207	26.10	4.60	0.089	0.000	15.0	4.1	38.9	18.6	0.047	0.000
Strath_GW552	7.04	337	185	0	127	14.60	46.28	0.046	0.000	13.0	2.9	33.0	13.6	0.001	0.000
Strath_GW553	7.23	315	173	3	137	26.00	6.70	0.001	0.000	21.0	1.4	25.0	13.0	0.001	0.000
Strath_GW554	6.05	80	44	0	22	8.10	10.60	0.038	0.000	4.0	1.0	8.5	2.1	0.144	0.000
Strath_GW555	6.92	344	207	0	115	23.50	42.40	0.001	0.000	13.0	4.1	37.6	10.7	0.223	0.000
Strath_GW556	6.23	229	128	0	114	12.40	3.43	0.058	0.000	7.0	3.1	22.8	9.3	0.146	0.000
Strath_GW557	7.19	507	307	0	130	20.80	113.00	0.001	0.000	38.0	2.7	40.1	16.4	0.133	0.000
Strath_GW558	6.6	408	245	0	191	7.20	34.40	0.083	0.730	12.0	6.4	43.5	15.0	0.083	0.000
Strath_GW559	6.88	182	111	0	27	21.70	36.50	0.092	0.000	22.0	3.8	9.1	3.9	0.261	0.000
Sample ID	**pH**	**EC**	**TDS**	**CO_3**	**HCO_3**	**Cl**	**SO_4**	**NO_3**	**F**	**Na**	**K**	**Ca**	**Mg**	**Fe**	**Mn**

		μS/cm	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
Strath_GW560	6.56	526	316	0	146	15.40	117.00	0.001	0.000	49.0	1.5	36.8	13.9	0.260	0.000
Strath_GW561	6.99	167	92	0	137	16.40	0.10	0.170	0.000	11.0	2.7	27.4	11.2	0.001	0.000
Strath_GW562	6.94	455	273	0	110	28.40	91.90	0.236	0.340	56.0	2.6	20.1	12.6	0.010	0.000
Strath_GW563	7.33	619	340	0	300	43.60	0.10	0.112	0.000	40.0	3.4	51.0	21.7	0.001	0.000
Strath_GW564	6.86	1153	634	0	560	68.00	19.90	0.191	0.000	56.0	2.7	93.0	53.1	0.001	0.000
Strath_GW565	6.81	357	196	0	117	34.90	78.27	0.001	0.000	29.0	5.1	48.0	9.7	0.151	0.000
Strath_GW566	6.64	307	184	0	118	22.50	22.20	0.328	0.740	22.0	1.8	26.5	9.0	0.036	0.000
Strath_GW567	7.76	1014	556	0	270	24.50	241.00	0.001	0.000	42.0	13.0	95.8	38.9	0.089	0.000
Strath_GW568	6.91	561	348	0	127	22.50	138.00	0.570	0.000	26.0	3.1	57.1	18.8	0.118	0.000
Strath_GW569	7.31	365	146	0	165	10.90	43.70	0.001	0.000	12.0	2.1	39.2	17.2	0.001	0.000
Strath_GW570	7.29	667	408	0	183	16.30	154.00	0.001	0.000	32.0	4.8	65.0	23.2	0.301	0.000
Strath_GW571	7.04	163	90	0	59	10.90	17.90	0.097	0.000	15.0	1.8	9.8	5.6	0.001	0.000
Strath_GW572	7.36	617	378	0	224	28.90	81.00	0.001	0.000	35.0	5.9	58.3	19.3	0.122	0.000
Strath_GW573	7.22	327	199	0	130	19.00	29.00	0.001	0.000	14.0	3.4	34.0	10.7	0.071	0.000
Strath_GW574	7.33	471	259	2	248	10.90	9.50	0.107	0.000	6.5	1.4	58.8	17.4	0.001	0.000
Strath_GW575	6.94	319	175	0	264	10.90	0.10	0.001	0.000	16.0	4.1	48.0	15.6	0.001	0.000
Strath_GW576	6.27	123	74	0	38	12.60	10.40	0.136	0.590	8.0	1.8	10.0	4.0	0.136	0.000
Strath_GW577	6.86	572	343	0	134	20.70	139.00	0.150	0.740	19.0	2.9	54.0	26.1	0.031	0.000
Strath_GW578	7.08	244	134	0	113	17.00	5.00	0.001	0.000	12.0	1.4	22.6	9.6	0.001	0.000
Strath_GW579	7	191	105	0	104	10.90	0.10	0.121	0.000	15.0	4.3	12.6	8.3	0.306	0.000
Strath_GW580	6.96	244	134	0	147	21.80	0.10	0.152	0.000	17.0	1.5	33.6	10.7	0.001	0.000
Strath_GW581	7.02	244	134	0	167	10.90	0.10	0.163	0.000	18.0	1.9	24.4	10.7	0.001	0.000
Strath_GW582	5.8	200	120	0	82	18.30	6.75	0.068	0.000	11.0	3.0	17.0	7.3	0.072	0.000
Strath_GW583	6.7	818	498	0	389	59.30	6.19	0.114	0.000	38.0	5.2	72.9	33.5	0.010	0.000
Strath_GW584	5.52	546	299	0	290	10.50	19.60	0.213	0.000	9.0	4.2	68.1	19.0	0.046	0.000
Strath_GW585	6.93	963	584	0	137	32.50	310.00	0.234	0.000	35.0	1.8	99.0	37.8	0.129	0.000
Strath_GW586	5.8	105	63	0	25	12.30	14.40	0.011	0.000	9.0	1.3	7.6	3.0	0.056	0.000
Strath_GW587	6.74	838	459	0	325	41.10	90.60	0.215	0.000	30.0	3.9	92.8	28.6	0.099	0.000
Strath_GW588	7.01	892	491	0	418	64.00	12.00	0.079	0.000	51.0	2.5	89.6	27.1	0.001	0.000
Strath_GW589	5.53	419	231	0	189	36.20	3.17	0.173	0.000	21.0	4.5	41.5	13.2	0.201	0.000
Strath_GW590	7.15	333	183	0	224	14.60	0.10	0.100	0.000	21.0	5.1	35.2	14.7	0.001	0.000
Strath_GW591	7.25	411	247	2	195	13.50	23.90	0.177	0.600	20.0	2.5	34.5	18.2	0.020	0.000
Strath_GW592	7.46	292	175	4	95	22.60	25.00	0.468	0.570	25.0	2.9	20.6	8.7	0.027	0.000
Strath_GW593	6.96	351	193	0	90	11.60	82.00	0.089	0.000	10.0	1.6	38.0	13.8	0.001	0.000
Strath_GW594	6.7	339	205	0	155	26.60	4.76	0.127	0.000	15.0	2.5	32.2	12.9	0.091	0.000
Strath_GW595	6.95	249	137	0	105	6.30	28.60	0.236	0.000	7.8	1.2	25.4	10.6	0.001	0.000
Strath_GW596	6.6	488	292	0	250	29.20	11.30	0.135	0.000	20.0	4.5	46.8	19.0	0.030	0.000
Strath_GW597	7.16	274	151	0	225	14.60	0.10	0.120	0.000	29.0	3.8	32.0	11.7	0.093	0.000
Strath_GW598	6.78	543	300	0	280	24.40	7.28	0.001	0.000	22.0	5.0	59.0	17.0	0.118	0.000
Strath_GW599	7.1	990	605	0	448	52.00	52.80	0.050	0.000	46.0	6.0	88.0	40.8	0.000	0.000
Sample ID	**pH**	**EC**	**TDS**	**CO_3**	**HCO_3**	**Cl**	**SO_4**	**NO_3**	**F**	**Na**	**K**	**Ca**	**Mg**	**Fe**	**Mn**

		μS/cm	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
Strath_GW600	7.23	758	381	2	181	15.60	18.73	0.010	0.180	10.9	2.8	44.0	13.3	0.020	0.045
Strath_GW601	7.06	1281	768	0	292	37.00	92.00	0.720	0.000	78.0	4.0	50.0	21.3	0.613	0.000
Strath_GW602	8.2	179	95	9.6	45	14.30	10.92	0.010	0.710	11.0	2.0	12.0	6.8	0.518	0.000
Strath_GW603	7.1	990	605	0	448	52.00	52.80	0.050	0.000	46.0	6.0	88.0	40.8	0.000	0.000
Strath_GW604	7.81	1384	830	8	463	54.90	198.00	2.460	0.000	30.0	1.2	160.0	55.0	0.001	0.000
Strath_GW605	7.57	3380	2028	6	512	315.00	790.00	1.030	0.000	530.0	45.0	110.0	50.0	0.001	0.000
Strath_GW606	8.52	948	475	28.8	128	58.90	171.00	0.301	0.000	50.0	3.8	70.0	31.0	0.000	0.000
Strath_GW607	8.26	1359	693	24	275	56.20	301.00	1.290	0.000	51.0	5.9	122.0	58.0	0.000	0.000
Strath_GW608	7.71	3290	1694	48	565	103.00	883.00	0.032	0.000	95.0	16.0	343.0	136.0	0.000	0.000
Strath_GW609	8.39	744	380	28.8	183	41.90	106.00	0.381	0.000	44.0	4.0	68.0	25.0	0.000	0.000
Strath_GW610	8.23	1133	590	24	163	63.10	290.00	0.161	0.000	62.0	5.1	98.0	43.0	0.000	0.000
Strath_GW611	8.39	314	162	9.2	75	9.10	65.00	0.186	0.000	8.6	2.2	36.0	10.8	0.000	0.000
Strath_GW612	8.23	418	220	20	118	36.00	27.30	0.079	0.000	33.0	3.0	35.0	11.0	0.000	0.000
Strath_GW613	8.49	1152	590	33	305	101.00	126.00	1.030	0.000	93.0	8.7	103.0	31.0	0.000	0.000
Strath_GW614	8.61	1292	670	23	103	97.00	320.00	0.001	0.000	86.0	9.8	97.0	37.0	0.000	0.000
Strath_GW615	8.09	649	340	14.2	76	51.00	161.00	0.006	0.000	48.0	3.2	44.0	24.6	0.000	0.000
Strath_GW616	8.62	413	221	19.2	127	26.00	33.40	0.332	0.000	23.0	1.4	39.0	14.6	0.000	0.000
Strath_GW617	8.34	518	270	29.2	153	34.00	34.90	0.849	0.000	29.0	1.7	49.0	17.5	0.000	0.000
Strath_GW618	8.48	416	215	14	120	39.60	30.00	0.235	0.000	38.0	3.1	30.0	11.6	0.000	0.000
Strath_GW619	8.6	949	476	39	328	77.20	25.30	2.140	0.000	70.0	3.2	86.0	24.0	0.000	0.000
Strath_GW620	8.44	607	312	28.8	230	38.20	15.70	0.360	0.000	35.0	3.1	58.0	19.4	0.000	0.000
Strath_GW621	8.17	1242	636	33.2	295	104.00	182.00	0.282	0.000	99.0	5.6	108.0	35.0	0.000	0.000
Strath_GW622	8.08	1805	930	23	372	102.00	400.00	0.601	0.000	97.0	7.1	176.0	59.0	0.000	0.000
Strath_GW623	8.48	676	350	19.2	180	54.00	77.60	0.756	0.000	48.0	3.3	50.0	24.0	0.000	0.000
Strath_GW624	8.6	1072	555	30.6	130	85.00	250.00	0.062	0.000	83.0	5.7	88.0	33.0	0.000	0.000
Strath_GW625	8.27	1349	700	28.8	210	89.10	325.00	0.559	0.000	87.0	2.7	116.0	48.0	0.000	0.000
Strath_GW626	8.32	510	366	14.2	61	54.00	101.00	0.017	0.000	50.0	3.1	39.0	11.0	0.000	0.000
Strath_GW627	7.88	451	235	9.6	90	31.00	90.00	0.001	0.000	29.0	2.7	42.0	13.0	0.000	0.000
Strath_GW628	8.32	434	225	14.4	68	30.10	92.00	0.001	0.000	28.0	4.0	40.0	12.8	0.000	0.000
Strath_GW629	8.57	368	187	9.6	52	34.00	72.60	0.015	0.000	22.0	2.3	36.0	11.0	0.000	0.000
Strath_GW630	8.1	442	225	22	80	25.70	80.00	0.076	0.000	24.0	2.3	46.0	12.2	0.000	0.000
Strath_GW631	8.47	392	198	20	117	12.40	47.70	0.001	0.000	11.0	2.5	43.0	15.0	0.000	0.000
Strath_GW632	8.48	975	503	28	408	38.40	48.20	0.025	0.000	36.0	3.6	112.0	30.0	0.000	0.000
Strath_GW633	8.51	640	334	12	56	40.70	190.00	0.001	0.000	38.0	2.9	60.0	21.0	0.000	0.000
Strath_GW634	8.23	773	395	19.2	127	45.00	180.00	0.001	0.000	39.0	4.8	80.0	24.0	0.000	0.000
Strath_GW635	8.03	382	198	10	66	21.00	87.10	0.001	0.000	23.0	4.6	39.0	10.0	0.000	0.000
Strath_GW636	8	306	158	9.6	65	29.80	40.00	0.045	0.000	27.0	2.5	20.0	10.0	0.000	0.000
Strath_GW637	8.08	423	215	9.6	163	21.00	31.80	0.001	0.000	20.0	6.6	37.0	16.1	0.000	0.000
Strath_GW638	8.23	306	160	15	78	18.00	36.90	0.001	0.000	15.0	1.7	31.0	10.0	0.000	0.000
Strath_GW639	8.11	272	140	8	80	24.00	23.00	0.001	0.000	21.0	2.3	22.1	8.1	0.000	0.000
Sample ID	**pH**	**EC**	**TDS**	**CO_3**	**HCO_3**	**Cl**	**SO_4**	**NO_3**	**F**	**Na**	**K**	**Ca**	**Mg**	**Fe**	**Mn**

		μS/cm	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
Strath_GW640	8.35	198	100	4.8	65	14.00	16.40	0.001	0.000	12.0	1.9	16.5	7.2	0.000	0.000
Strath_GW641	8.14	141	75	5	40	13.00	10.30	0.001	0.000	12.0	0.8	12.0	3.8	0.000	0.000
Strath_GW642	8.12	135	70	7	40	12.90	4.80	0.004	0.000	11.0	0.9	11.0	3.8	0.000	0.000
Strath_GW643	8.25	229	118	9	80	14.00	13.70	0.038	0.000	10.0	2.3	20.9	8.9	0.000	0.000
Strath_GW644	8.1	253	130	12	75	18.50	17.40	0.148	0.000	17.0	1.7	23.0	7.7	0.000	0.000
Strath_GW645	8.17	162	88	8	30	21.00	12.60	0.065	0.000	20.0	1.3	10.0	2.8	0.000	0.000
Strath_GW646	8.04	174	90	7	43	19.20	12.30	0.163	0.000	18.0	1.2	10.2	5.1	0.000	0.000
Strath_GW647	8.1	220	115	12	52	14.80	25.70	0.057	0.000	13.0	2.8	18.5	7.5	0.000	0.000
Strath_GW648	7.97	714	365	28.8	285	9.10	42.10	0.001	0.000	21.0	9.0	73.4	24.3	0.000	0.000
Strath_GW649	8.03	184	96	7.2	55	9.10	13.50	0.001	0.000	16.0	3.5	10.2	4.8	0.000	0.000
Strath_GW650	8.07	299	155	12	63	19.40	48.70	0.001	0.000	18.0	3.5	24.8	10.0	0.000	0.000
Strath_GW651	8.66	375	195	19.2	150	9.10	7.70	0.001	0.000	20.0	4.4	32.0	13.0	0.000	0.000
Strath_GW652	8.45	281	150	14.4	102	10.80	17.10	0.001	0.000	9.0	1.7	32.0	10.0	0.000	0.000
Strath_GW653	8.26	204	110	12	59	9.10	10.20	0.001	0.000	13.0	3.6	14.2	6.0	0.000	0.000
Strath_GW654	8.26	295	155	9.6	62	9.10	47.70	0.001	0.000	16.0	2.9	19.0	11.0	0.000	0.000
Strath_GW655	8.32	781	398	22	240	17.40	125.00	0.008	0.000	13.0	4.9	83.0	27.4	0.000	0.000
Strath_GW656	8.55	217	124	14.4	62	9.10	10.90	0.001	0.000	14.0	2.5	15.1	6.6	0.000	0.000
Strath_GW657	8.52	247	130	16.8	63	9.10	16.00	0.039	0.000	15.0	3.2	18.0	7.0	0.000	0.000
Strath_GW658	8.24	1142	598	28.8	102	10.70	315.00	0.001	0.000	56.0	7.4	86.0	32.0	0.000	0.000
Strath_GW659	8.6	798	404	24	113	10.70	186.00	0.098	0.000	36.0	4.5	60.0	26.6	0.000	0.000
Strath_GW660	8.85	484	260	21	224	9.10	6.30	0.103	0.000	39.0	3.9	34.6	14.8	0.000	0.000
Strath_GW661	8.22	523	275	24	81	8.90	101.00	0.029	0.000	30.0	5.8	35.2	13.6	0.000	0.000
Strath_GW662	8.26	264	140	9.6	46	5.80	49.20	0.041	0.000	17.0	3.3	18.0	7.0	0.000	0.000
Strath_GW663	8.39	354	183	14.4	93	10.70	42.50	0.065	0.000	11.0	3.6	32.6	12.1	0.000	0.000
Strath_GW664	8.18	313	160	12	79	7.40	43.40	0.257	0.000	13.0	3.2	27.2	10.0	0.000	0.000
Strath_GW665	8.43	248	135	7.2	54	7.40	41.10	0.062	0.000	12.0	3.1	19.0	7.9	0.000	0.000
Strath_GW666	8.51	284	150	14.4	79	5.80	29.40	0.045	0.000	22.0	3.5	17.0	8.8	0.000	0.000
Strath_GW667	8.51	350	180	16	89	9.10	43.20	0.069	0.000	19.0	3.9	27.0	10.0	0.000	0.000
Strath_GW668	8.48	254	141	7.2	78	15.70	17.10	0.552	0.000	18.0	2.9	17.2	8.1	0.000	0.000
Strath_GW669	8.49	260	143	9.6	103	4.10	16.70	0.139	0.000	11.0	2.9	22.0	10.0	0.000	0.000
Strath_GW670	8.62	427	238	24	148	10.70	20.30	0.025	0.000	25.0	3.3	35.0	13.0	0.000	0.000
Strath_GW671	8.26	246	130	9.6	92	9.10	11.50	0.022	0.000	8.0	3.1	23.1	9.1	0.000	0.000
Strath_GW672	8.65	288	153	12	127	7.40	5.00	0.052	0.000	9.0	2.8	27.0	12.1	0.000	0.000
Strath_GW673	8.54	382	200	14	110	9.10	46.10	0.160	0.000	30.0	3.1	24.2	10.8	0.000	0.000
Strath_GW674	8.39	326	172	18	91	7.40	30.30	0.073	0.000	23.0	2.4	23.0	9.3	0.000	0.000
Strath_GW675	8.48	250	130	16	80	4.10	16.20	0.439	0.000	14.0	1.7	19.2	8.2	0.000	0.000
Strath_GW676	8.57	293	151	17	82	9.10	23.60	0.144	0.000	16.0	2.4	20.0	10.7	0.000	0.000
Strath_GW677	8.67	396	201	24	97	12.40	36.70	0.445	0.000	26.0	2.7	28.0	11.0	0.000	0.000
Strath_GW678	8.33	247	129	14.4	60	7.40	24.00	0.154	0.000	15.0	2.3	17.8	7.7	0.000	0.000
Strath_GW679	8.61	320	170	17	102	12.40	16.00	0.737	0.000	12.0	2.7	25.6	13.6	0.000	0.000
Sample ID	**pH**	**EC**	**TDS**	**CO_3**	**HCO_3**	**Cl**	**SO_4**	**NO_3**	**F**	**Na**	**K**	**Ca**	**Mg**	**Fe**	**Mn**

		μS/cm	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
Strath_GW680	7.76	243	128	12	83	4.10	18.60	0.254	0.000	10.0	1.3	20.1	9.7	0.000	0.000
Strath_GW681	7.74	271	140	16	86	7.40	17.00	0.294	0.000	10.0	0.8	24.0	10.1	0.000	0.000
Strath_GW682	7.48	281	150	0	106	10.70	31.70	0.045	0.000	11.0	1.9	27.4	9.5	0.000	0.000
Strath_GW683	7.26	336	180	0	122	7.40	49.30	0.299	0.000	17.0	4.4	29.8	9.6	0.000	0.000
Strath_GW684	7.78	443	240	17	63	10.70	89.30	0.049	0.000	24.0	8.4	30.7	11.4	0.000	0.000
Strath_GW685	8.43	468	244	19.2	130	9.10	58.20	0.104	0.000	19.0	3.1	39.8	16.6	0.000	0.000
Strath_GW686	8.08	300	160	12	81	9.10	35.40	0.151	0.000	18.0	4.1	20.0	9.9	0.000	0.000
Strath_GW687	8.7	470	240	19.2	90	14.00	74.20	0.118	0.000	19.0	5.6	37.4	15.8	0.000	0.000
Strath_GW688	8.55	358	185	14.4	83	9.10	53.90	0.116	0.000	12.0	3.7	29.0	13.0	0.000	0.000
Strath_GW689	8.38	234	125	7.2	40	10.70	40.30	0.154	0.000	10.0	3.8	17.1	7.8	0.000	0.000
Strath_GW690	8.05	340	182	12	156	7.40	9.30	0.117	0.000	6.0	1.8	34.6	16.0	0.000	0.000
Strath_GW691	8.19	239	124	14.4	81	3.40	14.70	0.071	0.000	5.0	1.7	23.0	10.2	0.000	0.000
Strath_GW692	8.54	275	142	16	88	9.10	14.30	0.308	0.000	8.0	2.8	26.0	9.6	0.000	0.000
Strath_GW693	8.51	260	140	9.6	70	12.40	25.40	0.310	0.000	11.0	2.1	22.0	8.7	0.000	0.000
Strath_GW694	7.49	352	180	0	141	12.40	36.60	0.623	0.000	10.0	2.1	33.6	14.6	0.000	0.000
Strath_GW695	7.51	403	210	8	89	12.40	96.00	0.161	0.000	10.0	3.8	40.0	18.5	0.000	0.000
Strath_GW696	8.46	540	277	22	180	39.00	11.10	0.153	0.000	28.0	5.4	43.2	18.8	0.004	0.021
Strath_GW697	7.09	891	449	0	349	64.10	47.10	0.001	1.220	62.0	4.6	81.2	21.1	0.010	0.001
Strath_GW698	6.81	1162	587	0	523.4	50.00	58.10	0.001	1.140	53.0	5.5	151.6	19.2	0.050	0.001
Strath_GW699	6.69	763	383	11	375	35.70	6.80	0.010	0.060	31.4	4.1	68.0	33.0	0.301	0.167
Strath_GW700	6.73	498	250	0	179	34.10	42.10	0.001	0.810	31.6	3.3	44.4	13.6	0.010	0.001
Strath_GW701	6.79	671	339	0	312.4	50.10	8.18	0.001	0.570	49.8	4.8	62.0	16.5	0.250	0.001
Strath_GW702	7.61	696	348	19.2	270	50.10	8.50	0.001	0.440	51.0	7.3	64.8	9.5	0.040	0.001
Strath_GW703	7.49	567	277	34	78	40.20	47.60	0.001	0.710	37.0	7.7	40.6	8.6	0.240	0.001
Strath_GW704	6.77	580	292	0	275.2	32.10	9.22	1.120	1.290	36.0	2.4	70.0	9.2	0.040	0.001
Strath_GW705	7.82	298	156	14.4	76	10.20	46.20	0.010	0.010	12.1	3.4	32.0	10.7	0.140	0.010
Strath_GW706	7.2	973	487	0	505.2	46.10	11.60	0.001	1.330	35.0	3.8	106.8	35.6	0.030	0.001
Strath_GW707	6.95	796	399	0	335	72.20	11.00	0.001	0.540	70.0	3.4	75.0	9.7	0.001	0.001
Strath_GW708	6.69	471	239	0	213	36.10	6.53	0.001	0.970	37.0	3.9	43.0	9.6	0.330	0.001
Strath_GW709	6.04	317	190	0	150	21.30	4.71	0.132	0.000	14.0	2.4	28.8	12.6	0.686	0.001
Strath_GW710	6.02	187	112	0	64	23.30	7.89	0.039	0.000	18.0	0.7	13.8	4.5	0.397	0.001
Strath_GW711	6.06	145	87	0	61	11.20	6.43	0.019	0.000	8.0	1.5	14.5	3.5	1.443	0.001
Strath_GW712	6.51	810	485	0	426	30.60	11.40	0.739	0.000	23.0	1.5	87.1	32.8	0.578	0.003
Strath_GW713	6.4	1121	673	0	550	67.50	13.40	0.102	0.000	41.0	12.4	111.0	43.3	0.277	0.012
Strath_GW714	6.5	855	513	0	422	55.10	3.43	0.149	0.000	35.0	2.4	92.3	28.6	0.229	0.001
Strath_GW715	6.16	280	170	0	124	21.40	7.90	0.053	0.000	16.0	2.1	26.1	8.8	0.618	0.076
Strath_GW716	6.02	160	100	0	72	12.60	3.10	0.039	0.000	8.0	2.3	17.9	3.6	0.131	0.028
Strath_GW717	6.26	240	200	0	120	12.80	3.51	0.063	0.000	8.6	2.5	24.2	8.9	0.618	0.001
Strath_GW718	6.8	350	230	0	156	26.80	8.94	0.046	0.000	18.0	2.8	28.9	14.6	0.131	0.001
Strath_GW719	6.96	990	650	0	471	42.10	47.20	0.651	0.000	35.0	6.6	98.6	39.9	0.229	0.001
Strath_GW720	6.97	720	470	0	342	23.70	43.80	0.743	0.000	24.0	4.7	73.4	28.7	0.375	0.001

Strath_GW721	6.75	730	470	0	373	34.70	9.57	0.146	0.000	26.0	1.6	77.9	27.2	0.180	0.001
Strath_GW722	6.01	190	120	0	74	21.70	3.57	0.058	0.000	12.0	3.4	16.9	5.4	0.083	0.001
Strath_GW723	6.84	950	620	0	370	46.40	102.00	0.005	0.000	64.0	6.4	76.4	33.3	0.131	0.006
Strath_GW724	6.59	570	370	0	289	16.50	23.60	0.002	0.000	19.0	2.4	69.8	16.0	0.423	0.001
Strath_GW725	6.32	350	230	0	157	27.60	4.29	0.855	0.000	20.0	1.6	36.4	9.3	0.229	0.001
Strath_GW726	6.93	1260	820	0	648	34.20	47.60	0.121	0.000	42.0	4.9	124.0	54.2	0.229	0.131
Strath_GW727	6.77	850	560	0	361	79.60	15.70	0.243	0.000	50.0	5.4	72.1	31.3	0.175	0.240

10.4.4 Geochemical Modelling Data: Saturation Indices

GEOCHEMICAL MODELLING DATA: SATURATION INDICES FOR CALCITE, GYPSUM, HALITE, DOLOMITE AND pCO_2

Sample ID	Calcite	Gypsum	Halite	Dolomite	pCO_2		Sample ID	Calcite	Gypsum	Halite	Dolomite	pCO_2
Strath_GW01	-0.6972	-2.5562	-8.0862	-1.2663	0.25396		Strath_GW201	-0.7703	-3.4791	-7.2344	-1.603	0.06167
Strath_GW02	-0.6798	-2.6127	-7.6363	-1.2237	0.22985		Strath_GW202	-0.7716	-3.9612	-7.1118	-1.573	0.06569
Strath_GW03	-0.8809	-3.0063	-8.1838	-1.6338	0.04318		Strath_GW203	-0.9247	-3.3742	-7.4019	-1.9584	0.03172
Strath_GW04	-2.0838	-4.8372	-8.8379	-4.3081	0.02224		Strath_GW204	-0.6204	-4.0137	-6.8901	-1.307	0.04116
Strath_GW05	-1.7152	-2.9056	-8.5718	-3.3048	0.01537		Strath_GW205	-0.5913	-3.1527	-6.89	-1.2385	0.04531
Strath_GW06	-1.9356	-2.9339	-8.6436	-3.7602	0.01954		Strath_GW206	-1.8921	-3.5567	-7.8929	-3.9133	0.01438
Strath_GW07	-0.5257	-2.5189	-7.8602	-1.0024	0.03372		Strath_GW207	-1.9884	-3.1488	-7.8175	-4.0561	0.00864
Strath_GW08	-2.2038	-4.2208	-9.0252	-4.3535	0.02113		Strath_GW208	0.0387	-1.9282	-6.661	-0.0687	0.04655
Strath_GW09	-0.7312	-4.5169	-8.514	-1.338	0.02851		Strath_GW209	0.0452	-1.9813	-6.3515	-0.0827	0.04085
Strath_GW10	-0.0632	-1.9493	-7.6174	-0.2232	0.01564		Strath_GW210	-0.2623	-1.4892	-6.2176	-0.5921	0.05522
Strath_GW11	-1.8275	-3.2508	-8.7093	-3.5045	0.06066		Strath_GW211	0.2285	-1.7774	-6.7204	0.3579	0.09383
Strath_GW12	-1.8289	-3.6046	-8.7641	-3.9583	0.00711		Strath_GW212	0.4363	-1.2689	-5.8622	0.7958	0.15082
Strath_GW13	0.5817	-1.1691	-5.9625	1.1692	0.08034		Strath_GW213	-0.2552	-1.49	-6.2178	-0.5777	0.05621
Strath_GW14	-2.1003	-4.1257	-9.0183	-4.3258	0.00276		Strath_GW214	0.2285	-1.7774	-6.7204	0.3579	0.09383
Strath_GW15	-2.438	-5.4281	-9.6954	-4.848	0.03672		Strath_GW215	0.4363	-1.2689	-5.8622	0.7958	0.15082
Strath_GW16	-2.0717	-3.4219	-8.2234	-4.6355	0.02873		Strath_GW216	-0.2732	-1.9293	-6.3189	-0.5947	0.11008
Strath_GW17	-0.319	-2.4456	-7.1253	-0.8833	0.04315		Strath_GW217	-2.3399	-4.2146	-8.4327	-4.7422	0.03294
Strath_GW18	0.129	-1.67	-7.7512	0.4213	0.04476		Strath_GW218	-0.6249	-2.9845	-6.988	-1.3419	0.05103
Strath_GW19	0.4267	-1.0949	-6.0372	0.9315	0.11397		Strath_GW219	-0.3658	-3.263	-6.8824	-0.7872	0.02582
Strath_GW20	-0.435	-1.98	-7.1301	-0.8537	0.09881		Strath_GW220	-0.4574	-3.0347	-6.9975	-0.9542	0.02735
Strath_GW21	-0.4598	-4.0713	-5.6266	-0.5649	0.01706		Strath_GW221	-0.9674	-3.1239	-7.4474	-2.0361	0.02566
Strath_GW22	-0.728	-2.6425	-7.3583	-1.5366	0.00004		Strath_GW222	-0.9772	-3.592	-7.5606	-2.054	0.03776
Strath_GW23	-0.6534	-2.2747	-7.8177	-1.4894	0.03612		Strath_GW223	-1.5918	-3.9918	-7.8106	-3.3559	0.0863
Strath_GW24	-0.618	-2.2178	-8.2335	-1.418	0.01202		Strath_GW224	-0.4268	-3.3542	-7.7183	-0.9784	0.04768
Strath_GW25	-1.8748	-3.3226	-8.1	-4.0163	0.02948		Strath_GW225	-0.9062	-2.5044	-8.0361	-1.8314	0.00093
Strath_GW26	-2.4578	-3.7693	-8.5452	-5.0554	0.03057		Strath_GW226	-0.4268	-3.3535	-7.7183	-0.9784	0.04768
Strath_GW27	-0.2145	-2.0752	-6.9736	-0.6509	0.03607		Strath_GW227	-0.9671	-3.1869	-6.921	-1.9085	0.00303
Strath_GW28	-1.6803	-3.1531	-8.7832	-3.4694	0.01044		Strath_GW228	-0.1982	-2.3207	-7.8456	-0.5212	0.01649
Strath_GW29	-0.0151	-2.5873	-6.785	-0.2972	0.09846		Strath_GW229	-1.2876	-2.8238	-8.1971	-2.5358	0.00023
Strath_GW30	-1.1555	-3.0996	-7.7163	-2.5392	0.06736		Strath_GW230	-0.0293	-1.9003	-6.866	-0.2086	0.02243
Strath_GW31	-0.3235	-2.8495	-6.9816	-1.0285	0.05975		Strath_GW231	-1.0619	-2.7458	-8.0186	-2.0799	0.00091
Strath_GW32	-1.1218	-2.5286	-8.0948	-2.4894	0.02524		Strath_GW232	-1.9884	-3.1488	-7.8175	-4.0561	0.00864
Strath_GW33	-0.255	-1.9331	-7.4119	-1.0342	0.03493		Strath_GW233	-0.2315	-2.3383	-7.2257	-0.4927	0.00377
Strath_GW34	-2.4567	-4.1175	-8.9125	-5.0154	0.04645		Strath_GW234	-0.0814	-1.9756	-7.2778	-0.2301	0.01384
Strath_GW35	-0.8515	-2.6049	-8.2872	-1.9232	0.02665		Strath_GW235	-1.0084	-2.7458	-7.8844	-2.1652	0.0005
Strath_GW36	-0.918	-2.4079	-7.8401	-1.7975	0.01863		Strath_GW236	-0.0637	-2.1264	-7.4276	-0.3943	0.01321
Strath_GW37	-2.072	-4.1041	-9.5435	-4.1789	0.15582		Strath_GW237	-0.8017	-2.5039	-7.9427	-1.6123	0.00166
Strath_GW38	-2.7419	-4.2038	-9.1407	-5.5448	0.12494		Strath_GW238	-0.3457	-2.3276	-7.7049	-0.845	0.01099
Strath_GW39	-1.587	-3.0149	-8.6336	-3.2521	0.02598		Strath_GW239	-0.8055	-2.5426	-7.9633	-1.6041	0.00076
Strath_GW40	-2.3089	-3.6723	-9.3758	-4.3588	0.07199		Strath_GW240	-0.3868	-2.5356	-8.6995	-0.7862	0.01044

Strath_GW41	0.2671	-1.9199	-5.7263	0.58	0.02215		Strath_GW241	0.0647	-2.1352	-6.2336	-0.1241	0.01431
Strath_GW42	-1.3691	-2.9221	-8.74	-2.797	0.01928		Strath_GW242	-0.1984	-2.4351	-5.7755	-0.449	0.05658
Strath_GW43	-0.64	-2.8136	-8.4975	-1.351	0.06617		Strath_GW243	0.0686	-1.1747	-6.2857	-0.0749	0.01511
Strath_GW44	-0.7924	-1.6703	-8.2093	-1.8721	0.0225		Strath_GW244	0.1405	-1.985	-6.7239	0.1084	0.0515
Strath_GW45	-0.3817	-2.1167	-8.7832	-1.0224	0.07603		Strath_GW245	0.0648	-1.7611	-7.0259	0.085	0.01896
Strath_GW46	-0.4236	-2.6579	-6.8462	-0.8934	0.04858		Strath_GW246	-1.0376	-2.5175	-7.7823	-2.0484	0.00044
Strath_GW47	-2.5734	-4.4443	-9.286	-5.0752	0.11393		Strath_GW247	-0.5348	-2.9071	-7.5496	-1.194	0.00445
Strath_GW48	-1.4079	-2.7816	-8.0991	-2.8495	0.01652		Strath_GW248	-0.0237	-1.6634	-7.7934	-0.069	0.05125
Strath_GW49	-0.7075	-2.6205	-8.2321	-1.2753	0.05075		Strath_GW249	-0.3807	-1.7506	-7.2188	-0.8271	0.0035
Strath_GW50	-0.6753	-2.7426	-7.4392	-1.419	0.02768		Strath_GW250	-1.6653	-2.9736	-7.8439	-3.3076	0.00188
Strath_GW51	-1.458	-3.1681	-8.4047	-2.9059	0.04363		Strath_GW251	-0.6853	-2.5963	-7.4196	-1.3467	0.00084
Strath_GW52	-1.788	-3.8943	-7.5279	-3.6608	0.06112		Strath_GW252	-0.7255	-3.9643	-7.2324	-1.4428	0.07332
Strath_GW53	-1.452	-2.8757	-7.7253	-2.8541	0.03356		Strath_GW253	-1.5516	-3.2475	-8.3009	-2.9992	0.0039
Strath_GW54	-0.7958	-2.7876	-7.8886	-1.6146	0.05698		Strath_GW254	-0.6204	-4.0137	-6.8901	-1.307	0.04116
Strath_GW55	-0.5732	-2.549	-7.7252	-1.2391	0.0785		Strath_GW255	-0.4261	-2.5783	-7.1732	-0.9045	0.0352
Strath_GW56	-0.1758	-2.0371	-7.1817	-0.5659	0.07624		Strath_GW256	0.2682	-1.2955	-6.5986	0.2585	0.01835
Strath_GW57	-0.0075	-2.1614	-6.5353	-0.1732	0.08098		Strath_GW257	-1.5753	-3.4623	-7.9939	-3.0029	0.00322
Strath_GW58	-0.9536	-2.7741	-7.9149	-1.7476	0.03563		Strath_GW258	-0.3801	-2.2857	-7.4054	-0.738	0.01239
Strath_GW59	0.9397	-1.2337	-4.9938	1.3796	0.21112		Strath_GW259	-0.8317	-2.4793	-8.005	-1.6516	0.00145
Strath_GW60	-0.0653	-2.5085	-6.9043	-0.1488	0.07391		Strath_GW260	-1.5918	-3.993	-7.8106	-3.3559	0.0863
Strath_GW61	0.2807	-1.5392	-6.6024	0.1924	0.09469		Strath_GW261	-0.4714	-2.3642	-7.5203	-0.8809	0.01885
Strath_GW62	0.1167	-1.6827	-5.9478	0.2692	0.09865		Strath_GW262	-0.2278	-2.2207	-7.4398	-0.5764	0.0188
Strath_GW63	0.3656	-1.4508	-6.2252	0.5354	0.06606		Strath_GW263	-1.337	-2.7125	-8.0762	-2.6963	0.02231
Strath_GW64	0.0882	-1.7919	-5.5964	0.3864	0.04941		Strath_GW264	-0.3411	-2.165	-7.8846	-0.5815	0.03628
Strath_GW65	-1.3352	-2.7157	-8.0559	-2.837	0.06355		Strath_GW265	-0.786	-2.5924	-7.5035	-1.6571	0.00041
Strath_GW66	-0.4735	-2.4852	-7.8523	-1.3251	0.04277		Strath_GW266	-1.2572	-2.7267	-8.0474	-2.5103	0.00409
Strath_GW67	-0.9531	-3.1644	-8.5617	-2.0889	0.03513		Strath_GW267	-1.193	-2.5345	-8.1266	-2.3556	0.00038
Strath_GW68	-1.2125	-3.1108	-8.4986	-2.5346	0.03274		Strath_GW268	-0.6663	-2.5444	-7.2477	-1.4026	0.00737
Strath_GW69	-1.2659	-2.6895	-8.0353	-2.4439	0.01286		Strath_GW269	-0.5282	-2.5826	-7.2685	-1.0091	0.01349
Strath_GW70	-0.6847	-1.8353	-7.2519	-1.5996	0.01613		Strath_GW270	-0.9247	-3.3746	-7.4019	-1.9584	0.03172
Strath_GW71	-0.088	-2.806	-6.3301	0.2068	0.04023		Strath_GW271	-0.6935	-2.6311	-7.794	-1.3193	0.00302
Strath_GW72	0.1673	-2.2739	-5.588	0.107	0.03571		Strath_GW272	-1.157	-2.7895	-7.9961	-2.3127	0.00321
Strath_GW73	-0.7295	-2.7534	-7.0175	-1.403	0.0164		Strath_GW273	-0.5133	-2.4773	-7.8745	-1.1795	0.00049
Strath_GW74	-1.7654	-3.3066	-8.4883	-3.3688	0.01719		Strath_GW274	-1.2031	-2.684	-7.6922	-2.1655	0.00047
Strath_GW75	-1.4581	-3.225	-8.0637	-3.0068	0.02301		Strath_GW275	-0.9772	-3.5917	-7.5606	-2.054	0.03776
Strath_GW76	-0.507	-2.21	-7.9496	-1.7458	0.06018		Strath_GW276	-0.3196	-2.4293	-7.7138	-0.6638	0.00879
Strath_GW77	-1.6616	-2.8896	-8.5188	-3.4098	0.01016		Strath_GW277	-0.9083	-2.5745	-7.6411	-1.9018	0.00074
Strath_GW78	-1.0943	-3.2054	-8.0262	-2.4483	0.03541		Strath_GW278	-1.3574	-2.591	-8.0629	-2.719	0.00022
Strath_GW79	-1.4216	-3.402	-8.462	-2.7747	0.05436		Strath_GW279	-0.196	-2.3713	-7.1255	-0.4476	0.03106
Strath_GW80	-0.7372	-2.4101	-8.5046	-1.7295	0.03429		Strath_GW280	-0.2116	-2.3276	-7.6423	-0.4897	0.00469
Strath_GW81	-2.2912	-4.3546	-8.9737	-4.7253	0.00867		Strath_GW281	-0.719	-2.6339	-7.656	-1.4023	0.00601
Strath_GW82	-2.4828	-4.3473	-9.288	-4.8916	0.01649		Strath_GW282	-0.291	-3.1774	-7.3914	-0.666	0.03457
Strath_GW83	-0.0682	-2.2816	-6.8066	-0.4195	0.06187		Strath_GW283	-1.8921	-3.5568	-7.8929	-3.9133	0.01438

Strath_GW84	0.2323	-1.8632	-8.2123	0.4156	0.08412		Strath_GW284	-1.7467	-2.8628	-7.85	-3.4086	0.00023
Strath_GW85	-0.8223	-2.9054	-6.6015	-1.7234	0.00875		Strath_GW285	-0.4637	-3.0342	-6.9974	-0.9667	0.02693
Strath_GW86	0.1064	-2.152	-6.7046	0.242	0.07578		Strath_GW286	-0.4447	-2.4493	-7.1662	-0.9557	0.01726
Strath_GW87	-1.6833	-3.7526	-9.1771	-3.3305	0.01657		Strath_GW287	-0.818	-2.4907	-8.5553	-1.6484	0.00107
Strath_GW88	-1.3042	-3.3817	-8.3516	-2.5386	0.11866		Strath_GW288	-0.7614	-2.4353	-7.7437	-1.546	0.04707
Strath_GW89	-0.4579	-1.9533	-7.3529	-0.9945	0.02403		Strath_GW289	-1.2323	-2.7267	-7.9372	-2.4692	0.00043
Strath_GW90	-0.773	-2.9143	-7.9356	-1.4073	0.05631		Strath_GW290	-0.7941	-2.6498	-7.9751	-1.5849	0.0092
Strath_GW91	-0.9613	-3.0544	-7.6651	-1.9635	0.03699		Strath_GW291	-1.1148	-2.8285	-8.5733	-2.1935	0.00249
Strath_GW92	-1.0163	-3.1522	-7.8779	-2.0634	0.03273		Strath_GW292	-0.0311	-1.4397	-6.5109	-0.1325	0.01349
Strath_GW93	-1.6684	-3.9437	-9.4081	-3.2982	0.18097		Strath_GW293	0.4591	-1.5315	-7.5317	0.9266	0.06176
Strath_GW94	-0.0343	-1.9872	-7.4348	-0.0493	0.03546		Strath_GW294	-0.8067	-2.7128	-8.3863	-1.7841	0.00049
Strath_GW95	-1.1899	-2.4259	-8.4715	-2.2794	0.43645		Strath_GW295	-0.9748	-2.6632	-8.3847	-1.9098	0.0021
Strath_GW96	-1.1869	-2.0388	-8.3497	-2.336	0.03051		Strath_GW296	0.1738	-1.7221	-6.7888	0.1766	0.01825
Strath_GW97	-0.8536	-2.5791	-8.1367	-1.7159	0.02721		Strath_GW297	0.2231	-1.7756	-6.7332	0.3472	0.09242
Strath_GW98	-0.3758	-2.3717	-8.0479	-0.7276	0.02663		Strath_GW298	-0.6125	-2.5794	-7.9653	-1.3898	0.00068
Strath_GW99	0.2146	-1.2491	-6.8343	-0.0189	0.0549		Strath_GW299	-1.101	-2.7904	-8.0954	-2.136	0.00053
Strath_GW100	0.3712	-1.7432	-7.5928	0.7744	0.07246		Strath_GW300	0.0182	-1.7285	-6.737	-0.0015	0.03339
Strath_GW101	0.3374	-0.8135	-6.109	0.01	0.05642		Strath_GW301	0.0986	-1.811	-7.0404	0.1406	0.01735
Strath_GW102	-0.4268	-2.3203	-8.0615	-0.7604	0.06268		Strath_GW302	-0.2542	-2.2259	-6.458	-0.5192	0.05882
Strath_GW103	-0.583	-2.0695	-7.9122	-1.1171	0.04166		Strath_GW303	0.0639	-1.9278	-6.7777	-0.0181	0.04939
Strath_GW104	-0.443	-2.5461	-8.3446	-0.8577	0.03226		Strath_GW304	-2.3399	-4.2138	-8.4327	-4.7422	0.03294
Strath_GW105	-0.687	-2.4439	-7.9773	-1.3381	0.0277		Strath_GW305	-0.3044	-1.6251	-6.4503	-0.6406	0.00322
Strath_GW106	-0.3526	-1.9934	-7.9951	-0.667	0.02627		Strath_GW306	-0.3442	-2.1684	-7.5845	-0.7685	0.00965
Strath_GW107	-0.5866	-1.7099	-7.3503	-1.1018	0.02772		Strath_GW307	-0.8375	-2.7369	-8.0001	-1.5824	0.00603
Strath_GW108	0.0622	-1.3483	-7.3243	0.1659	0.0409		Strath_GW308	-0.7908	-2.7749	-8.0185	-1.5406	0.00179
Strath_GW109	-1.1067	-2.9265	-8.1922	-2.1407	0.05296		Strath_GW309	-0.9106	-2.5929	-8.0216	-1.9414	0.00025
Strath_GW110	-0.024	-1.0287	-6.6227	-0.0057	0.03669		Strath_GW310	-0.5573	-2.0773	-6.7705	-1.2523	0.00794
Strath_GW111	0.1683	-1.7326	-7.5548	-0.095	0.04167		Strath_GW311	-0.611	-2.6073	-7.7281	-1.2711	0.00829
Strath_GW112	0.1725	-1.5911	-7.2603	0.0487	0.0555		Strath_GW312	-1.6238	-2.9875	-8.9175	-3.2019	0.00038
Strath_GW113	-0.1846	-1.9497	-6.8379	-0.5966	0.01532		Strath_GW313	-1.9791	-3.089	-8.8115	-4.1414	0.00095
Strath_GW114	0.0499	-2.464	-7.4474	-0.1396	0.03349		Strath_GW314	-0.5803	-2.6432	-7.7585	-1.1134	0.00068
Strath_GW115	-0.0419	-1.4701	-7.0347	-0.1237	0.01417		Strath_GW315	-0.5903	-3.1512	-6.9155	-1.2365	0.04533
Strath_GW116	0.0235	-2.5825	-7.4175	-0.2173	0.03577		Strath_GW316	-0.2892	-2.2524	-7.1062	-0.6336	0.00968
Strath_GW117	-0.3557	-1.496	-7.3803	-0.6743	0.01631		Strath_GW317	-0.1423	-1.6911	-7.2265	-0.4123	0.00583
Strath_GW118	0.2179	-2.2822	-7.0633	0.2002	0.0612		Strath_GW318	-1.0496	-2.682	-7.9212	-2.0517	0.1008
Strath_GW119	0.3648	-1.6911	-7.183	0.206	0.01863		Strath_GW319	-0.7282	-1.7099	-6.9046	-1.4767	0.00675
Strath_GW120	0.3859	-2.0273	-7.4662	0.3648	0.07979		Strath_GW320	-1.1598	-2.5829	-7.9994	-2.3406	0.00077
Strath_GW121	0.232	-1.6841	-7.0713	-0.1391	0.04447		Strath_GW321	-0.7365	-2.479	-8.1208	-1.6342	0.00566
Strath_GW122	-0.4479	-1.7238	-6.7859	-0.8382	0.03628		Strath_GW322	-1.17	-2.6446	-8.3151	-2.2821	0.00025
Strath_GW123	-0.0551	-1.29	-6.9919	-0.1234	0.03821		Strath_GW323	-0.4447	-2.411	-7.3261	-0.9589	0.00866
Strath_GW124	0.3053	-0.6566	-5.9076	-0.0371	0.03992		Strath_GW324	0.2797	-2.1906	-6.4213	0.3487	0.00637
Strath_GW125	-0.7375	-2.2675	-7.4257	-1.4286	0.05815		Strath_GW325	-0.9399	-2.6006	-8.1009	-1.851	0.00785
Strath_GW126	-0.1771	-1.7464	-7.5929	-0.7233	0.03449		Strath_GW326	-0.9287	-2.6041	-7.9229	-1.7269	0.03552

Strath_GW127	0.1875	-1.3788	-7.1253	0.0016	0.04688		Strath_GW327	-0.4484	-2.5451	-7.6896	-0.8801	0.0083
Strath_GW128	0.4245	-1.2514	-6.5173	0.2496	0.12686		Strath_GW328	-0.3961	-2.7972	-7.1887	-0.9492	0.02121
Strath_GW129	0.4531	-1.2949	-6.2376	0.3087	0.09065		Strath_GW329	-0.7156	-3.4813	-7.3336	-1.4937	0.07024
Strath_GW130	-1.0829	-2.7632	-8.4404	-2.3829	0.00045		Strath_GW330	-1.7288	-2.9235	-8.3407	-3.4941	0.00084
Strath_GW131	0.2369	-1.4326	-6.855	-0.161	0.05274		Strath_GW331	-0.3659	-3.2627	-6.8824	-0.7872	0.02582
Strath_GW132	-1.7803	-3.773	-8.9097	-3.5922	0.05631		Strath_GW332	-0.1802	-2.2557	-7.2845	-0.3486	0.02092
Strath_GW133	-1.6678	-3.6129	-8.5381	-3.4669	0.01983		Strath_GW333	-1.0762	-2.4708	-8.078	-2.1184	0.00033
Strath_GW134	-2.1271	-3.6131	-8.5925	-4.434	0.00845		Strath_GW334	-1.7953	-3.4388	-8.6956	-3.6878	0.02688
Strath_GW135	-0.5145	-2.6773	-7.4378	-1.1581	0.00316		Strath_GW335	-0.052	-1.8997	-6.8316	-0.1731	0.0153
Strath_GW136	-1.9914	-2.6725	-8.6012	-3.977	0.0008		Strath_GW336	-0.4362	-2.282	-7.3055	-0.9056	0.01
Strath_GW137	-0.6728	-2.9645	-8.3775	-1.3949	0.00663		Strath_GW337	-1.4327	-2.8003	-7.9322	-2.898	0.0003
Strath_GW138	-1.6305	-2.9163	-8.1805	-3.2297	0.00351		Strath_GW338	-0.9511	-2.7405	-8.3084	-1.8695	0.00365
Strath_GW139	-1.4228	-2.7034	-8.3452	-2.9915	0.00552		Strath_GW339	-0.547	-2.5486	-7.6782	-1.1046	0.00205
Strath_GW140	-1.7773	-3.3137	-8.7595	-3.6817	0.00323		Strath_GW340	-1.5043	-2.6536	-8.2428	-3.0929	0.00022
Strath_GW141	-2.0551	-3.5791	-8.6616	-4.2464	0.00086		Strath_GW341	-0.2391	-2.2265	-7.1571	-0.5146	0.0119
Strath_GW142	-1.1399	-2.4604	-8.1857	-2.3606	0.00251		Strath_GW342	-0.8517	-2.6399	-7.7153	-1.7909	0.00224
Strath_GW143	-1.1464	-2.7049	-8.0918	-2.2904	0.00485		Strath_GW343	-0.2742	-3.0562	-6.7605	-0.7235	0.01865
Strath_GW144	-1.9856	-3.222	-8.8101	-3.9501	0.01714		Strath_GW344	-0.2161	-4.0835	-6.8777	-0.5468	0.02234
Strath_GW145	-1.6087	-3.1209	-8.7192	-3.2508	0.00173		Strath_GW345	-0.5815	-3.5516	-8.6438	-1.2114	0.00468
Strath_GW146	-2.1189	-3.0664	-8.6554	-4.4742	0.00275		Strath_GW346	-0.8494	-3.29	-8.2992	-1.7831	0.00525
Strath_GW147	-1.8135	-2.9305	-8.3672	-3.8299	0.00525		Strath_GW347	-0.9066	-3.0431	-8.2395	-1.9059	0.03194
Strath_GW148	-1.3091	-2.5158	-8.3619	-2.7059	0.01747		Strath_GW348	-0.3814	-2.213	-7.8285	-0.8967	0.02867
Strath_GW149	-2.1443	-3.3232	-8.6616	-4.4896			Strath_GW349	-1.3116	-2.5791	-7.9168	-2.6457	0.04554
Strath_GW150	-1.4166	-3.016	-8.3552	-3.0115	0.0018		Strath_GW350	-1.9653	-3.1366	-8.5156	-4.0581	0.02803
Strath_GW151	-1.7254	-3.6179	-8.6071	-3.5501	0.00602		Strath_GW351	-1.3339	-2.6645	-8.2223	-2.7056	0.04454
Strath_GW152	-1.7659	-3.238	-8.7597	-3.7264	0.01311		Strath_GW352	-1.6631	-3.0051	-8.2283	-3.4256	0.02327
Strath_GW153	-1.4039	-2.8231	-8.6174	-2.8093	0.00347		Strath_GW353	-0.616	-2.0839	-8.1398	-1.3119	0.05219
Strath_GW154	-1.5776	-3.066	-8.7985	-3.1306	0.00175		Strath_GW354	-1.5758	-2.5747	-8.2913	-3.19	0.28443
Strath_GW155	-1.9784	-3.004	-8.6669	-4.1051	0.01341		Strath_GW355	-0.2221	-1.2403	-7.7432	-0.5154	0.09288
Strath_GW156	-1.8408	-3.2406	-8.6085	-3.663	0.00254		Strath_GW356	-0.6686	-2.0842	-7.9889	-1.4076	0.05935
Strath_GW157	-2.1257	-4.0311	-8.7106	-4.3732	0.00032		Strath_GW357	-0.4288	-1.803	-8.1527	-1.0181	0.04755
Strath_GW158	-1.8119	-3.0701	-8.4051	-3.6642	0.00539		Strath_GW358	-1.0492	-3.1843	-8.0672	-2.1753	0.04183
Strath_GW159	-1.12	-4.3528	-8.1969	-2.5519	0.05359		Strath_GW359	-0.8858	-3.2932	-8.1568	-1.8482	0.03166
Strath_GW160	-1.4237	-4.5962	-8.6323	-2.7415	0.03914		Strath_GW360	-0.9895	-3.2225	-8.115	-2.0823	0.03351
Strath_GW161	-0.5746	-3.1804	-8.1872	-1.0278	0.00745		Strath_GW361	-2.1213	-3.8519	-8.1543	-4.2993	0.01773
Strath_GW162	-1.1159	-4.3926	-8.4457	-2.2345	0.04607		Strath_GW362	-0.8049	-3.1506	-8.1783	-1.728	0.10958
Strath_GW163	-0.0483	-0.9889	-6.3592	-0.594	0.00652		Strath_GW363	-0.5786	-2.8834	-8.0607	-1.2284	0.11734
Strath_GW164	0.4988	-0.9719	-5.7375	0.5807	0.21319		Strath_GW364	-0.4976	-2.9022	-8.0336	-1.0654	0.10298
Strath_GW165	0.0232	-2.0319	-6.9896	0.0226	0.00845		Strath_GW365	-0.7876	-2.9998	-8.1881	-1.5997	0.05884
Strath_GW166	0.4592	-1.687	-4.9963	0.7079	0.16808		Strath_GW366	-0.3273	-2.5559	-8.3702	-0.7297	0.06355
Strath_GW167	0.2087	-1.6307	-6.2542	0.1839	0.01049		Strath_GW367	-0.7699	-2.735	-8.0591	-1.5973	0.02984
Strath_GW168	-0.965	-2.81	-7.3977	-1.9828	0.00292		Strath_GW368	-0.461	-1.9113	-7.683	-0.9991	0.05003
Strath_GW169	0.0397	-2.1501	-6.7267	-0.064	0.11254		Strath_GW369	-1.0557	-3.2107	-8.09	-2.2252	0.03423

Strath_GW170	-0.8851	-3.5916	-7.4983	-1.7315	0.07329		Strath_GW370	-0.1739	-2.6141	-8.0261	-0.4156	0.06313
Strath_GW171	-0.8247	-2.6645	-7.7185	-1.8096	0.00343		Strath_GW371	-0.6522	-2.873	-8.2217	-1.3867	0.02132
Strath_GW172	0.1279	-2.4079	-6.5995	0.1491	0.22717		Strath_GW372	-1.392	-2.8504	-8.5331	-2.8376	0.04214
Strath_GW173	0.086	-1.9011	-6.6676	0.057	0.01196		Strath_GW373	-2.0342	-3.3103	-8.1652	-4.1262	0.06004
Strath_GW174	0.0624	-1.9623	-6.5632	-0.1416	0.00843		Strath_GW374	-1.0899	-3.1352	-7.9101	-2.1846	0.0291
Strath_GW175	0.1964	-2.8694	-7.2291	0.1483	0.19661		Strath_GW375	-0.6393	-2.8613	-8.7023	-1.488	0.00276
Strath_GW176	0.0537	-2.9458	-6.9115	-0.0181	0.0104		Strath_GW376	-0.3637	-2.071	-7.7377	-0.5886	0.00476
Strath_GW177	-0.1642	-2.5029	-7.2404	-0.5581	0.00773		Strath_GW377	-1.7445	-3.006	-8.2645	-3.4961	0.03949
Strath_GW178	-0.6738	-4.8475	-7.8917	-1.3973	0.19193		Strath_GW378	-1.5038	-3.3385	-8.1919	-3.0428	0.05906
Strath_GW179	-1.011	-5.0105	-8.3045	-1.9695	0.05536		Strath_GW379	-0.7496	-2.2143	-7.7213	-1.666	0.07287
Strath_GW180	-0.7127	-3.2282	-7.562	-1.4751	0.0228		Strath_GW380	-1.2372	-3.6889	-7.8301	-2.5234	0.07065
Strath_GW181	-0.5174	-4.827	-7.7821	-1.004	0.07885		Strath_GW381	-1.1445	-2.3539	-8.1371	-1.3555	0.03555
Strath_GW182	-0.3368	-2.5038	-7.0208	-0.7927	0.09925		Strath_GW382	-1.3399	-3.2601	-8.1471	-2.5176	0.06161
Strath_GW183	-0.2812	-2.9959	-7.266	-0.6868	0.06978		Strath_GW383	-1.9839	-3.2495	-8.4916	-4.0448	0.0013
Strath_GW184	-1.2874	-2.991	-8.2377	-2.5434	0.00973		Strath_GW384	-2.2853	-3.6039	-8.6435	-4.624	0.00087
Strath_GW185	-0.0502	-2.334	-7.8799	-0.2529	0.00175		Strath_GW385	-1.1117	-3.5597	-7.962	-2.2011	0.04064
Strath_GW186	-0.3153	-2.3763	-7.4855	-0.8238	0.00919		Strath_GW386	-1.3464	-2.5821	-8.1769	-2.8722	0.00786
Strath_GW187	-0.4344	-2.5601	-7.3187	-0.8763	0.00058		Strath_GW387	-2.2214	-3.3632	-8.5239	-4.5501	0.01023
Strath_GW188	-0.5371	-2.4592	-7.6375	-1.0939	0.00059		Strath_GW388	-1.8364	-2.927	-8.2828	-3.8552	0.00209
Strath_GW189	-0.7959	-2.6882	-7.4541	-1.618	0.00516		Strath_GW389	-1.8858	-3.5829	-8.8089	-3.708	0.00114
Strath_GW190	-0.3001	-2.2933	-7.5266	-0.6883	0.00844		Strath_GW390	-1.1853	-3.0678	-8.1991	-2.3751	0.01755
Strath_GW191	-0.5402	-2.5773	-6.7465	-1.1054	0.01141		Strath_GW391	-0.8157	-2.1869	-8.0689	-1.8394	0.0298
Strath_GW192	0.0944	-2.2399	-6.8355	-0.1721	0.00147		Strath_GW392	-2.3895	-3.6762	-8.3041	-4.9259	0.01585
Strath_GW193	0.3059	-1.9764	-6.4919	0.2721	0.01822		Strath_GW393	-1.154	-2.1322	-7.8052	-2.4004	0.04241
Strath_GW194	-0.9263	-4.1175	-7.2337	-1.9437	0.02114		Strath_GW394	-2.7503	-3.0259	-8.0866	-5.5616	0
Strath_GW195	-0.4963	-4.0148	-7.3506	-1.1907	0.0121		Strath_GW395	-0.3987	-3.6757	-7.3856	-0.8295	0.00519
Strath_GW196	-0.2818	-3.9035	-6.611	-0.9174	0.0064		Strath_GW396	-0.9968	-2.7353	-8.6008	-2.0995	0.00932
Strath_GW197	-1.1583	-4.3104	-7.9562	-2.2471	0.02173		Strath_GW397	-0.8671	-4.2702	-8.7336	-1.8142	0.02705
Strath_GW198	-0.7638	-3.8365	-7.5386	-1.6675	0.03814		Strath_GW398	-0.2906	-2.5747	-7.1346	-0.7037	0.01276
Strath_GW199	-1.0616	-4.9084	-8.0411	-2.2875	0.00155		Strath_GW399	-0.5401	-2.6283	-6.6158	-1.0621	0.00544
Strath_GW200	-0.4983	-3.2658	-6.4175	-1.0687	0.0073		Strath_GW400	-0.4709	-2.8308	-7.6845	-0.8908	0.00791

Sample ID	Calcite	Gypsum	Halite	Dolomite	pCO_2		Sample ID	Calcite	Gypsum	Halite	Dolomite	pCO_2
Strath_GW401	-0.0457	-2.1902	-7.1937	-0.3136	0.00921		Strath_GW601	-0.343	-1.8078	-7.1125	-0.7192	0.02492
Strath_GW402	0.0423	-3.5941	-7.672	-0.0707	0.01156		Strath_GW602	-1.627	-3.1044	-8.3295	-3.1601	0.00029
Strath_GW403	-1.0448	-3.1443	-8.532	-2.0377	0.01231		Strath_GW603	0.0619	-1.8814	-7.2055	0.133	0.03444
Strath_GW404	-0.9105	-2.7272	-8.1515	-1.7772	0.01736		Strath_GW604	0.2698	-1.1588	-7.3851	0.4121	0.00679
Strath_GW405	-0.7079	-2.7008	-7.9252	-1.5608	0.00369		Strath_GW605	-0.0061	-0.8952	-5.4255	-0.0342	0.01249
Strath_GW406	-1.5856	-3.3483	-8.7934	-3.4251	0.0014		Strath_GW606	-0.5754	-1.4358	-7.1082	-1.1733	0.00037
Strath_GW407	-0.2398	-1.8019	-7.0444	-0.4925	0.00363		Strath_GW607	-0.0774	-1.0825	-7.1422	-0.1486	0.00143
Strath_GW408	-0.7585	-2.3051	-7.4127	-1.6837	0.00364		Strath_GW608	0.521	-0.4383	-6.6577	0.9631	0.00986
Strath_GW409	-0.7827	-2.1415	-7.6421	-1.5101	0.03407		Strath_GW609	-0.4086	-1.6216	-7.3059	-0.9161	0.00073
Strath_GW410	-1.7725	-2.9032	-8.3785	-3.5845	0.01506		Strath_GW610	-0.3788	-1.1465	-6.9996	-0.7885	0.00092
Strath_GW411	-0.2683	-1.9717	-7.0219	-0.6758	0.04826		Strath_GW611	-0.9972	-1.97	-8.6522	-2.1819	0.00031
Strath_GW412	-0.2213	-1.6447	-6.5847	-0.7356	0.00422		Strath_GW612	-0.81	-2.3626	-7.4742	-1.7824	0.0007
Strath_GW413	1.1608	-1.0114	-6.2114	2.1149	0.3088		Strath_GW613	-0.0561	-1.4548	-6.6168	-0.2962	0.00095
Strath_GW414	-1.7223	-1.4478	-6.9727	-3.5588	0.00006		Strath_GW614	-0.5894	-1.1109	-6.6728	-1.2725	0.00024
Strath_GW415	-1.34	-2.1214	-7.81	-2.8135	0.00265		Strath_GW615	-0.9801	-1.6108	-7.1796	-1.8831	0.00061
Strath_GW416	0.1504	-1.3168	-8.1297	0.1228	0.00225		Strath_GW616	-0.7378	-2.2446	-7.7739	-1.5625	0.0003
Strath_GW417	-0.7066	-1.3696	-8.4308	-1.5578	0.00037		Strath_GW617	-0.575	-2.1614	-7.5631	-1.2568	0.00069
Strath_GW418	-0.9805	-3.0023	-7.6054	-1.9313	0.00134		Strath_GW618	-0.8709	-2.3874	-7.3718	-1.8145	0.0004
Strath_GW419	-0.8782	-2.4882	-8.1023	-1.8032	0.00382		Strath_GW619	-0.0568	-2.1633	-6.8453	-0.3239	0.0008
Strath_GW420	-0.7259	-1.5621	-7.4403	-1.4645	0.04029		Strath_GW620	-0.336	-2.4604	-7.4359	-0.8045	0.00082
Strath_GW421	-0.9885	-2.4566	-8.0511	-2.0226	0.03364		Strath_GW621	-0.0688	-1.3001	-6.5811	-0.2926	0.0019
Strath_GW422	-1.2136	-2.7656	-8.8764	-2.6555	0.01044		Strath_GW622	0.166	-0.8725	-6.6191	0.1854	0.00288
Strath_GW423	-1.2633	-2.4129	-8.122	-2.5518	0.02694		Strath_GW623	-0.5315	-1.8588	-7.1534	-1.0444	0.00059
Strath_GW424	-1.0125	-1.7222	-7.7499	-2.0734	0.01112		Strath_GW624	-0.5082	-1.2282	-6.74	-1.1144	0.00031
Strath_GW425	-0.747	-2.6251	-8.2899	-1.647	0.02618		Strath_GW625	-0.2188	-1.0638	-6.7107	-0.4937	0.00107
Strath_GW426	-1.2711	-2.6043	-8.1702	-2.6223	0.02588		Strath_GW626	-1.0896	-1.7975	-7.1268	-2.3959	0.00029
Strath_GW427	-0.4716	-1.5384	-7.3232	-1.124	0.00025		Strath_GW627	-0.8817	-1.8105	-7.602	-1.9387	0.00118
Strath_GW428	-0.6641	-1.5558	-7.2938	-1.4685	0.00946		Strath_GW628	-1.021	-1.8154	-7.6286	-2.2033	0.00032
Strath_GW429	-0.6657	-2.3986	-7.235	-1.1971	0.00231		Strath_GW629	-1.1654	-1.9358	-7.6755	-2.5109	0.00014
Strath_GW430	-0.3412	-1.3176	-7.9988	-0.9562	0.07883		Strath_GW630	-0.8862	-1.8151	-7.7638	-2.014	0.00063
Strath_GW431	-0.1739	-2.3035	-8.5868	-0.559	0.86196		Strath_GW631	-0.7344	-2.0526	-8.4155	-1.5879	0.0004
Strath_GW432	-1.3614	-3.2682	-8.9859	-2.8184	0.03604		Strath_GW632	0.1321	-1.8088	-7.4418	0.035	0.00131
Strath_GW433	-0.9688	-3.3791	-8.5967	-1.9846	0.0685		Strath_GW633	-0.988	-1.4186	-7.3808	-2.1043	0.00017
Strath_GW434	-2.07	-3.2072	-9.0044	-4.4074	0.01989		Strath_GW634	-0.5207	-1.3504	-7.3318	-1.2339	0.00073
Strath_GW435	-0.587	-3.1222	-8.3778	-1.1813	0.08497		Strath_GW635	-1.0365	-1.8332	-7.8673	-2.3306	0.00062
Strath_GW436	-0.9727	-2.2355	-8.7022	-2.0317	0.04811		Strath_GW636	-1.295	-2.3998	-7.636	-2.5532	0.00066
Strath_GW437	-0.0442	-1.5969	-7.4879	-0.2608	0.05752		Strath_GW637	-0.6564	-2.2949	-7.9286	-1.3339	0.00136
Strath_GW438	-0.794	-2.3611	-8.2798	-1.5723	0.11837		Strath_GW638	-1.0277	-2.2563	-8.111	-2.2084	0.00046
Strath_GW439	-0.6196	-2.9812	-8.4486	-1.3332	0.0325		Strath_GW639	-1.1486	-2.5789	-7.8359	-2.3933	0.00063
Strath_GW440	-0.4874	-3.053	-7.8942	-1.0327	0.07813		Strath_GW640	-1.3446	-2.8159	-8.3057	-2.7092	0.0003
Strath_GW441	-0.2685	-2.8066	-7.9009	-0.604	0.04546		Strath_GW641	-1.6699	-3.1106	-8.33	-3.4987	0.0003

Strath_GW442	-0.5338	-3.2374	-7.668	-1.2213	0.55949		Strath_GW642	-1.7003	-3.4693	-8.3692	-3.521	0.00031
Strath_GW443	-0.1585	-1.2189	-7.5762	-0.3788	0.04509		Strath_GW643	-1.1596	-2.8106	-8.3881	-2.349	0.00046
Strath_GW444	-0.9036	-2.5493	-8.113	-1.8493	0.03036		Strath_GW644	-1.1517	-2.6726	-8.0385	-2.4382	0.00061
Strath_GW445	-0.7826	-1.5986	-7.7783	-1.6677	0.05546		Strath_GW645	-1.8761	-3.1013	-7.9008	-3.965	0.00021
Strath_GW446	-0.7881	-1.6941	-7.6712	-1.6134	0.05953		Strath_GW646	-1.7176	-3.118	-7.9877	-3.3958	0.0004
Strath_GW447	-1.6509	-2.9541	-8.962	-3.3599	0.01729		Strath_GW647	-1.3996	-2.5835	-8.2488	-2.8524	0.00042
Strath_GW448	-0.9711	-2.0017	-8.0074	-2.0598	0.07582		Strath_GW648	-0.1648	-1.9722	-8.2865	-0.4682	0.003
Strath_GW449	-1.2421	-2.5784	-8.1269	-2.5207	0.05995		Strath_GW649	-1.6106	-3.0759	-8.3625	-3.2083	0.00053
Strath_GW450	-1.3533	-2.7289	-8.3837	-2.7462	0.04009		Strath_GW650	-1.219	-2.2283	-7.9988	-2.4958	0.00054
Strath_GW451	-0.9301	-1.9933	-8.024	-1.9268	0.05281		Strath_GW651	-0.7299	-2.9335	-8.2846	-1.5084	0.00033
Strath_GW452	-1.1905	-2.1553	-7.7848	-2.4785	0.07069		Strath_GW652	-0.8864	-2.5646	-8.5523	-1.9372	0.00037
Strath_GW453	-1.0151	-1.6799	-8.0046	-2.1197	0.06766		Strath_GW653	-1.44	-3.0668	-8.4545	-2.9134	0.00033
Strath_GW454	0.3446	-0.6944	-7.349	0.6258	0.93691		Strath_GW654	-1.3345	-2.3395	-8.3758	-2.5698	0.00035
Strath_GW455	-0.7191	-1.368	-7.3471	-1.5099	0.67614		Strath_GW655	-0.2169	-1.4859	-8.2193	-0.5801	0.00112
Strath_GW456	-0.9288	-1.7687	-7.8059	-1.9625	0.08968		Strath_GW656	-1.3955	-3.0187	-8.4236	-2.8096	0.00018
Strath_GW457	-1.5628	-2.1392	-8.3214	-3.2097	0.0325		Strath_GW657	-1.3211	-2.7914	-8.3963	-2.7122	0.00019
Strath_GW458	-2.0625	-3.1408	-8.4747	-4.1893	0.04115		Strath_GW658	-0.63	-1.1359	-7.8082	-1.3663	0.00056
Strath_GW459	-0.8596	-1.5382	-7.7672	-1.7	8.66049		Strath_GW659	-0.6873	-1.4398	-7.9857	-1.3991	0.00028
Strath_GW460	-1.2287	-3.1881	-8.2276	-2.4829	0.13316		Strath_GW660	-0.5434	-3.0212	-8.002	-1.112	0.00032
Strath_GW461	-0.6017	-2.9962	-8.0755	-1.283	0.11369		Strath_GW661	-1.0026	-1.8293	-8.1273	-2.0857	0.00049
Strath_GW462	-1.1328	-3.3292	-8.0619	-2.3437	0.05675		Strath_GW662	-1.4793	-2.3284	-8.5417	-3.0329	0.00026
Strath_GW463	-0.39	-2.6721	-7.7911	-0.828	0.06131		Strath_GW663	-0.9369	-2.1872	-8.4735	-1.9663	0.00038
Strath_GW464	-0.7138	-3.1409	-7.9444	-1.4818	0.03122		Strath_GW664	-1.0779	-2.2364	-8.5578	-2.2529	0.00053
Strath_GW465	-0.9474	-3.4964	-7.9734	-1.9175	0.03065		Strath_GW665	-1.3824	-2.3815	-8.5866	-2.809	0.0002
Strath_GW466	-0.5268	-3.1158	-7.9597	-1.0303	0.04138		Strath_GW666	-1.2652	-2.5775	-8.4303	-2.4776	0.00025
Strath_GW467	-0.7508	-3.0012	-8.0309	-1.5414	0.02402		Strath_GW667	-1.0333	-2.2474	-8.3047	-2.1603	0.00028
Strath_GW468	-0.0477	-2.8418	-7.2227	-0.0874	0.07587		Strath_GW668	-1.2566	-2.7958	-8.0833	-2.4999	0.00026
Strath_GW469	-0.7583	-2.9569	-7.9569	-1.5346	0.02433		Strath_GW669	-1.0354	-2.7156	-8.8822	-2.0726	0.00034
Strath_GW470	-1.2059	-3.4251	-8.2547	-2.3841	0.01445		Strath_GW670	-0.7079	-2.4893	-8.1203	-1.5047	0.00036
Strath_GW471	-1.3902	-2.8355	-8.1479	-2.8962	0.0245		Strath_GW671	-1.0569	-2.8478	-8.6727	-2.1772	0.00051
Strath_GW472	-0.9886	-3.1319	-8.2125	-2.0802	0.02869		Strath_GW672	-0.86	-3.167	-8.7157	-1.7261	0.00029
Strath_GW473	-0.4014	-2.9136	-7.9289	-0.8458	0.07446		Strath_GW673	-0.9967	-2.2768	-8.1089	-2.0062	0.00032
Strath_GW474	-0.6099	-2.9904	-7.9957	-1.2807	0.04549		Strath_GW674	-1.0819	-2.4526	-8.3086	-2.218	0.00037
Strath_GW475	-1.2686	-3.3728	-8.0182	-2.7379	0.02063		Strath_GW675	-1.1947	-2.7686	-8.7742	-2.4184	0.00027
Strath_GW476	-0.2776	-2.1834	-8.1192	-0.5381	0.02585		Strath_GW676	-1.1786	-2.6099	-8.3738	-2.2892	0.00022
Strath_GW477	-0.703	-4.8082	-8.3284	-1.4994	0.02578		Strath_GW677	-0.9823	-2.3098	-8.0358	-2.0318	0.00021
Strath_GW478	-0.5209	-4.7231	-8.4767	-1.1138	0.06944		Strath_GW678	-1.3531	-2.6283	-8.4873	-2.731	0.00029
Strath_GW479	-0.3455	-4.656	-8.436	-0.9015	0.03728		Strath_GW679	-0.9841	-2.6936	-8.368	-1.9019	0.00025
Strath_GW480	-1.4776	-5.1053	-8.3205	-2.9566	0.01179		Strath_GW680	-1.1626	-2.6974	-8.9214	-2.3015	0.00147
Strath_GW481	-1.4351	-5.1076	-8.131	-3.1195	0.0108		Strath_GW681	-1.0747	-2.6706	-8.6669	-2.1848	0.00159
Strath_GW482	-1.026	-4.9259	-8.1167	-2.1119	0.01485		Strath_GW682	-0.9437	-2.3655	-8.4699	-2.0084	0.00356
Strath_GW483	-0.4418	-2.1144	-8.4414	-0.8794	0.02113		Strath_GW683	-0.864	-2.1616	-8.4456	-1.8825	0.00676
Strath_GW484	-1.5038	-1.9711	-8.4625	-3.2293	0.0062		Strath_GW684	-1.157	-1.9168	-8.1398	-2.4112	0.00105

Strath_GW485	-0.6669	-1.9786	-7.9305	-1.478	0.02736		Strath_GW685	-0.7311	-2.0108	-8.3147	-1.5046	0.00048
Strath_GW486	-0.8594	-2.5973	-7.9435	-1.6824	0.01176		Strath_GW686	-1.1919	-2.4416	-8.3243	-2.3511	0.00068
Strath_GW487	-0.627	-1.6025	-8.521	-1.6364	0.0169		Strath_GW687	-0.919	-1.9294	-8.127	-1.8769	0.00018
Strath_GW488	-0.6726	-1.9782	-7.9304	-1.4893	0.02699		Strath_GW688	-1.0407	-2.1367	-8.5063	-2.0932	0.00024
Strath_GW489	-0.8776	-2.5963	-7.923	-1.7187	0.01126		Strath_GW689	-1.5533	-2.4267	-8.5039	-3.1108	0.00017
Strath_GW490	-0.4368	-1.6379	-8.5269	-0.9865	0.02702		Strath_GW690	-0.6817	-2.8272	-8.8978	-1.3558	0.0014
Strath_GW491	-0.5297	-1.4351	-7.7323	-0.9542	0.01733		Strath_GW691	-1.1127	-2.7426	-9.3035	-2.2379	0.00053
Strath_GW492	-0.8927	-1.617	-7.6005	-1.839	0.36264		Strath_GW692	-1.0297	-2.7118	-8.6742	-2.1512	0.00026
Strath_GW493	-0.7117	-2.0376	-7.0874	-1.6008	0.02318		Strath_GW693	-1.2026	-2.5291	-8.4008	-2.4688	0.00022
Strath_GW494	-0.0941	-1.9505	-7.9287	-0.4311	0.04507		Strath_GW694	-0.7515	-2.2558	-8.4541	-1.5257	0.00459
Strath_GW495	-0.8252	-4.9026	-7.9959	-1.6556	0.01787		Strath_GW695	-0.9065	-1.8069	-8.4609	-1.8146	0.00274
Strath_GW496	-1.0398	-4.9639	-8.032	-1.9865	0.01403		Strath_GW696	-0.55	-2.7026	-7.5173	-1.1184	0.00062
Strath_GW497	-0.3208	-4.7239	-7.8841	-0.6415	0.03451		Strath_GW697	-0.0575	-1.9124	-6.9776	-0.3582	0.02768
Strath_GW498	-0.8239	-4.8878	-8.1497	-1.6832	0.01205		Strath_GW698	0.3454	-1.6337	-7.1674	0.1368	0.07791
Strath_GW499	-0.9658	-4.9089	-7.9634	-2.0991	0.0106		Strath_GW699	-0.0856	-2.8171	-7.5227	-0.1397	0.07499
Strath_GW500	-0.5351	-4.7608	-8.3638	-1.1461	0.01674		Strath_GW700	-0.5512	-2.1139	-7.5239	-1.2766	0.03324
Strath_GW501	-1.1878	-1.9936	-7.8401	-2.3491	0.00705		Strath_GW701	-0.1866	-2.7296	-7.1694	-0.6034	0.05001
Strath_GW502	-0.6826	-1.4841	-7.165	-1.6797	0.00873		Strath_GW702	-0.221	-2.6735	-7.156	-0.9317	0.00654
Strath_GW503	-0.734	-1.4346	-7.7691	-1.3593	0.01256		Strath_GW703	-0.934	-2.0671	-7.3785	-2.2041	0.00252
Strath_GW504	0.2049	-2.2641	-7.0085	0.3809	0.07313		Strath_GW704	-0.1768	-2.6028	-7.4992	-0.8908	0.04635
Strath_GW505	-1.0065	-2.1901	-8.4234	-2.2924	0.00422		Strath_GW705	-1.03	-2.1519	-8.4517	-2.1984	0.00116
Strath_GW506	-1.1601	-2.5298	-8.2657	-2.2589	0.00981		Strath_GW706	0.2032	-2.4549	-7.3764	0.2756	0.03087
Strath_GW507	-1.6031	-2.9793	-8.3128	-3.1097	0.00554		Strath_GW707	-0.0855	-2.533	-6.8671	-0.7145	0.03693
Strath_GW508	-0.2935	-2.2849	-7.4423	-0.6178	0.03207		Strath_GW708	-0.4733	-2.9123	-7.4276	-1.2543	0.04353
Strath_GW509	0.0609	-2.1746	-7.1197	-0.1039	0.03979		Strath_GW709	-0.771	-3.183	-8.0688	-1.558	0.1384
Strath_GW510	-0.7191	-2.9395	-8.3933	-1.3822	0.0098		Strath_GW710	-1.419	-3.1905	-7.906	-2.9835	0.06281
Strath_GW511	-0.8368	-2.8542	-7.8056	-1.7864	0.00774		Strath_GW711	-1.4065	-3.238	-8.5718	-3.094	0.05487
Strath_GW512	-0.9928	-3.0066	-7.8878	-2.0238	0.00738		Strath_GW712	0.0632	-2.5108	-7.729	0.0477	0.12854
Strath_GW513	-0.2151	-2.6517	-8.0516	-0.3617	0.01579		Strath_GW713	0.2418	-2.4038	-7.1474	0.4214	0.21086
Strath_GW514	-0.2642	-2.6544	-7.3768	-0.6164	0.01318		Strath_GW714	0.0833	-3.0078	-7.2925	0.0041	0.13014
Strath_GW515	-0.7109	-3.0807	-8.379	-1.5976	0.01766		Strath_GW715	-0.8865	-2.9778	-8.0051	-1.9025	0.08713
Strath_GW516	-1.3764	-3.2044	-8.3483	-2.5928	0.00801		Strath_GW716	-1.2481	-3.4754	-8.5229	-2.8508	0.07084
Strath_GW517	-0.7835	-2.9849	-8.0557	-1.6071	0.01743		Strath_GW717	-0.9233	-3.3473	-8.4944	-1.9385	0.06723
Strath_GW518	-0.4035	-2.8282	-7.6092	-1.0215	0.01046		Strath_GW718	-0.7612	-2.9186	-7.8628	-1.4764	0.02493
Strath_GW519	-1.0222	-2.0119	-7.8041	-2.1004	0.01462		Strath_GW719	0.1314	-1.8864	-7.4164	0.2134	0.04995
Strath_GW520	-0.7994	-1.9673	-8.0781	-1.6916	0.03478		Strath_GW720	-0.0987	-1.9763	-7.8171	-0.2632	0.03593
Strath_GW521	-0.9627	-2.9457	-8.4457	-2.1064	0.00636		Strath_GW721	-0.0285	-2.6065	-7.6166	-0.1688	0.06508
Strath_GW522	-0.5251	-2.5855	-7.6877	-1.1322	0.01		Strath_GW722	-1.2694	-3.4547	-8.114	-2.6907	0.07424
Strath_GW523	-0.2968	-4.7671	-7.3745	-0.4621	0.01575		Strath_GW723	-0.0837	-1.6415	-7.1096	-0.1895	0.05184
Strath_GW524	-0.7065	-1.1643	-7.8532	-1.8546	0.00855		Strath_GW724	-0.1646	-2.2127	-8.0669	-0.6261	0.07355
Strath_GW525	-0.587	-3.1222	-8.3778	-1.1813	0.08497		Strath_GW725	-0.6558	-3.131	-7.8038	-1.561	0.07583
Strath_GW526	-0.8238	-6.8878	-8.1492	-1.6831	0.01205		Strath_GW726	0.3358	-1.8466	-7.4383	0.6574	0.07279
Strath_GW527	-0.9474	-3.4964	-7.9734	-1.9175	0.03065		Strath_GW727	-0.0875	-2.4429	-6.9767	-0.1927	0.05986

Strath_GW528	-0.7268	-2.7915	-7.9355	-1.583	0.01021							
Strath_GW529	-0.8125	-1.6357	-7.8307	-1.653	0.07022							
Strath_GW530	-0.121	-0.7021	-6.6011	-0.3297	0.05691							
Strath_GW531	-0.4874	-3.053	-7.8942	-1.0327	0.07813							
Strath_GW532	-0.6278	-1.298	-8.1804	-1.425	0.00868							
Strath_GW533	-0.2872	-2.2888	-7.4511	-0.5819	0.03265							
Strath_GW534	-0.9593	-2.838	-8.5001	-1.8837	0.01067							
Strath_GW535	-0.794	-2.3611	-8.2798	-1.5723	0.11837							
Strath_GW536	0.1715	-0.9959	-7.6438	0.1122	157.843							
Strath_GW537	-1.7679	-1.2505	-7.7756	-3.6116	0.05							
Strath_GW538	-0.6196	-2.9812	-8.4486	-1.3332	0.0325							
Strath_GW539	-0.7506	-3.0008	-8.0537	-1.5409	0.02403							
Strath_GW540	-0.3955	-4.7554	-8.3924	-0.6866	0.03057							
Strath_GW541	-0.9727	-2.2355	-8.7042	-2.0316	0.04811							
Strath_GW542	-1.1867	-1.8182	-8.2163	-2.466	0.01457							
Strath_GW543	-1.362	-3.2681	-8.9871	-2.8196	0.00883							
Strath_GW544	-0.3859	-1.3035	-8.3072	-1.0766	0.01791							
Strath_GW545	-0.4494	-4.7295	-7.8935	-1.0824	0.02106							
Strath_GW546	-0.4509	-0.8077	-7.5374	-0.9897	0.02083							
Strath_GW547	-0.6017	-2.9962	-8.0755	-1.283	0.11369							
Strath_GW548	-2.2611	-3.7012	-8.6185	-4.5793	0.00726							
Strath_GW549	-0.9269	-2.1572	-7.5199	-1.9407	0.0053							
Strath_GW550	-1.1328	-3.3292	-8.0619	-2.3437	0.05675							
Strath_GW551	-0.5268	-3.1158	-7.9597	-1.0303	0.04138							
Strath_GW552	-0.8076	-2.1623	-8.2695	-1.662	0.01165							
Strath_GW553	-0.8711	-3.0885	-7.806	-1.6836	0.00816							
Strath_GW554	-2.0582	-3.2075	-9.0045	-4.3838	0.02045							
Strath_GW555	-0.7916	-2.14	-8.0626	-1.7907	0.01391							
Strath_GW556	-0.9688	-3.3791	-8.5967	-1.9846	0.0685							
Strath_GW557	-0.7611	-1.7583	-7.6627	-1.5777	0.00833							
Strath_GW558	-0.5216	-2.1976	-8.616	-1.1654	0.04803							
Strath_GW559	-1.9865	-2.7124	-7.8508	-4.0043	0.00365							
Strath_GW560	-0.7504	-1.7775	-7.6831	-1.5913	0.03989							
Strath_GW561	-0.8213	-4.8599	-8.2837	-1.6879	0.01423							
Strath_GW562	-1.1132	-2.1036	-7.3532	-2.0958	0.01262							
Strath_GW563	-0.2792	-4.7156	-7.322	-0.5843	0.01389							
Strath_GW564	0.1694	-2.3146	-7.0097	0.4417	0.07437							
Strath_GW565	-0.7094	-1.8129	-7.5512	-1.7777	0.01806							
Strath_GW566	-0.9128	-2.5371	-7.8478	-1.9541	0.02737							
Strath_GW567	-0.1585	-1.2189	-7.5762	-0.3788	0.00451							
Strath_GW568	-0.6351	-1.5526	-7.7984	-1.4211	0.01541							
Strath_GW569	-0.6306	-2.1385	-8.4354	-1.2798	0.00809							
Strath_GW570	-0.4392	-1.4825	-7.8541	-0.9941	0.00919							

Strath_GW571	-1.6031	-2.9793	-8.3136	-3.1097	0.00554							
Strath_GW572	-0.3716	-1.772	-7.5614	-0.8861	0.00964							
Strath_GW573	-0.7736	-2.3358	-8.1207	-1.7093	0.0079							
Strath_GW574	-0.2843	-2.6514	-8.7064	-0.7538	0.01156							
Strath_GW575	-0.337	-4.6977	-8.3129	-0.8175	0.0303							
Strath_GW576	-1.7667	-3.1767	-8.5179	-3.591	0.02114							
Strath_GW577	-0.6385	-1.5846	-7.9718	-1.261	0.01821							
Strath_GW578	-0.9804	-3.2252	-8.227	-1.9902	0.00958							
Strath_GW579	-1.2524	-5.1419	-8.3172	-2.3433	0.01067							
Strath_GW580	-0.7118	-4.7891	-7.9746	-1.5769	0.0163							
Strath_GW581	-0.7893	-4.9112	-8.2481	-1.593	0.01618							
Strath_GW582	-1.2287	-3.1881	-8.2276	-2.4829	0.13316							
Strath_GW583	-0.0477	-2.8418	-7.2227	-0.0874	0.07587							
Strath_GW584	-0.1711	-2.3038	-8.5869	-0.5535	0.86788							
Strath_GW585	-0.4458	-1.0994	-7.5324	-0.9851	0.01546							
Strath_GW586	-2.0625	-3.1408	-8.4747	-4.1893	0.04115							
Strath_GW587	-0.0442	-1.5969	-7.4879	-0.2608	0.05752							
Strath_GW588	0.0624	-2.4786	-7.0651	-0.0489	0.03979							
Strath_GW589	-0.5337	-3.2373	-7.6704	-1.2212	0.5595							
Strath_GW590	-0.5289	-4.8037	-8.0634	-1.0928	0.01593							
Strath_GW591	-0.6086	-2.4507	-8.1205	-1.1535	0.01098							
Strath_GW592	-1.1099	-2.5804	-7.7879	-2.2544	0.00334							
Strath_GW593	-0.9114	-1.8729	-8.486	-1.9284	0.00989							
Strath_GW594	-0.7138	-3.1409	-7.9444	-1.4818	0.03122							
Strath_GW595	-0.9761	-2.4373	-8.8477	-1.9925	0.01197							
Strath_GW596	-0.3819	-2.673	-7.7913	-0.8119	0.06255							
Strath_GW597	-0.5647	-4.8327	-7.9219	-1.2222	0.01566							
Strath_GW598	-0.2398	-2.7786	-7.8307	-0.6757	0.04615							
Strath_GW599	0.0619	-1.8814	-7.2055	0.133	0.03444							
Strath_GW600	-0.5292	-2.442	-8.3177	-1.2362	0.0107							