Predicting geogenic groundwater fluoride:
Malawi as a case study

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Marc James Addison

Department of Civil and Environmental Engineering,

University of Strathclyde,

SCOTLAND

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DECLARATION

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Signed: Marc J. Addison, M.Sc., B.Sc.

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ABSTRACT

Geogenic fluoride contamination of groundwater causes the health condition fluorosis and is a global water degredation issue affecting an estimated 200 million people. It has been identified as a priority chemical contaminant of concern by the United Nations and will be a focus in many fluoride-vulnerable develping countries towards Sustainable Development Goal 6 (SDG 6) related to water quality. Predicting groundwater vulnerability to geogenic fluoride will be key to sustainably managing groundwater assets for SDG 6, however some developing nations may not have the resources or data available to develop a solution. Malawi has only sparse knowledge of issues with fluoride and fluorosis and it does not have access to comprehensive national groundwater fluoride data which is a hinderance to the development of a complex risk model. This thesis sought to fill the knowledge gap with a national data collation and a synthesis of geological, hydrogeological and hydro-geochemical analyses of fluoride occurrence, to develop an innovative prediction method to screen for groundwater fluoride contamination which can be applied nationally. National groundwater fluoride occurrence was documented for the first time in Malawi providing a master data set of groundwater fluoride spanning 50 years. Fluoride was found to occur from two distinct source types (lithological, hydrothermal), each of which was designated a fluoride risk factor using fluoride-lithology statistics from existing data and extrapolating where data were absent. The method was developed to be dynamic with prediction accuracy increasing as new data is acquired, and can be easily applied at any scale in any country for little expense. The prediction method developed will allow the Government of Malawi to manage its groundwater infrastructure assets for fluoride contamination in a targeted manner, boost their attainment potential for SDG 6, redefine their groundwater policy to include geogenic fluoride contamination and bring their groundwater fluoride standard in line with observed health risks.

Marc J. Addison

PREFACE

The main core of this thesis was developed as a series of papers to be published in peer review journals. Each results chapter of the thesis has its own abstract, introduction, methods, results, discussion, and conclusion. A bridge text between those chapters was written to link the chapters and provide context to the main aims and objectives of the thesis. The following peer-reviewed papers were published in the corresponding journals:

Paper 1 (Chapter 4)

Addison, M.J.; Rivett, M.O.; Robinson, H.; Fraser, A.; Miller, A.V.M.; Phiri, P.; Mleta, P.; Kalin, R.M. (2020). Fluoride occurrence in the lower East African Rift System, Southern Malawi. *Science of the Total Environment*, 712, 136260, DOI: https://doi.org/10.1016/j.scitotenv.2019.136260

Paper 2 (Chapter 5)

Addison, M.J.; Rivett, M.O.; Phiri, P.; Mleta, P.; Mblame, E.; Kanjaye, M.; Phiri, O.; Lakudzala, W.; Kalin, R.M. (2020). Identifying groundwater fluoride source in a weathered basement aquifer in Central Malawi: human health and policy implications. *Applied Sciences*, 10(14), 5006, DOI: https://doi.org/10.3390/app10145006

Paper 3 (Chapter 6)

Addison, M.J.; Rivett, M.O.; Phiri, P.; Mleta, P.; Mblame, M.; Wanangwa, G.; Kalin, R.M. (2020). Predicting groundwater vulnerability to geogenic fluoride risk: a screening method for Malawi and an opportunity for national policy redefinition. *Water*, 12(11), 3123, DOI: https://doi.org/10.3390/w12113123

Paper 4 (Chapter 7)

Addison, M.J.; Rivett, M.O.; Phiri, O.L.; Milne, N.; Milne, V.; McMahon, A.D.; Macpherson, L.M.D.; Bagg, J.; Conway, D.I.; Phiri, P.; Mblame, E.; Manda, I.; Kalin, R.M. (2021). 'Hidden hot springs' as a source of groundwater fluoride and severe dental fluorosis in Malawi. *Water,* 13(8), 1106, DOI: https://doi.org/10.3390/w13081106

NOVELTY STATEMENT

This research sought to make several contributions to knowledge with both global and local context. These comprise:

Global Novelty

- A new research approach for predicting groundwater vulnerability to geogenic fluoride was developed which is applicable in lesser developed countries where limited hydrochemical data prevents the development of comprehensive risk models.
- A screening method for groundwater fluoride prediction was developed which can be easily applied at national scale in any country.
- A new understanding of groundwater fluoride occurrence has been generated for peripheral locations within active continental rift systems, where magmatic activity has ceased but hydrothermal processes are still present.

Local Novelty

- National groundwater fluoride occurrence has been documented for the first time in Malawi providing a master data set of groundwater fluoride spanning 50 years.
- New knowledge and an integrated understanding of hydrogeological processes responsible for fluoride occurrence has been generated for Malawi for the first time. That includes specific geogenic sources and their corresponding fluoride risk factors.
- Tiered groundwater fluoride prediction maps have been generated for Malawi, including areas with no groundwater fluoride data.
- An evidence-based platform has been developed for redefining fluoride-relevant groundwater policy and updating fluoride standards in Malawi where there was none previously.

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LIST OF EQUATIONS

LIST OF ABBREVIATIONS AND ACRONYMS

cm	Centimetre
CJF	Climate Justice Fund
EC	Electrical Conductivity
GIS	Geographical Information System
GoM	Government of Malawi
GPS	Global Positioning System
IWRM	Integrated Water Resources Management
JMP	Joint Monitoring Project
Km	Kilometres
LSB	Lower Shire Basin
m	Metres
mm	Millimetre
masl	Metres above sea level
MDG	Millennium Development Goal
mg/L	Milligrams per litre
MIS	Management Information System
MoAIWD	Ministry of Agriculture, Irrigation and Water Development
MoFNR	Ministry of Forestry and Natural Resources
NGO	Non-Governmental Organisation
PI	Principal Investigator
RO	Research Objective
RQ	Research Question
SB	Shire Basin
SDG	Sustainable Development Goal
TA	Traditional Authority
TDS	Total Dissolved Solids

UN	United Nations
UNICEF	United Nations Children’s Fund
USEPA	United States Environment Protection Agency
WHO	World Health Organisation
WRA	Water Resource Area
WRU	Water Resource Unit
µS/cm	Micro siemens per centimetre

Chapter 1 INTRODUCTION

1.1 Overview and study area

Groundwater constitutes the most extensive reserve of freshwater globally (Morris et al., 2003). Arid regions rely heavily on groundwater resources for domestic use and agriculture, particularly during the dry season when surface water reserves are depleted. Rural populations in many developing countries abstract untreated, raw groundwater for drinking purposes directly from an aquifer via boreholes fitted with handpumps (Kalin et al., 2019). Groundwater is considered to be relatively clean compared to many surface water resources as it is often free from microbial or industrial contamination, however geogenic contamination can still occur where groundwater interacts with a contamination source. Dissolved fluoride is one of the primary geogenic groundwater contaminants which contributes to groundwater quality degradation globally. Groundwater fluoride contamination arises from dissolution of aquifer material and is most prominent in regions with fluoride-rich geology (Edmunds and Smedley, 2013). Increasing exploitation of groundwater resources will require more focus on geogenic contaminants in the future, particularly in countries striving to meet the water needs of an increasing population whilst working towards achieving Sustainable Development Goals (SDGs). The United Nations' Joint Monitoring Programme (JMP) classified fluoride and arsenic as the priority contaminants of concern globally (WHO and UNICEF, 2017), triggering an immediate need for groundwater data and research in developing countries.

The focus of this research was groundwater fluoride. Fluoride from drinking water causes the health condition fluorosis which ranges in severity depending on concentrations consumed (Oszvath, 2006). The initial interest in the subject was developed during an MSc research field visit to Malawi in June 2017. Visible signs of fluorosis (brown-black stained teeth) were prevalent but very little appeared to be understood as to the cause. Groundwater fluoride and its health implications were well-documented in other countries; however Malawi displayed a vacuum of knowledge of the contaminant, its occurrence, or the associated health effects which was surprising considering the prevalence of visible symptoms of fluorosis. When the JMP identified fluoride as one of its two global primary contaminants of concern it became clear that Malawi's significant knowledge gap pertaining to fluoride would hinder its ability to achieve SDG 6 water quality targets. This research sought to fill that knowledge gap with extensive geological and hydrogeological analyses to document the occurrence of fluoride for Malawi, identify the main geogenic sources and design a cost-effective prediction method which can screen for groundwater fluoride nationally by maximising use of existing groundwater data. The value of the research is threefold: 1) existing groundwater assets can be assessed for groundwater fluoride and if identified, replacement water supplies acquired, 2) future groundwater quality management can be conducted in a targeted manner, allowing the Government of Malawi and Non-Governmental Organisations (NGOs) to avoid fluoride-prone areas when drilling new groundwater assets, and 3) allow the Government of Malawi to redefine their groundwater policy documents to include geogenic contamination sources (including mitigation methods) and to bring their groundwater quality standard for fluoride in line with health risks. This research will significantly boost Malawi's SDG 6 attainment with respect to groundwater quality.

Malawi bears a regionally unique knowledge gap relating to fluoride and its associated health implications. It is a landlocked country in south-central Africa bordered by Mozambique, Tanzania and Zambia and has a burgeoning population of over 18.6 million (mostly rural) which is projected to double by 2038 (World Bank, 2020). It forms the southernmost extent of the western branch of the East African Rift System (EARS), an active continental rift associated with extensive volcanic and hydrothermal activity (Edmunds and Smedley, 2013). Its climate is described as semi-arid with distinct wet and dry seasons. Reliance on the arrival of annual wet season rains leaves it vulnerable to water scarcity from climate change, particularly in rural areas. Malawi has struggled with development despite making significant economic and structural reforms designed to sustain economic growth. Its low-diversity economy is heavily dependent on agriculture which employs almost 80% of the population, leaving the economy and the population sensitive to external shocks such as drought and flooding (World Bank, 2020).

1.2 Research Aim and Questions

1.2.1 Research Aim

The aim of this research was to develop a national prediction method to screen for groundwater fluoride contamination which can be applied in developing countries with limited groundwater data. Countries globally must review their drinking water fluoride occurrence as a requirement of the SDGs, specifically SDG 6: "Ensure access to water and sanitation for all". Comprehensive statistical risk models for groundwater contaminants can be developed where there are extensive national data sets available. Many developing countries do not have national groundwater data so an innovative solution to predicting groundwater fluoride risk was required which maximises the use of existing data which may be sporadic. Malawi was chosen as a case study as it is a country with limited knowledge of fluoride occurrence, does not yet have any method for predicting groundwater fluoride and only a sporadic groundwater data set was available. The development of a national prediction method for groundwater fluoride will boost Malawi's ability to achieve SDG 6 and provide an evidence-based framework for reviewing policy and assessing current groundwater infrastructure assets nationally.

1.2.2 Research Questions and Objectives

Five research questions (RQ) were developed to achieve the overall aim of the research. Those research questions and associated research objectives (RO) are detailed below:

RQ. 1: What is the current understanding/knowledge gaps with respect to groundwater fluoride in Malawi? (Paper 1).

- **RO. 1.1:** Collate all existing data and knowledge pertaining to fluoride occurrence in Malawi via an extensive literature review and data collation.
- **RO. 1.2:** Augment archive data with recent groundwater data and conduct preliminary geological and geochemical analyses to investigate main sources and controls on occurrence in Malawi's groundwater.

RQ. 2: Can groundwater fluoride risk be mapped using geology and limited groundwater data? (Paper 2).

- **RO. 2.1**: Conduct a case study to investigate 'source-extent' relationship between geology and groundwater fluoride.
- **RO. 2.2**: Develop method for predicting and mapping geology-based groundwater fluoride risk using groundwater data.

RQ. 3: What is the direct link between geogenic groundwater fluoride and human health risk in Malawi and is the current fluoride standard for drinking water aligned with health risks? (Papers 2 & 3).

- **RO. 3.1**: Quantify key link between geogenic fluoride and risk to human health via a human health risk assessment case study.
- **RO. 3.2**: Investigate difference between current Malawi and global fluoride standards and advocate policy review via stepped progression for fluoride in drinking water in Malawi.

RQ. 4: Can the groundwater fluoride prediction method developed be scaled nationally to cover all lithologies using existing data? (Paper 3).

- **RO. 4.1**: Create high resolution digitised map of Malawi's geology.
- **RO. 4.2**: Scale methodology for mapping geological fluoride nationally using existing statistical 'fluoride-lithology' correlations where present, and extrapolations where data are absent.

RQ. 5: Can the groundwater fluoride prediction method developed be refined to delineate hot spring influence from unconsolidated sediments? (Paper 4).

- **RO. 5.1**: Investigate and identify hidden hot spring locations within unconsolidated sediments using proxy indicators, including a collaboration with dentists to use dental data as additional proxy indicator locations where severe dental fluorosis occurs.
- **RO. 5.2**: Separate hidden hot spring-influenced water points from unconsolidated sediments in the risk model and recalculate accurate statistics for both hot springs and unconsolidated sediments.

1.3 Thesis Structure

This thesis is comprised of 8 main chapters (Figure 1.3.1). The results section (chapters 4-7) are written as individual peer-reviewed journal articles which have each been published in international journals. The chapters are as follows:

- Chapter 1 provides an overview of the research topic, the study area, and contains a description of the research aim with the research questions and research objectives involved in achieving the aim.

- Chapter 2 provides a general literature review of the broad research topic and highlights key challenges and general knowledge gaps which subsequently form the core of the thesis.

- Chapter 3 provides a descriptive methodology for the thesis outlining the research approach adopted to achieve the objectives of the thesis.

- Chapter 4 is the first chapter in the results section and explores the current knowledge of the occurrence of fluoride in Malawi's groundwater. Key Malawi-specific knowledge gaps were identified.

- Chapter 5 is the second chapter in the results section and is a local-scale exploration of the specific relationships between lithological sources of fluoride and occurrence in groundwater. The chapter develops an innovative solution to screening groundwater fluoride risk via geology-based risk maps. The direct link between geogenic sources of fluoride and human health (fluorosis) is quantified and the results used to advocate policy review in Malawi.

- Chapter 6 is the third chapter in the results section and comprises a scaling of the prediction method for screening for groundwater fluoride nationally. This chapter contains detailed catchment-level and national geogenic groundwater fluoride risk maps for Malawi.

- Chapter 7 is the fourth chapter in the results section and contains a refinement of the groundwater fluoride prediction method by delineating water points from the unconsolidated sediments of the rift basin in southern Malawi influenced by hydrothermal groundwater. This was achieved by using proxy indicators to identify hidden hot springs.

- Chapter 8 is a general discussion of the results of the whole thesis, including detail on how the aim, ressearch questions and objectives were achieved. This chapter also contains general conclusions and recommendations for future work.

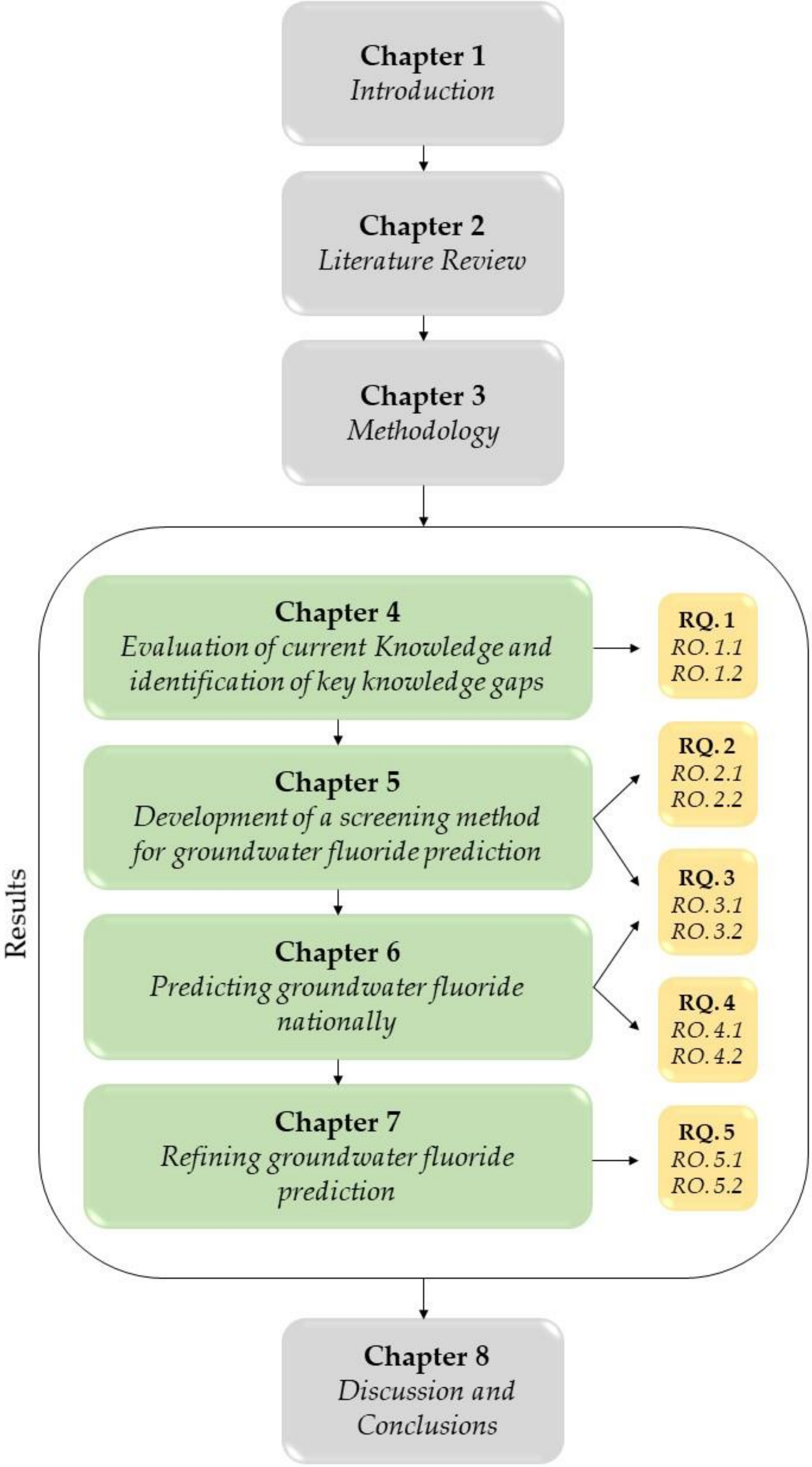

Figure 1.3.1. Flow diagram of the structure of the thesis.

Chapter 2 GENERAL LITERATURE REVIEW

2.1 Introduction

The previous chapter provided a background to the research and described the main aim, research questions and research objectives key to addressing the aim. Each chapter in the results section comprises a peer-reviewed journal article which contains more detailed literature reviews relevant to each study. This chapter aims to provide a more general overview of the literature relevant to the broad thesis topic, highlighting the general research gaps being filled by the thesis.

2.2 Drinking water and the development Goals

It is estimated that 80% of diseases globally arise from poor quality drinking water (Adimalla and Rajitha, 2018). International monitoring of drinking water has been ongoing since the 1930s and is currently overseen jointly by the World Health Organisation (WHO) and The United Nations Children's Fund (UNICEF) via their Joint Monitoring Programme (JMP). In 1992 the 'Dublin Principles', later updated by the 'Rio Principles', were developed and published as a means to begin to define and prioritise action on water poverty (UN, 2000). The Principles state:

- Fresh water is a finite and vulnerable resource, essential to sustain life, development, and the environment.
- Water development and management should be based on a participatory approach, involving users, planners, and policy makers at all levels.
- Women play a central role in providing, managing, and safeguarding water.
- Water has an economic value in all its competing uses and should be recognized as an economic good. ('Rio principles' updated this point to include social value).

Since the year 2000, monitoring has been carried out to support global development targets set out by the United Nations' (UN) for their 'Millennium Development Goals (MDGs) (Bartram et al., 2014; Truslove et al., 2019). More recently, those goals were updated to the Sustainable Development Goals (SDGs) (Truslove et al., 2019; UN, 2020). The 2030 agenda for the SDGs was launched in 2015 with the ambition of ending poverty, creating peace, prosperity, and equal human rights for everyone on the planet by 2030 (UN, 2020). There are 17 SDGs in total, one of which relates specifically to water: SDG 6 – 'Ensure availability and sustainable management of water and sanitation for all' (Truslove et al., 2019).

Water and socioeconomic development are intrinsically dependent upon one another (UN, 2000), something that is particularly evident in many African countries where a combination of poverty, low socioeconomic status, rural living, and water scarcity issues result in slow or sometimes static development. Widespread poverty results in limited access to adequate water and sanitation, however limited access to safe water results in increased incidence of communicable diseases. This means that limited access to safe water and sanitation is both a cause and a consequence of poverty (UN, 2000). Deaths from water-related complications and inadequacies exceed those caused by violence and unrest globally (Onipe et al., 2019), illustrating the need for focus on water in the SGDs. Surface water has historically been the primary source of domestic water across the globe; however rapidly growing populations, particularly in urban areas, have seen a decrease in surface water quality and availability (Chidya et al., 2016). Critical factors that may negatively affect surface water quality and availability include poor water infrastructure, poverty, large-scale industrial pollution, corruption, and climate change. In many developing countries those factors have resulted in an increased dependence on groundwater (Onipe et al., 2019).

Dependence on groundwater is growing exponentially with rapid population growth (Lapworth et al., 2020) and groundwater is now the primary developing world domestic water source relied upon to achieve SDG 6 (Xu et al., 2019). An estimated 75% of Africans rely on groundwater for their main domestic water supply (Onipe et al., 2019; UN, 2000), provided mostly by boreholes installed with handpumps (Lapworth et al., 2020), however groundwater accounts for only 15% of the continent's total renewable water resources (UN, 2000). This has seen a rapid increase in private sector investment to drill boreholes and wells across sub-Saharan Africa, most without prior hydrogeological knowledge or assessment of potential geo-hazards (Kalin et al., 2019). Many countries in sub-Saharan Africa have distinct wet and dry seasons resulting in increased water stress and water related poverty during dry seasons when groundwater is particularly relied upon. Groundwater used domestically in Africa is often raw with little or no treatment so understanding the characteristics of groundwater is key to managing public health as groundwater dependence increases (Lapworth et al., 2020).

Sustainable Development target 6.1 refers specifically to drinking water and states: “By 2030, achieve universal and equitable access to safe and affordable drinking water for all” (Table 2.2. 1). This target refers to drinking water from “boreholes and wells” that is “free of faecal and priority chemical contamination” (UN Water, 2016). The JMP classified fluoride and arsenic as priority chemical contaminants of concern globally in 2017 (WHO and UNICEF, 2017) meaning that all countries will be required to assess their water resources for both contaminants if they are to achieve SDG 6 targets.

Table 2.2. 1. Breakdown of SDG 6.1 description with normative interpretations (UN Water, 2016).

Target Text	Normative Interpretation
By 2030, achieve universal	Implies all exposures and settings including households, schools, health-care facilities, and workplaces
and equitable	Implies progressive reduction and elimination of inequalities among population subgroups
access	Implies sufficient water to meet domestic needs is reliably available close to home
to safe	Safe drinking water is free from pathogens and elevated levels of toxic chemicals at all times
and affordable	Payment for services does not present a barrier to access to or prevent people from meeting basic human needs
drinking water	Water used for drinking, cooking, food preparation and personal hygiene
for all	Suitable for use by men, women, girls, and boys of all ages, including people with disabilities

Given the 2017 JMP classification of fluoride as a global level priority contaminant (WHO and UNICEF, 2017), all countries must now assess drinking water supplies for fluoride in order to meet global indicator 6.1.1: “Proportion of population using safely managed drinking water services”, within the SDG 6.1 envelope. The global indicator is specific about the data used and how it may be achieved, specifically the use of household surveys, population records and water quality testing for priority contaminants (namely fluoride) (Table 2.2. 2).

Table 2.2. 2. Data required for global indicator 6.1.1 (UN Water, 2016).

1st step of progressive monitoring (*example*)	**2nd step of progressive monitoring (*example*)**	**3rd step of progressive monitoring (*example*)**
Household surveys combined with population records for information on access and type of services. No information on water quality and reporting to the basic level but not to the safely managed services level. Disaggregation of household data by place of residence, subnational region, and wealth.	Inclusion of water quality testing for faecal contamination in household survey instruments. Incomplete data from utilities and national authorities on availability and quality of drinking water services. Disaggregation of data by informal settlements and locally important marginalized groups.	Inclusion of water quality testing for faecal contamination and priority chemicals (arsenic and fluoride) by utilities and/or in household survey instruments. High temporal and spatial resolution of institutional/utility data. Disaggregation of data by intrahousehold characteristics.

Over 200 million people globally are affected by excess fluoride in groundwater (Amini et al., 2008; Onipe et al., 2019), with an estimated 80 million of those in East Africa. Most of those at risk are poor, of low socioeconomic status and living rurally. The WHO set a global standard for fluoride in drinking water of 1.5 mg/L (WHO and UNICEF, 2017) to mitigate health risks posed. Few countries permit groundwater fluoride concentrations in excess of the current WHO standard (Onipe et al., 2019), however some do, for example: Malawi in East Africa where the standard for drinking water from raw groundwater sources (untreated) is currently 6 mg/L (pre-1994 WHO standard) (Malawi Bureau of Standards, 2005).

With the population of sub-Saharan Africa predicted to increase to 2 billion by 2050 and the predominantly low socioeconomic status of most of its inhabitants (Onipe et al., 2019), this illustrates an urgent need for better Integrated Water Resources Management (IWRM) for the region and suggests a growing need for intervention from both governmental and non-governmental organisations to achieve SDG 6. Characterising water quality from groundwater sources, particularly with respect to priority contaminants, will be key to assessing progress towards SDG 6 and to underpinning future investment (Lapworth et al., 2020). Inadequate and unsustainable funding arrangements are a key roadblock to IWRM in Africa illustrating a need for institutional reform, underpinned by the Dublin principles (UN, 2000). The Covid-19 pandemic has negatively impacted SDG progress in many developing countries as funds and resources are diverted toward immediate healthcare. A UN update report on SDG progress stated that even before the pandemic, global progress has so far been insufficient to achieve SDG goals by the 2030 deadline (UN, 2020). This presents a significant challenge for developing countries looking to beat the pandemic whilst also achieving SDG targets. The report outlines data gaps, particularly access to data on water resources as a significant hinderance to assessing country-level SDG (6) progress, meaning that any SDG-led independent research aiming to fill such data and knowledge gaps will become increasingly important. "Investments and innovation" are therefore key to responding to SDGs, particularly now due to the implications of Covid-19. Key challenges identified from the report specifically relevant to SDG 6 in Malawi include - Inadequate public awareness and stakeholder engagement, Inadequate research for water resources development and Inadequate private sector participation in financing (UN, 2020).

2.3 Health Implications of fluoride in drinking water

Fluoride can be detrimental to human health, hence the JMP focus as a primary contaminant of concern globally and its inclusion in SDG indicators (WHO and UNICEF, 2017). Drinking water is the primary pathway of fluoride to humans (Onipe et al., 2019). Health effects occur in two forms: fluoride deficiency and excess fluoride. Human bodies require fluoride to strengthen teeth and bones during the early stages of development in children. Fluoride deficiency occurs when concentrations from a main drinking water source fall consistently below 0.5 mg/L and manifests as dental caries and tooth rot (Edmunds and Smedley, 2013; Onipe et al., 2019; Ozsvath, 2006). Many countries with drinking water concentrations below 0.5 mg/L will add fluoride to water and dental products to promote oral health (Edmunds and Smedley, 2013). The optimal concentration range for fluoride in drinking water is small at 0.5 – 1.5 mg/L, concentrations within that range will promote the healthy development of teeth and bones in infants and children (Onipe et al., 2019; Ozsvath, 2006). Concentrations in excess of 1.5 mg/L cause increasing severity of the condition fluorosis (Amini et al., 2008; Edmunds and Smedley, 2013; Ozsvath, 2006), from dental fluorosis (1.5 – 4 mg/L), to skeletal fluorosis (4 – 6 mg/L) to crippling fluorosis (>6 mg/L) (Edmunds and Smedley, 2013; Haimanot et al., 1987; Ozsvath, 2006) and even renal failure (Young et al., 2011) and cancer (Onipe et al., 2019). The damage from fluorosis is permanent and occurs when excess fluoride accumulates in the body and replaces too much apatite in teeth and bones making them weak and brittle (DenBesten and Li, 2011). This manifests as brown-black staining of teeth in dental fluorosis cases. Whilst this may be considered as an aesthetic concern, it can be an indication of more serious forms of fluorosis. Skeletal fluorosis occurs when consistent ingestion of concentrations >4 mg/L (from drinking water) begins to weaken bones and manifests as deformed appendages of increasing severity, depending on concentrations consumed. Crippling fluorosis occurs when the damage from skeletal fluorosis is severe enough to permanently cripple an individual (Haimanot et al., 1987; Ozsvath, 2006). The WHO standard (upper limit) for fluoride in drinking water is based on a global average ambient temperature of 16 °C, however there is evidence to suggest that higher ambient temperatures facilitate the onset of fluorosis at lower concentrations of drinking water fluoride (Hossain and Patra, 2019).

Cases of fluorosis are reported from fluoride provinces across the globe, particularly in China, India, United States of America, Mexico, Argentina, and many East African countries within the EARS including Tanzania, Ethiopia, and Kenya (Agrawal et al., 1997; Amini et al., 2008; Bo et al., 2003; Chen et al., 2012; Ghiglieri et al., 2012; Nair et al., 1984; Olaka et al., 2016; Onipe et al., 2019; Shorter et al., 2010; Tekle-Haimanot et al., 2006). Dental fluorosis is most extensive and is found in any country with rural populations drinking raw groundwater with fluoride concentrations exceeding the WHO standard of 1.5 mg/L (WHO and UNICEF, 2017). The most severe cases of fluorosis (dental – crippling) are often associated with the rift valley in East Africa and are concentrated along the main rift zone. Fluorosis is well documented in other EARS countries (Ghiglieri et al., 2012; Nair et al., 1984; Olaka et al., 2016; Tekle-Haimanot et al., 2006), however Malawi is contrary to that. There were only two local scale published studies which investigated fluorosis (Msonda et al., 2007; Sajidu et al., 2008) and no published attempt to document the condition nationally. That presented a significant knowledge gap for Malawi where there is a requirement for the condition to be documented and the risk from geogenic sources quantified. Malawi's location on the EARS means it is a prime target for geogenic fluoride sources (thus, fluorosis), particularly along active rift faults and hydrothermal environments, both of which are common in Malawi (Kaonga et al., 2014; Kirkpatrick, 1969; Wedmore et al., 2020).

An objective for Malawi to achieve SDG 6 (with respect to fluoride) is to lower its national standard for fluoride in drinking water from raw groundwater sources from 6 mg/L to the globally accepted WHO standard of 1.5 mg/L. This will bring fluoride policy in line with health risks. The first step to achieving that objective in Malawi will be to quantify (for the first time) the direct link between geogenic sources of fluoride in groundwater and human health risks. Policy update in that regard can be advocated once the Malawi-specific health risks are quantified and documented.

2.4 Groundwater Fluoride

Drinking water is the primary fluoride pathway to humans globally (Amini et al., 2008). Surface water generally has low fluoride concentrations (Edmunds and Smedley, 2013) and bottled or piped drinking water is usually treated and free from harmful chemical and microbial contaminants. Fluoride occurrence in groundwater is the most significant source (Onipe et al., 2019) meaning that populations who abstract raw groundwater are most at risk from harmful concentrations. Groundwater is often regarded as safe due to appearing clear and clean compared to many surface water sources, however dissolved chemical contaminants are an invisible danger including Sodium (Na), Calcium (Ca), Magnesium (Mg), Iron (Fe), Fluoride (F), Arsenic (As) and Lead (Pb), (Onipe et al., 2019). Globally, elevated groundwater fluoride occurs in distinct fluoride provinces including countries such as India, China and the United States of America (Amini et al., 2008), however it is most prevalent in East African countries, particularly those within the EARS (Edmunds and Smedley, 2013; Ghiglieri et al., 2012; Nair et al., 1984; Olaka et al., 2016; Onipe et al., 2019; Tekle-Haimanot et al., 2006). In East Africa where groundwater is the primary domestic water source, groundwater fluoride occurrence is predominantly from natural sources, rather than anthropogenic (Onipe et al., 2019).

Fluoride is the 13th most abundant element in Earth's crust (625 mg/kg) (Qasemi et al., 2018) and exists in trace amounts in all groundwater (Amini et al., 2008). Fluoride occurrence in groundwater arises from interaction with geogenic sources (geology) and is documented as occurring from two main geogenic source types: lithological and hydrothermal (Edmunds and Smedley, 2013; Reddy et al., 2010; Sracek et al., 2015). Each lithological source contains various combinations of fluoride-bearing minerals which dissolve in groundwater. Fluoride-bearing minerals include fluorite, hornblende, amphibole, biotite, villiaumite and Topaz (Amini et al., 2008; Bath, 1980; Mapoma et al., 2017; Onipe et al., 2019). Some lithologies contain higher relative content of fluoride-bearing minerals and thus produce groundwater fluoride signatures which have higher dissolved fluoride concentrations than others. Leaching experiments have shown that fluoride content of rock is directly proportional to fluoride concentrations in groundwater (McCaffery and Willis, 2001). Alkaline igneous lithologies such as granites, syenites and carbonatites (and their meta-equivalents) are well documented globally as producers of particularly elevated groundwater fluoride concentrations (Abelgawad et al., 2009; Amini et al., 2008; Berger et al., 2016; Ghiglieri et al., 2012; Naseem et al., 2010; Onipe et al., 2019). Elevated fluoride in groundwater is also associated with low calcium environments so lithologies with low relative calcium content (for example: alkaline igneous lithologies) are additionally conducive to elevated fluoride (Amini et al., 2008; Bath, 1980).

Hydrothermal sources of fluoride produce some of the most elevated groundwater fluoride concentrations (Kundu et al., 2002; Lottermosser and Cleverley, 2007; Sracek et al., 2015), particularly in the EARS where some hot springs have recorded concentrations as high as 1000 mg/L (Edmunds and Smedley, 2013). Elevated geothermal temperature drives hydrothermal activity and acts as a catalyst, increasing dissolution rates of fluoride-bearing minerals into groundwater. That process, coupled with long residence times in deep reservoirs results in excessive fluoride concentrations recorded in hot springs and hydrothermal systems (Edmunds and Smedley, 2013; Onipe et al., 2019). Historical hydrothermal activity additionally results in mineralised fluorite (CaF_2) along fractures which were originally conduits for hydrothermal groundwater (Broom-Fendley et al., 2017; Carter and Bennett, 1973). Such mineralisation can be a significant source of groundwater fluoride where interactions occur with modern shallow groundwater.

Fluoride occurrence in the groundwater of almost all EARS countries has been well documented both locally and nationally (Ghiglieri et al., 2012; Nair et al., 1984; Olaka et al., 2016; Tekle-Haimanot et al., 2006), In contrast, very little knowledge was available of its occurrence in Malawi which is located at the southern periphery of the Western Branch of the EARS. Only a few sporadic studies looking at fluoride within more general groundwater quality studies were available (Bath, 1980; Pritchard et al., 2008) and no published knowledge was available of national fluoride occurrence presenting a significant knowledge (and data) gap. Sources of fluoride in Malawi’s groundwater had only been inferred previously and it was suggested that a detailed geological assessment was required to fill the knowledge gap and understand the specifics of fluoride-geology relationships in detail in Malawi (Onipe et al., 2019).

In the pursuit of SDG 6 targets, increasing pressure is on countries globally to manage their groundwater assets for fluoride in a targeted manner. National risk maps based on geostatistical risk modelling techniques have been the most effective method by which to target those water supplies most at risk from fluoride contamination. The method has been developed both nationally (for example, India) and globally (Amini et al., 2008; Podgorski et al., 2018) with great success. Those risk maps (sometimes referred to as probability maps) were developed based on extensive and comprehensive national data sets collated from multiple sources and consider a wide variety of fluoride sources and pathways. Such geostatistical risk modelling is not possible in many developing countries due to lack of data and resources, so there is an immediate need for an innovative solution to screening groundwater fluoride risk which is applicable in the developing world. Prediction mapping should never replace testing, however it can be used as a screening method where groundwater testing is not possible.

2.5 Climate Justice Fund (CJF) Water Futures Programme

The Climate Justice Fund (CJF) Water Futures Programme is a programme which was set up with a research grant from the Scottish Government. The programme aims to "Support the Government of Malawi to achieve SDG 6 by 2030". The programme is run through the University of Strathclyde, funded by the Scottish Government and is part of their wider international development initiative managed through the Hydro Nation agenda. The main objectives of the program are to conduct SDG 6-led research and provide technical evidence and knowledge from research to decision makers within the Malawian Government. The core (ongoing) technical initiative of the programme is to map every water point in the country (>120,000), developing a dynamic and 'live' national Management Information System (MIS) on the open-source MIS platform 'mWater'. This tool will enable the Malawian Government to proactively manage each of its water supply infrastructure assets nationally with up-to-date data, something essential to achieving SDG 6 targets. The programme is split into four main work streams:

1) Data for decision making.

2) Research and knowledge exchange.

3) Capacity building.

4) Policy support.

The programme is driven by workstream 2 (Research and knowledge exchange) which underpins the other three work streams. Data is collected to conduct research, the evidence-based outputs of which are used to assist decision making with key stakeholders, assist in capacity building and providing key SDG 6 policy support to the Government of Malawi. The primary research outputs from the programme are published papers from PhD and MSc projects which were set up to fill key knowledge gaps. The research and knowledge exchange work stream is multi-faceted and comprises four primary branches of research spanning a variety of SDG 6-centred outputs. The active branches of research (including outputs) are as follows:

Integrated Water Resources Management (IWRM)

Transboundary aquifer assessments are key to managing shared water resources yet surprisingly are overlooked in many countries. Malawi is a landlocked country which shares land borders with Mozambique, Zambia, and Tanzania meaning it is surrounded by shared aquifer resources. Inadequate characterisation of hydraulically connected cross-border systems may result in the creation of unsustainable and incompatible national policies between countries. A case study of transboundary aquifers for Malawi and its neighbours resulted in a realistic approach being developed for transboundary aquifer assessment which facilitates international collaboration and may result in sustainable policy development (Fraser et al., 2018). A national border assessment was subsequently conducted for Malawi which identified 38 previously undefined transboundary aquifers providing the Government of Malawi with valuable data and knowledge towards achieving SDG 6 for transboundary aquifer management (Fraser et al., 2020).

Groundwater-surface water interactions are a core part of IWRM research and until recently little understood in Malawi. Lake, climate, and river data were collated to develop proxy indicators for temporal variations in groundwater contribution to Lake Malawi via its inflow rivers (baseflow) using historical data spanning 120 years (Kelly et al., 2020a). Malawi is notorious for limited access to scientific data, particularly water resource data. A catchment-scale study was thus conducted for the Bua river catchment to develop a method to assess whether temporal variations in baseflow could be meaningfully estimated using sporadic river data. The study was successful, and the method has been advocated for use in other gauged catchments with limited data (Kelly et al., 2019a). The method was subsequently used to assess baseflow contribution to the largest and most significant river basin in Malawi, the Shire river catchment (Kelly et al., 2019b) and then nationally to demonstrate the method's ability to be adapted to any scale (Kelly et al., 2020b). Understanding baseflow is essential to managing surface water and groundwater resources for SDG tracking, particularly during the dry season when populations in arid environments are most dependent on groundwater.

Historically Malawi has relied on sample analyses from abroad to analyse isotope variations as it did not have access to isotope tracer tools or facilities. The CJF working collaboratively with the Government of Malawi set up an isotope facility in Malawi's capital city, Lilongwe to conduct an in-country isotope seasonal variation study for the first time (Banda et al., 2019). The study was successful in augmenting baseflow studies with stable isotope characterisation of surface water and groundwater nationally, the results of which are assisting the Government of Malawi with SDG 6-led policy reform. An additional stable isotope characterisation was carried out for the Shire River Basin (another first) to develop an isotopic baseline for the catchment which future IWRM studies can be assessed against (Banda et al., 2020).

Groundwater infrastructure asset management

Improving groundwater infrastructure asset management is key to achieving SDG 6. Developing countries such as Malawi where the majority of the population live in rural areas and rely on raw groundwater for their domestic supply must develop innovative new strategies to manage increasingly vast numbers of groundwater assets. Pivotal to that aim is mapping current groundwater assets in a dynamic way where data on each water point can be updated in a 'live' system. The CJF carried out a pilot study in Malawi analysing a time series of 25,000 water points using the MIS platform 'mWater'. The study successfully created a real-time asset register of water infrastructure which has now been adopted by the Government of Malawi and is being deployed nationally (Miller et al., 2018). The programme additionally employed an innovative method for assessing the functionality of groundwater infrastructure (mostly boreholes fitted with Afridev handpumps) called 'borehole forensics'. The study dismantled boreholes to assess problematic construction patterns and compared the results with drilling records to assess common issues with poorly functioning borehole assets (Mannix et al., 2018). Many boreholes are drilled without proper geological or hydrogeological knowledge resulting in water points which become stranded assets when they inevitably break down and become abandoned due to water quality and/or poor construction issues (Kalin et al., 2019). The CJF aims to not only map and manage borehole infrastructure in Malawi, but also to develop accountability for major stakeholders (drilling companies and NGOs) so that the Government of Malawi can take control of its water infrastructure assets in the pursuit of SDG goals.

Rural water point sustainability

New boreholes are drilled every day in Malawi, however sustainability has been a challenge. To prevent the accumulation of future stranded groundwater assets the CJF carried out a sustainability study of existing boreholes fitted with Afridev handpumps.

The first stage of the study assessed whether targets set out in the MDGs impacted the sustainability of water supply infrastructure. Results showed that the drive for coverage in the wake of MDG targets negatively impacted the sustainability of water assets in Malawi and will prove a challenge for SDG targets moving forward, where there is an immediate need for proactive monitoring and better-quality infrastructure to reduce the burden on rural communities (Truslove et al., 2019). The financial burden of borehole maintenance usually falls to local communities, so an investigation of the tariffs set by service providers vs affordability was carried out. Wide heterogeneity was found between communities in terms of financing maintenance of boreholes and subsequently many were found to be unsustainable under their current arrangements. Access to funds was shown to be a primary barrier to clean water for many communities in Malawi which will need to be addressed for SDG tracking (Truslove et al., 2020a).

Groundwater quality

A primary objective for SDG 6 tracking and for better IWRM is the transition from sporadic and isolated groundwater quality surveys to an integrated national systematic approach to groundwater quality monitoring in Malawi. The CJF developed a conceptual model-based framework for a pragmatic approach to groundwater quality monitoring in the developing world via a case study in Malawi's alluvial aquifer system (Chikwawa District). The model is advocated for use as a pilot to be applied nationally by the Government (Rivett et al., 2018). Conceptualisation of local-scale heterogeneities in hydrological and hydrogeological environments is key to meeting long term community water supply needs for rural communities so research is ongoing into such environments in Malawi, including the Lake Chilwa catchment (Rivett et al., 2020). Malawi is prone to typical developing world rural groundwater quality challenges and the CJF actively conducts research to assess the most significant contamination types which affect rural populations. Research areas include microbial contamination of groundwater from pit latrines (Back et al., 2018) and groundwater salinity (Rivett et al., 2019a). Key to SDG 6 targets are the priority chemical contaminants of concern identified by the JMP: arsenic and fluoride. To assist the Government of Malawi with those contaminants, the CJF carried out a national investigation into arsenic occurrence and found that groundwater contamination from arsenic was minimal and did not pose a national risk, except from hot springs (Rivett et al., 2019b). There has been no attempt to assess the other priority contaminant fluoride.

This thesis comprises one part of a larger body of research within work stream 2 of the CJF programme. Over 70 MSc and PhD projects have been involved in the programme since 2010, including my own MSc thesis which was a field-based study investigating groundwater salinity in the Lower Shire Basin of Malawi's Southern Region (Addison, 2017). Many rural communities with groundwater quality problems (including salinity) were visited providing a perspective on the human implications of poor groundwater quality in rural communities. Many people were overly reliant on drinking water that would be completely unacceptable elsewhere, simply due to a lack of alternatives, illustrating the importance of good quality groundwater sources. A recurring theme from conversations with rural communities were reports of specific water points which caused "black teeth" in people who drank from them. The condition (dental fluorosis) I later discovered to be a result of excess dissolved fluoride in groundwater. I also discovered there to be an apparent vacuum of knowledge pertaining to the condition or its cause in Malawi, something that was surprising considering the prevalence and severity of reported cases in rural communities. The fluoride knowledge gap, discovered initially during my MSc research in Malawi and later outlined by the CJF research and knowledge exchange work stream as a priority, coupled with the focus on fluoride in SDG 6 indicators, triggered a scientific and anthropological curiosity which formed the basis of the research in this thesis.

2.6 Summary

This chapter provided an overall review of published literature relevant to the broad research topic and highlights key challenges for SDG 6 attainment in developing countries (including Malawi). Key challenges include:

- Inadequate public awareness and stakeholder engagement. This has been a significant challenge which can be overcome with increased collaborative efforts with scientists and key stakeholders, particularly decision makers within the government.
- Inadequate research for water resources development. This challenge can be addressed by increased SDG 6-led international research which aims to assist the governments of developing countries with SDG targets.
- Inadequate private sector participation in financing. A common barrier to SDG 6 in developing countries. SDG 6-led research from the private sector internationally will be a key tool in addressing the issue and research efforts

such as this thesis may provide the tools needed to underpin financial planning from private stakeholders.

This chapter also highlighted key general knowledge gaps which form the core of the research contained within this thesis. It was identified by the UN that groundwater resource data gaps are a primary hinderance to assessing SDG 6 progress and will be a focus of future research. Additionally, SDG global indicator 6.1.1 states that data from household surveys, population records and water quality testing are primary data sets to be used for SDG 6 tracking and thus will be the focus of any SDG 6-led research. In the wake of the Covid-19 pandemic, investment and innovation will be key to responding to the SDGs. Key knowledge gaps identified are:

- Knowledge Gap 1 (Local): There is very little data available for groundwater fluoride or knowledge of its occurrence for Malawi compared to other EARS countries, highlighting an immediate need for groundwater fluoride research. It was suggested that a national geological assessment was required to fill the knowledge gap due to groundwater fluoride being geogenic in origin.
- Knowledge Gap 2 (Local): Very little data is available and even less is understood of the health implications of Malawi's groundwater fluoride. There is a need to quantify the direct link from geogenic groundwater fluoride sources and human health risks so that policy reform (for fluoride) can be justifiably advocated.
- Knowledge Gap 3 (Global and local): There is a need for an innovative method to screen for groundwater fluoride risk from geogenic sources in developing countries which makes the best use of existing sporadic groundwater data and can be deployed easily with minimal resources.

Chapter 3 METHODOLOGY

3.1 Introduction

The review of literature identified key knowledge gaps relevant to geogenic fluoride, including knowledge of various geogenic fluoride sources, specific health links and methods for predicting groundwater vulnerability. The main issue faced was a fundamental lack of resources available to developing countries with which to create risk models for groundwater fluoride. An innovative solution to mapping risk was therefore required, where the use of existing (sporadic) data could be maximised to produce a predictive screening method to map geogenic groundwater fluoride risk. One that was effective at national scales and could be easily updated with continuous addition of new data.

The results section of this thesis was developed as a series of consecutive, peer-reviewed journal articles (papers). Each results chapter comprises one article, therefore contains an independent materials and methods section relevant to each article, written in the format of the journal it was published in. This chapter will address the materials and methods for the whole thesis and will reference the methods of each publication where appropriate, to avoid repetition.

3.2 Research Philosophy

A scientific approach was adopted throughout the development of this research: observations, followed by hypothesising to generate ideas, and subsequent testing of hypotheses to come to reasonable conclusions and practical recommendations based on data and observations. The approach is characterised as a 'pragmatist research philosophy' which is focussed on the importance of practical results with the researcher having complete freedom when determining how the methodology is developed, depending on the results (Žukauskas et al., 2018). The majority of analysis is quantitative however there is some qualitative analysis and discussion where the experimental results interface with human health and policy. An additional theme integrated into the research methodology was stakeholder engagement. When conducting research that invariably impacts people and society, the engagement of stakeholders is particularly important. Stakeholders can vary from politicians and water sector officials to 'end user' stakeholders (i.e. water point users). This research was concerned with a natural contaminant (fluoride) which directly affects human health for better or worse, so continued cooperation with government stakeholders was sought out. Rapport was built via direct communication with various groundwater-relevant Government of Malawi officials who reviewed each manuscript carefully for accuracy prior to publication. Stakeholder engagement in that regard was maximised by the addition of collaborative stakeholders as co-authors on every published article, maximising visibility of the research outcomes within the Government of Malawi.

3.3 Research Materials

3.3.1 Data

The four main data types used in this research were: groundwater data (for geochemical analyses); geological data; national water point data and dental data. Groundwater data was comprised of a combination of both existing and new groundwater data for Malawi. The existing data, referred to throughout the thesis and various published articles as the 'Archive' data set was a collation of all available groundwater geochemical data from literature, and data provided by the Government of Malawi which covered southern Malawi and contained at the very least a fluoride concentration. That data set in particular was used extensively and formed the basis for the groundwater fluoride prediction method developed herein. New, local-scale groundwater geochemical data was collected reactively in order to test hypotheses, the results of which were published and will be discussed in detail in the following sections. Geological data was digitised from existing scanned geological maps and updates discovered in literature (Canon, 1970; Wedmore et al., 2019). Water point data was utilised from a 'live' data bank developed and curated in mWater in an ongoing collaboration between the Government of Malawi and the Government of Scotland-funded Climate Justice Fund (CJF) Water Futures Programme. Dental fluorosis data comprised of non-medical and medical data on dental fluorosis. Non-medical dental fluorosis indicator data was obtained from the Government of Malawi from a household survey in October 2019 and medical dental fluorosis data was obtained from the Scottish charity Smileawi (operating in Malawi), working with the University of Glasgow Dental School, collected during a collaborative venture in Malawi in 2019.

3.3.1.1 Archive groundwater data

The archive groundwater data set comprised two primary regional archive sets of data spanning the past 50 years and covering southern Malawi: one from the

Government of Malawi, ministry of Agriculture, Irrigation and Water Development (now the Ministry of Forestry and Natural Resources) containing georeferenced geochemical groundwater data from boreholes and wells collected between 1980 and 2014; and the other obtained from literature (Bath, 1980) which was originally obtained from the Government of Malawi archives spanning 1970- 1980, augmented by his own 1980 survey data, containing geochemical profiles from boreholes and wells which had not been georeferenced. The latter were included in the preliminary geochemical analysis of Malawi groundwater fluoride (Chapter 4) but were excluded from subsequent analyses due to a lack of corresponding spatial coordinates. The former was used extensively in this research: in the preliminary analysis of groundwater fluoride in Malawi (Chapter 4), the main data set used to calculate lithology-fluoride statistics for southern Malawi which formed the basis of the groundwater fluoride prediction model developed herein (Chapter 6), and the data set used to locate and identify hidden hot springs using geochemical proxy indicators in southern Malawi (Chapter 7). Detailed descriptions on those archive data and how they were used in this research are available in their respective chapters (Addison et al., 2020a; Addison et al., 2020c; Addison et al., 2020d). All data used were subjected to strict QA/QC protocols before inclusion into any subsequent analysis – only those data which ion balanced within <5 % uncertainty were considered.

3.3.1.2 New groundwater data

Three sets of new groundwater data were collected by the CJF and used within this research. The first was an existing data set and was comprised of data collected by University of Strathclyde Hydrogeology M.Sc. students in Malawi conducting groundwater quality and hydrothermal surveys between 2016 – 2018 (Fraser, 2016; Robinson, 2018). Those data are referred to herein as the ‘2016 – 2018’ data set. They comprise complete geochemical profiles for boreholes, wells, and hot springs from the rift valley in southern Malawi. They were used in preliminary analysis of groundwater fluoride occurence in Malawi (Chapter 4), included into statistical analysis for the development of a groundwater fluoride prediction method (Chapter 6) and finally used to identify proxy indicators exclusive to Malawi hot springs (Chapter 7). Detailed descriptions of those data and how they were used are provided in their respective chapters (Addison et al., 2020a; Addison et al., 2020c; Addison et al., 2020d).

The remaining two sets of ‘new’ groundwater data were collected specifically for this research: one was collected in a local study of the groundwaters of TA Mazengera in central Malawi and included full geochemical profiles for 39 boreholes, wells, and natural springs (Chapter 5); the second was comprised of full geochemical profiles for 17 boreholes which were sampled reactively after being identified as possible hidden hot spring locations using dental data (Chapter 7). Detailed descriptions of those data, how they were collected and how they were used are provided in their respective chapters (Addison et al., 2020b; Addison et al., 2020d).

3.3.1.3 Geological data

Geological data was used extensively in this research. Digital geological data was not available for Malawi so lithologies and structural geology had to be digitised from existing geological maps (Canon, 1970) and from structural geological updates found in Malawi literature (Wedmore et al., 2019). The 1:250,000 scale maps were obtained by the CJF previously and comprised 10 high resolution PDF files covering all of Malawi, scanned from originals held by the Geological Survey of Malawi's headquarters in Zomba. The scanned maps were subsequently georeferenced and digitised using ArcGIS (10.6) software for this research in a significant effort to digitise the geology of the entire country. Digitised geology was used in all papers included within this thesis (Addison et al., 2020a; Addison et al., 2020b; Addison et al., 2020c; Addison et al., 2020d) to present digital fluoride-geology maps, and most notably for fluoride-lithology statistical calculations used to develop the groundwater fluoride prediction method developed herein. A detailed description of digital geological data and how they were digitised and used in geostatistical analyses is provided in chapter 6 (Addison et al., 2020c).

3.3.1.4 National water point data

The largest data set used in this research was a national set of water point data. Efforts to develop a live data set of all of Malawi's water points are ongoing and are core to the CJF overall aim of assisting Malawi to achieve SDG 6. Over 120,000 water points of every type (groundwater, surface water, piped networks) have so far been mapped since 2010 (intensively since 2016) in the joint venture between the CJF and the Government of Malawi into a master live data set hosted by the 'mWater' MIS platform (www.mwater.co) (Kalin et al., 2019). Direct groundwater water points were extracted from mWater and used in the groundwater fluoride prediction method developed to estimate numbers of water points and water point users who are currently at risk within the various geogenic fluoride risk categories developed

(Chapter 6). A detailed description of water point data and how they were refined and used within the method is provided in chapter 6 (Addison et al., 2020c).

3.3.1.5 Dental Fluorosis Data

Dental fluorosis indicator data (non-medical) on the visible symptoms of dental fluorosis was obtained from the Government of Malawi. They conducted a Traditional Authority (TA)-scale household survey in TA Mazengera in central Malawi using local enumerators in October 2019. The survey was anonymous, and people were asked numerous water supply-related questions on their doorstep including one 'yes/no' question on the visible symptoms of dental fluorosis: "*Does anyone in your household suffer from black/brown staining of the teeth?*". The "yes" answers were used in this research to calculate indicatory lithology-fluorosis statistics in TA Mazengera to corroborate the lithology-fluoride statistics developed in the local-scale study (Chapter 5). A detailed description of non-medical dental fluorosis indicator data and how they were used is provided in chapter 5 (Addison et al., 2020b).

Data on incidence of dental fluorosis (medical data), particularly severe dental fluorosis, were obtained from the Scottish dental charity Smileawi working with the University of Glasgow Dental School who were conducting a survey of oral health in Malawian school children in June 2019. The opportunity to work together with dentists arised from direct communication and regular meetings with both parties and it was agreed that both groundwater scientists and dentists involved would benefit from the collaboration. Sharing of data resulted in locations with confirmed incidence of severe dental fluorosis identified by the oral health survey being used as proxy indicator locations for three hidden hot springs in southern Malawi which were identified by this research in an attempt to refine the groundwater fluoride prediction method developed (Chapter 7). A detailed description of medical dental fluorosis data and how they were used is provided in chapter 7 (Addison et al., 2020d).

3.3.2 Software

Various software packages were used during the research process to analyse data, create maps, and calculate statistics. Each software used is presented below. Detailed explanations on how and when each software was used are provided in relevant chapters (papers).

- **ArcGIS Desktop (10.6)**. ArcGIS is a platform used to create, edit, view, manage, and analyse spatial data. Developed by ArcGIS (https://www.arcgis.com/index.html).
- **Microsoft Excel 2016 (16.0)**. Excel is tool used to store, analyse, interrogate, view and model numerical data. Licenced to the University of Strathclyde and developed by Microsoft.
- **mWater**. mWater is a free and open-source online portal which anyone can use. It is a Management Information System (MIS) developed to track and monitor water sources worldwide, particularly in developing countries. It was designed to be deployed via surveys on mobile phones where survey results can be uploaded instantly to the platform creating live data sets which are easily accessible. Developed by mWater (www.mwater.co).

3.4 Research Methods

The research method employed was to divide the project into four main stages (*identification of knowledge gap – development and testing of method – application and scaling of method – refinement and validation of method*), with each stage to be written as a paper and published in a peer-review journal. Stage 1 (chapter 4) was an assessment of current knowledge and the identification of key Malawi-specific knowledge gaps. Stage 2 (chapter 5) was the initial development of a groundwater fluoride prediction method applied at a local scale, a preliminary investigation into the effects of geogenic groundwater fluoride on human health and the repercussions for national groundwater policy. Stage 3 (chapter 6) was the scaling of the groundwater fluoride prediction method developed in stage 2 nationally and an estimation of water points and water point users at risk from elevated groundwater fluoride, along with a detailed analysis of fluoride-relevant policy. Stage 4 (chapter 7) was a refinement of the national prediction method developed during stage 3. The approach was substantially achieved and resulted in four published papers. Each stage is detailed below.

3.4.1 Stage 1 - Evaluation of key knowledge gaps

The first stage of the research was to evaluate all known literature in order to identify key knowledge gaps. This was done via an exhaustive data/literature mining effort to collate all existing groundwater fluoride data and knowledge in Malawi. Groundwater data was obtained from the Government of Malawi archives, journal literature and published or grey literature reports. Fluoride concentration data were analysed in ArcGIS to examine spatial distributions of fluoride concentrations in Malawi and to examine spatial relationships with geology to determine potential geological controls on groundwater fluoride. Groundwater data with complete geochemical profiles were analysed in Microsoft Excel (16.0) to examine the geochemical controls on fluoride in groundwater and assist in tracking geogenic sources. Specific relationships were analysed to determine if known fluoride geochemical patterns were present in Malawi groundwater, such as fluoride-temperature (known relationship where hot springs have particularly increased fluoride with increased groundwater temperatures) and a fluoride-calcium relationship to determine if fluorite (CaF_2) equilibration was present in Malawi. A cursory investigation was conducted into the difference between global (WHO) and local (Malawi Government) recommended guideline concentrations for fluoride in drinking water so that key management challenges for the Government of Malawi could be identified and subsequent recommendations could be made with respect to groundwater policy (for fluoride). Stage 1 of the research was written as a journal article and published (Chapter 4).

3.4.2 Stage 2 – Development and testing of prediction method

Once it was identified that a national groundwater data set with complete geochemistry for Malawi was not available with which to create a risk model, the development of a new and innovative solution was required to predict groundwater fluoride. Fluoride in groundwater arises from water-rock interactions, where a geogenic fluoride source (lithological or hydrothermal) interacts with groundwater. Hot springs (hydrothermal) were identified as site-specific sources of particularly elevated groundwater fluoride by stage 1 (Chapter 4) and as a result were relatively straightforward to map and predict once hot spring locations had been identified. More diffuse concentrations resulting from groundwater interaction from shallow lithological sources of fluoride (weathered basement aquifers) posed a key challenge to predict, so a local-scale study was conducted to investigate the influence specific lithologies had on local groundwater fluoride concentrations. A location within the weathered basement aquifer in Malawi was chosen as it is the most dominant aquifer system nationally. Fluoride-lithology statistics were calculated to determine which lithologies posed a greater risk of elevated groundwater fluoride and a hierarchy of fluoride risk factors were thus developed based on the statistical likelihood (translated to risk) of each lithology to produce raw groundwater with fluoride concentrations exceeding the WHO guideline standard of 1.5 mg/L (thus, causing dental fluorosis). Lithologies were then mapped per their calculated groundwater fluoride risk factor to produce a geology-based local groundwater fluoride prediction map.

The purpose of developing a (national) groundwater fluoride prediction method was not only to manage groundwater assets, but also to develop an evidence-based justification for a review of national groundwater (fluoride) policy to assist Malawi achieve SDG6 targets. A direct geology-human health link between groundwater fluoride and dental fluorosis was additionally investigated during the local study via a Human Health Risk Assessment (United States Environment Protection Agency, 2019) to develop evidence to justify the importance of updating policy. Recommendations were presented on groundwater policy update in Malawi (for fluoride). Stage 2 of the research was written as a journal article and published (Chapter 5).

3.4.3 Stage 3 – Application of prediction method at national-scale

The method for predicting groundwater fluoride developed in stage 2 (Chapter 5) needed to be adapted and scaled nationally to include all lithologies. The method was effective at the local scale where groundwater fluoride concentrations were available and could be attributed to specific lithologies, but national groundwater data was unavailable for Malawi. A regional groundwater data set published in stage 1 (Chapter 4), provided by the Government of Malawi, contained groundwater geochemical data spanning southern Malawi. Fluoride-lithology statistics were calculated for those lithologies where the archive groundwater data occurred, and groundwater fluoride risk factors were developed for each lithology using the same method developed during the local study (Chapter 5). Hot springs were treated as a separate 'site-specific' geogenic sources and assigned their own risk factor, lithologies were treated as 'generic' geogenic sources and assigned generic risk factors which covered any water point within each lithology. A detailed investigation of compositional mineralogy was then conducted for all remaining lithologies nationally for which there were no corresponding groundwater data (fluoride concentrations) from which to calculate statistical groundwater fluoride risk. Groundwater fluoride risk factors were thus extrapolated to all lithologies nationally which had similar mineralogical compositions where such extrapolations could be justified with data.

The groundwater fluoride prediction method needed to not only predict which groundwaters were more vulnerable from geogenic fluoride sources, but also to predict which water points and water point users may be at risk nationally. Statistics for the numbers of water points and water point users at risk from each fluoride risk classification were calculated using national water point data from mWater. Data were filtered for ‘functional’ and ‘partly functional but in need of repair’ direct groundwater sources so that statistics could be calculated for water points which currently produce groundwater. Statistics were additionally calculated for ‘not functional’ water points as those may still pose a risk if drilled into a lithology with a high-risk factor for groundwater fluoride and are repaired.

A detailed investigation into fluoride-specific policy within the national standard documents was conducted and comparisons made with the global standard (WHO). Specific recommendations were presented on updating fluoride policy documents and also on the implications of reducing the Malawian groundwater fluoride standard of 6 mg/L to match the WHO global drinking water standard of 1.5 mg/L via stepped progression. Stage 3 of the research was written as a journal article and published (Chapter 6).

3.4.4 Stage 4 – Refinement of the groundwater fluoride prediction method

The unconsolidated sediments lithology which contained six individual sub-groups presented the only unconsolidated generic geogenic source of groundwater fluoride. It represented the rift basin sediments which fill the rift valley, concealing the onshore rift floor and was most extensive in southern Malawi. The lithology was characterised by a moderate-low risk factor for groundwater fluoride (Chapter 6) but contained sporadic anomalously high groundwater fluoride concentrations where it occurred within the rift basin. That posed uncertainty for accurately predicting groundwater fluoride risk within the unconsolidated sediments as it was hypothesised that they represented hidden hydrothermal activity in the rift valley (Chapter 6). For accuracy it was necessary to delineate those anomalously elevated fluoride concentrations that were related to hydrothermal activity (hidden hot springs), so that a more accurate risk factor for unconsolidated sediments could be calculated without influence from hydrothermal systems.

Southern Malawi’s rift valley was investigated for evidence of hidden hot springs via the development of a multi-faceted set of hot spring proxy indicators. Geochemical proxy indicators for (Malawi) hot springs were identified from CJF data collected from hot springs and shallow (non-hydrothermal) groundwater located in basin sediments in southern Malawi’s rift valley. Proxy indicators were thus applied to the regional archive data set to identify hidden hot spring locations from geochemical data. Dental data was used to identify additional hidden hot spring locations where increased incidence of severe dental fluorosis were confirmed by dentists in a collaboration with the Scottish charity Smileawi (active in Malawi) and the University of Glasgow Dental School. Hidden hot spring locations identified were subsequently removed from the groundwater fluoride risk statistics for unconsolidated sediments (Chapter 6), which were then recalculated for an updated groundwater fluoride risk factor. Hidden hot spring locations were added to the site-specific 'Hot springs' groundwater fluoride risk category which was also recalculated to provide an updated and more accurate risk factor for the category. A final groundwater fluoride risk map for Malawi with prediction statistics was developed in ArcGIS (10.6) which included all updated statistics and risk factors. Stage 4 of the research was written as a journal article and published (Chapter 7).

3.5 Summary

This chapter described the overall research approach adopted to achieve the aim of developing an alternative groundwater fluoride prediction method which could be applied in the developing world where limited data and resources prevent the development of complex risk models. The research philosophy was described, the various data sets and software used were described and explained. The research method was presented as a four-stage process (*identification of knowledge gap – development and testing of method – application and scaling of method – refinement and validation of method*), with each stage representing a paper written as an article to be published in a peer-review journal. The methods involved in every stage and how they contributed to the overall aim of the research were explained in detail. More detailed descriptions on specific methods employed for each stage are available in the methods sections of each paper in the following chapters. The next chapter presents the results of stage 1 of the methodology.

Chapter 4 EVALUATION OF KEY KNOWLEDGE GAPS

4.1 Introduction

The previous chapter outlined the overall methods employed to achieve the aim of the research. Chapter 2 identified key general knowledge gaps related to the broad thesis topic. The literature review in this chapter is Malawi-specific, addresses stage 1 of the research method and addresses research question (RQ) 1 (including research objectives (RO) 1.1 and 1.2). The chapter comprises the results of a data and literature collation which represented (at the time) all knowledge and data available on the occurrence of fluoride in the groundwater of Malawi. Literature on fluoride occurrence in Malawi was sporadic, local-scale and extremely rare compared to other EARS countries. There was no published knowledge of groundwater fluoride at national-scale and very little linking the health effects of fluorosis.

This chapter analysed all collated groundwater data for geochemical patterns to fluoride occurrence. The results show hydrochemical control on groundwater fluoride concentrations where fluorite (CaF_2) equilibration is dominant in the majority of Malawi groundwater and that there is groundwater temperature sensitivity where all groundwater samples >32 °C were hot springs. Results additionally showed geological control where the most elevated fluoride concentrations occur in hot springs or in water points along rift faults in the rift valley. Results show the Malawian standard for fluoride in drinking water from boreholes and wells at 6 mg/L is significantly higher than the globally accepted WHO standard of 1.5 mg/L. Fluoride concentrations >6 mg/L in Malawi were shown to be exclusive to hot springs and due to their site-specific nature represented relatively straightforward risk management. Diffuse concentrations between the WHO and Malawi guideline standards (1.5 – 6 mg/L) were significantly more extensive and appeared to be related to lithological sources presenting a key groundwater fluoride risk management challenge.

This chapter was written as a journal paper which was published in the international journal ‘Science of the Total Environment’ in April 2020 as follows:

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4.2 Paper

Fluoride occurrence in the lower East African Rift System, Southern Malawi

Marc J. Addison [a, *], Michael O. Rivett [a], Helen Robinson [a], Aimee Fraser [a], Alexandra M. Miller [a], Peaches Phiri [b], Prince Mleta [b], Robert M. Kalin [a]

[a] Department of Civil & Environmental Engineering, University of Strathclyde, Glasgow, Scotland, G1 1XJ

[b] The Ministry of Agriculture, Irrigation and Water Development, Regional Irrigation and Water Development Office, Lilongwe Headquarters, Private Bag 390, Lilongwe, Malawi

*Correspondence: marc.addison@strath.ac.uk;

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Non-standard abbreviations: SB (Shire Basin); LSB (Lower Shire Basin)

Highlights

- Groundwater fluoride documented (*n* = 1365) in Malawi groundwater at EARS periphery
- Fluoride >6 mg/l at 3.4% occurrence, less than EARS elsewhere, but locally significant
- Geological control: Excessive >6 mg/l fluoride only occurs in hot springs >32 °C
- Hydrochemical control: fluorite control, calcium, pH and temperature sensitivity
- Troublesome >1.5–6 mg/l fluoride of diffuse occurrence a key management challenge

Abstract

Countries located on the East African Rift System (EARS) are vulnerable to fluoride in their groundwater; a vulnerability for the developing country of Malawi at the southern rift periphery that is not well characterised. Groundwater fluoride occurrence in Malawi is documented here to better understand and manage fluoride risks posed. Available literature and Gov't of Malawi archive fluoride data spanning some fifty years have been collated and augmented by our own 2016–18 surveys of groundwater quality in Southern Malawi, targeting deep-sourced springs. In total, fluoride data for 1365 borehole, spring and hot spring samples were assembled. Statistically, 83% of samples were below the 1.5 mg/l WHO limit, concentrations in the 1.5–6 mg/l range between former (pre-1993) and current WHO guidelines at 14%, and those with fluoride above the current Malawi (former WHO) 6 mg/l guideline, at 3%. A lower occurrence than in other zones of the EARS, but indicative of a need for a Malawi Gov't management policy revision and associated management strategies endorsed by several documented incidences of dental fluorosis in proximity to high fluoride groundwater. Increased fluoride is related to increased groundwater temperatures signifying the importance of geothermal groundwater provenance. Temperature data may indeed be used as a proxy indicator of fluoride risk; samples with a temperature >32 °C, contained >6 mg/l fluoride. Structural geological controls appear to allow deep geothermal groundwaters to come to the near surface, as evidenced by increased fluoride in springs and boreholes close to faulted areas. Hydrochemical evaluation shows that fluoride concentrations are influenced by fluorite equilibration and sensitivity to calcium and pH. Recommendations are made to further document the occurrence of fluoride and enhance management of risks due to fluoride in drinking water in Malawi. With fluoride as a key indicator within Sustainable Development Goal number 6, the current Malawi standard and waters with concentration between 1.5 and 6 mg/l will come under increased scrutiny and pose a key challenge to assessment and management efforts.

1 Introduction

Fluoride and arsenic are the two chemical contaminants of concern globally for “safely managed drinking water” identified by the UN's Joint Monitoring Programme (WHO and UNICEF, 2017). Securing safe drinking water across the developing world including countries such as Malawi in Africa has been driven by meeting Millennium and now Sustainable Development Goals (M/SDGs) specifically SDG 6, to “achieve universal and equitable access to safe and affordable drinking water for all” (Truslove et al., 2019). Fluoride at low concentration is beneficial to dental health and often added to water supplies and dental products, cognisant that ingestion of excessive concentrations is detrimental (Edmunds and Smedley, 2013). The World Health Organisation (WHO) (2017) drinking-water guideline is 1.5 mg/l; below this, concentrations promote teeth and bone growth; above, fluoride replaces apatite in teeth causing dental fluorosis (DenBesten and Li, 2011). Prolonged, excessive exposure causes skeletal fluorosis (Haimanot et al., 1987), reported in China, Tanzania and India

(Agrawal et al., 1997; Bo et al., 2003; Chen et al., 2012; Shorter et al., 2010). Despite the health risks, especially to children, some developing countries, including Malawi, retain the pre-1993 WHO guideline of 6 mg/l in their regulations (Malawi Standards, 2005). The more stringent guideline may be perceived too onerous, a perception not necessarily underpinned by data. Developing countries may lack resources to undertake sufficient fluoride analysis to fully document occurrence. Moreover, if health impacts seem rare, complacent settling for the higher guideline may occur with latent problems remaining undiagnosed.

Given that fluoride in supply invariably originates from groundwater (Amini et al., 2008), and groundwater is the primary developing-world water resource relied upon to meet SDG 6 (Xu et al., 2019), managing groundwater fluoride risk is a priority. Fluoride arises from groundwater dissolution of fluoride-rich lithologies, including clay minerals and micas (Battaleb-Looie et al., 2012), hornblende, amphibole and biotite in metamorphic Basement rocks (Bath, 1980; Mapoma et al., 2017), and (Basement) volcanic rocks, especially of alkaline composition (Ghiglieri et al., 2012). Manifestation of fluoride in deep-source springs or shallow groundwater may arise from discharge of hydrothermal groundwater from (Basement) rocks at depth, short-circuiting via fault pathways to surface (Edmunds and Smedley, 2013), recognising concentration of fluoride may occur in late stage hydrothermal fluids and pegmatitic mineralisation (Bath, 1980). Groundwater supplies within rift systems may be vulnerable where hydrothermal fluid discharge pathways to surface are prevalent as found in parts of the East African Rift System (EARS) (Hochstein, 2005). Groundwater fluoride problems are well known in the central to northern parts of the EARS (Chavula, 2012); in Kenya elevated fluoride occurs in proximity to rift volcanic rocks (Nair et al., 1984), further north in Ethiopia it is associated with near-surface volcanic rocks and active volcanoes (Tekle-Haimanot et al., 2006). Secondary sources of hydrothermally precipitated fluorite (CaF2) may arise; upon groundwater calcium increase, fluorite may precipitate on sediments, fault surfaces or in caves, to later re-dissolve upon the return of suitable hydrochemical conditions (Maltsev and Korshunov, 1998). Due to equilibrium geochemical reactions, high sodium, low calcium, and increased pH together promote elevated fluoride concentrations, at times up to hundreds of mg/l (Edmunds and Smedley, 2013).

Malawi ranks 172 out of 189 in the 2019 Human Development Report (UN, 2019) and receives significant international aid. Some 85% of its burgeoning 18 million population are rural, primarily depending upon groundwater for safe drinking-water supply (Upton et al., 2018). This is mostly delivered from tens of thousands of hand-pumped boreholes that continue to be drilled under aid programmes (Kalin et al., 2019). Malawi's location towards the southern extreme of the lower EARS western branch renders it susceptible to groundwater fluoride, a susceptibility that is only poorly documented at present. EARS countries with active rift volcanism such as Tanzania, Kenya and Ethiopia appear to exhibit the highest rift valley fluoride (Ghiglieri et al., 2012; Nair et al., 1984; Tekle-Haimanot et al., 2006). Whilst Malawi does not currently host active volcanism, the Rift Valley floor in Southern Malawi experiences active rifting and is judged susceptible to fluoride, by researchers historically involved (Bath, 1980) alongside others generally reviewing Malawi's groundwater quality (BGS, 2004; Mapoma and Xie, 2014; UN, 1989; Upton et al., 2018). The early work of Kirkpatrick (1969) on Malawi's thermal springs notes frequent excessive fluoride. Such fluoride concerns are set within known groundwater quality concerns, notably salinity in some of the alluvial (superficial) aquifers (Monjerezi et al., 2011; Rivett et al., 2018a) and possibly arsenic that although generally low, may be more elevated in supplies containing hydrothermal groundwater contributions (Rivett et al., 2018b).

The above work allows preliminary conclusions of sporadic fluoride in groundwater in contact with EARS Basement geology and, although not appearing widespread in superficial deposits, some occurrences above the 6 mg/l former WHO guideline that are acknowledged worrisome (Mapoma and Xie, 2014). Of added concern we contend are occurrences in groundwater above the current WHO 1.5 mg/l guideline that are observed but poorly documented, alongside at least some evidences of dental fluorosis in Malawi dating back to Bath (1980) together with more recent reports (Msonda et al., 2007; Pritchard et al., 2008; Sajidu et al., 2007). Added management concerns are that where physical symptoms of dental fluorosis do occur in Malawi, but these appear to be regarded as ‘cosmetic’. Also, where records of fluorosis could exist within hospitals, health offices or schools, these appear not to be collated to drive a response. Moreover, recognising Malawi's shortage of dentists, only 36 exist in 2019 (Khamula and Faiti, 2018), a lack of problem diagnosis is very probable.

Our aim is hence to document groundwater fluoride occurrence in Malawi, not only to help safeguard water supply to vulnerable populations, but also to understand and manage fluoride risks that may be posed at this peripheral location within the African continental rift system. We hence collate and evaluate available data pertaining to groundwater fluoride in Malawi. We also add to this data from our own recent sampling campaigns in Southern Malawi that allow improved insight into the significance of hydrothermal groundwater and springs of deep groundwater provenance in particular. The geological and geographical relationships of fluoride in groundwater in Malawi allow recommendations to be made on the improved quantification of the groundwater fluoride problem in Malawi with subsequent development of appropriate policy and management response priorities.

2 Materials and Methods

2.1 Geological and hydrogeological setting

Malawi occurs as an elongate plateau towards the southern extreme of the western branch of the lower EARS that structurally dominates its landform (Fig. 1) (Habgood, 1963; Upton et al., 2018). Recent continental rifting occurs, but Malawi is without current active volcanism (Hochstein, 2005). Its Miocene-recent structural geology (see Fig. 1) is mainly influenced by the EARS and is bound by many faults. Elevation rises steeply where the rift valley is bounded by large NW-SE and SW-NE trending normal faults. Elevations span from around 30 m in the valley floor at Malawi's southern border with Mozambique to over 3000 m in the highlands. Our descriptions focus towards Southern Malawi, the lower rift valley region judged (hydro)geologically at most fluoride risk (Bath, 1980). Most available fluoride data and our subsequent field surveys occur there.

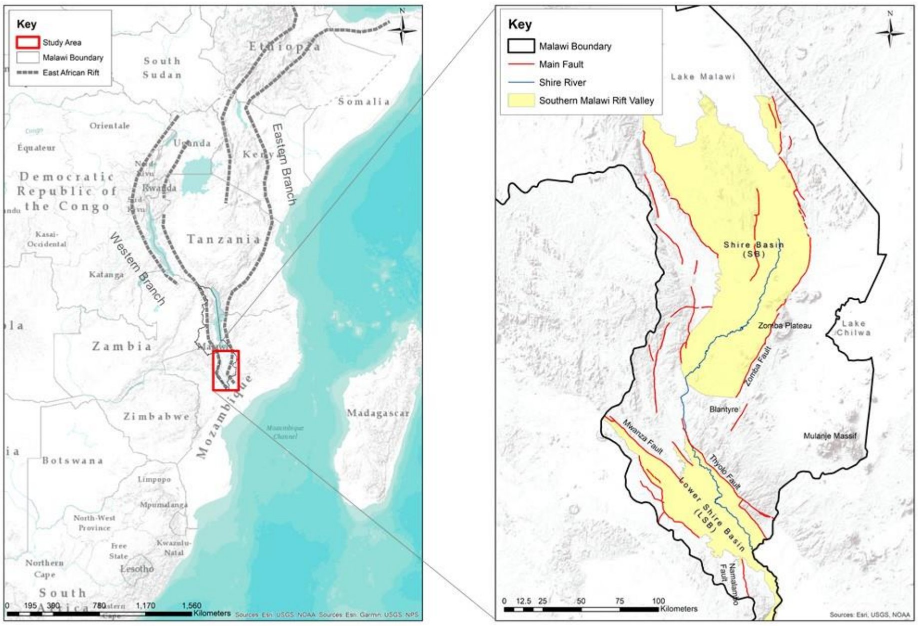


Figure. 1. Left: Malawi's position on the western branch of the lower EARS with study area. Right: Topographic map of Malawi showing rift valley, major faulting, and other study area features of interest.

Upper Jurassic intrusive volcanics of the Chilwa Alkaline Province (CAP) exposed by weathering in Southern Malawi occur as isolated topographic highs (the Mulanje Massif and Zomba Plateau) and comprise mainly granites, syenites and carbonatites (Fig. 1). Regional-scale, normal-faulted blocks of Precambrian and Lower Palaeozoic Basement gneiss and granulite occur, with Quaternary colluvium, alluvium and lacustrine basins forming wide rift valley plains in the Shire Basin (SB) (Fig. 1). The Shire River, the only outflow from Lake Malawi, follows the rift valley exploiting the low terrain. Highly fractured sequences of igneous and sedimentary rocks of the Karoo Supergroup form the southwest flank of the Lower Shire Basin (LSB). Remnants of EARS heat occur as hydrothermal boreholes and hot springs located on major rift faults, for instance in the Mwanza valley and along strike of the Zomba fault; occurrence is sufficient to cause on-going interest in establishing Malawi's geothermal resource potential (Dulanya, 2006; Msika et al., 2014; Robinson, 2018).

Three main aquifer types occur in (Southern) Malawi; fractured Precambrian and Lower Palaeozoic Basement, weathered Basement and Quaternary superficial deposits (BGS, 2004; Smith-Carington and Chilton, 1983; Upton et al., 2018). Fractured Basement often underlies relatively thin weathered Basement. Permeability of these high-grade, crystalline metamorphic and metaigneous rocks arises from their fracture network, with near-vertical fractures (alongside faulting) allowing deep-shallow flow connectivity. Storage though is limited, with low, but still sufficient yields of 0.25–0.5 l/s for rural water supplies to village communities nominally serving 250 people. They provide drinking water to over 60% of Malawians (Chimphamba et al., 2009). Weathered Basement aquifers are shallow, saprolite aquifers resulting from in-situ weathering of Basement rocks. Where boreholes penetrate granular horizons within the saprolite, yields of c. 2 l/s are common, with increased yields where recharged by overlying permeable superficial deposits (can be limited as units are often semi-confined by clays) (Mkandawire, 2004).

Rift valley Quaternary - Tertiary superficial deposits form the most productive aquifer of highest borehole yields. They arise from erosion and mass wasting of rift escarpment Basement rock with yields potentially exceeding 10 l/s. Deposit thickness varies due to the tilted, block-faulted nature of underlying Basement sequences, but may be up to 150 m where sediments have accumulated against large normal faults on the rift valley's eastern flank. Coarse-grained, poorly sorted alluvial fans form basin flank, permeable aquifer units along rift escarpments and may receive recharge contributions of typically good quality water from recently recharged adjoining Basement rock. In contrast, flows into the shallow superficial deposits from deeper units are typically of poor-quality groundwater. Data are sparse, but may include transmission of hydrothermal water from depth along conductive fault-lines (Dulanya, 2006; Msika et al., 2014; Robinson, 2018), or hydraulic leakage from the underlying Karoo sedimentary aquifers containing evaporite beds (of halite) (Monjerezi and Ngongondo, 2012).

2.2 Review of literature and archive groundwater fluoride data

Our research on fluoride occurrence in Malawian groundwater was conducted under the Climate Justice Fund: Water Futures Programme ('CJF') that aims to support the Government of Malawi in meeting SDG 6 (www.cjfwaterfuturesprogramme.com) (Kalin et al., 2019). Review of the literature and archive data was undertaken to collate all existing groundwater fluoride data in Malawi. Review included journal literature, published or grey literature reports, and the extraction of archive data held by the Government's Ministry of Agriculture, Irrigation and Water Development (MoAIWD) discussed further below. Some datasets, perhaps unpublished or not formally collated, may also be held by NGOs (non-governmental organisations) facilitating (international) aid. Efforts were made to source all data, however, suspect data is not presented here, one example is a large dataset that was excluded from our collation as fluoride concentration data reported by this NGO appeared anomalous (a consistent error was suspected, but not proven).

2.2.1 Data quality assurance/quality control (QA/QC)

Where appropriate supporting major-ion data exist, we have adopted a quality assurance – quality control (QA/QC) data-screening protocol of using only the data for analysis where calculated ion balances are better than the conventionally accepted 5%. Some peer review published fluoride data are presented for which supporting major ion data were not available and hence ion balance checks are not possible. It should be recognised that good ion balances do not necessarily guarantee the validity of the fluoride data in that positive and negative ion errors may cancel out and that the balance may not be that sensitive to fluoride errors as the fluoride ion contribution is typically a small component of the balance (96% of samples had <5% fluoride contribution to anions).

2.2.2 MoAIWD and predecessor organisation archive data

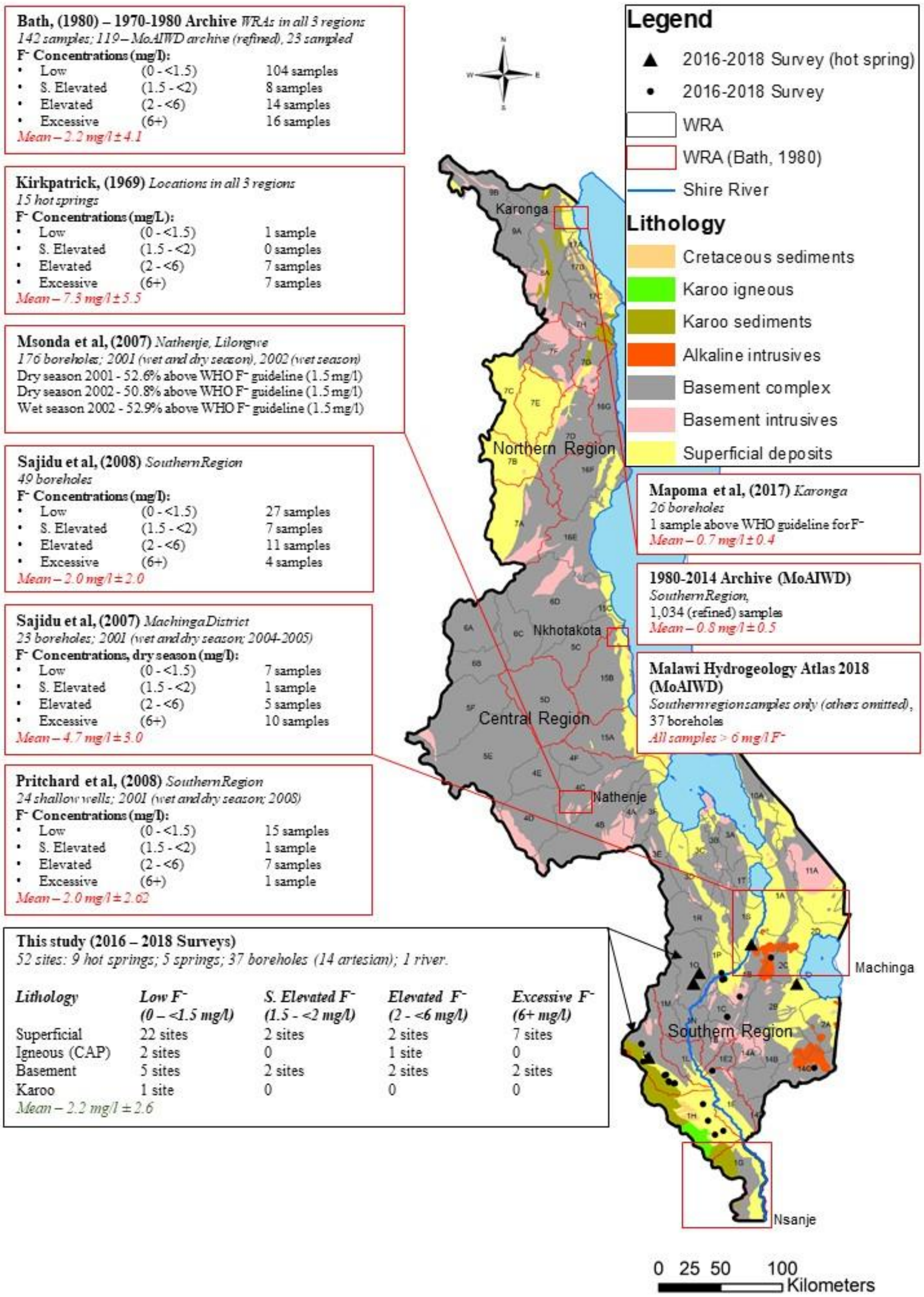
Regarding the MoAIWD archive, Malawi has struggled to establish a regularly sampled national groundwater quality monitoring network (Rivett et al., 2018a). A monitoring network failed to be established under the 1986 National Water Resources Master Plan (Malawi Department of Water, 1986), but was recommended by the Ministry of Water Development (2003) as a statutory provision within Malawi's National Water Policy. The MoAIWD subsequently initiated a network using 35 purpose drilled monitoring wells in 2009–10 (MoAIWD, 2017a). However, budgetary constraints since have resulted in sparse groundwater quality data and infrequent periodic sampling (MoAIWD, 2017b). Combined with the fact that collation of records into a single Management Information System (MIS) remains an on-going MoAIWD effort, fragmentary collation of archive groundwater quality data (incl. fluoride data) is apparent. Archived data held by the MoAIWD are mostly from its own laboratory facilities that are recognised to be limited, and in need of modernisation.

The MoAIWD archive of groundwater quality data is mostly from the sampling of hand-pumped groundwater supply 'water points' used for village community water supply. Water points of all types are being evaluated for SDG6 by the CJF Programme, the majority of the over 115,000 rural water supplies across Malawi are dependent on groundwater (Kalin et al., 2019). Linking this georeferenced data with MoAIWD groundwater quality archive sample data is problematic as the latter may not be geo-referenced with coordinate locations and are simply identified by a village name whose location may not be clear, or the precise water point is unclear (many villages now have multiple water points after successive water development programmes (Truslove et al., 2019)).

We have gathered two primary sets of archive data: (i) a '1980 – 2014 archive' gathered from the MoAIWD records; and, (ii) a '1970–80 archive' originally gathered by Bath (1980) from the Geological Survey (of Malawi) and augmented by his own 1980 survey data. A third set of archive data has been selectively drawn from, (iii) the 'Hydrogeological Atlas for Malawi' published internally in 2018 (Malawi Government, 2018). The detail of each set is described below, including QA-QC applied.

Regarding (i) the 1980–2014 archive dataset gathered contained 1959 samples of which 72% (n = 1401 samples) had ion balance estimates. Of these, 74% balanced within 5% and were used herein for the 1980–2014 archive data analysis (n = 1034 samples).

Regarding (ii) the 1970–1980 archive, the Bath (1980) British Geological Survey advisory report provides data on a 234 groundwater sample data set for which fluoride data were available. Of these, 209 samples were extracted in 1980 by Bath from the Geological Survey (of Malawi) archive 'Cardex system' of >1000 major element analyses (some partial) on groundwater sample data "accumulated over the last ten years or so", referred to herein as the '1970–1980 archive' data set (in the absence of specific dates). Analysis was by colourimetry initially and specific ion electrode latterly, noting that the older analyses in particular are flagged by Bath as "might be unreliable". Of the 209 samples extracted 49 samples had insufficient data to calculate ion balances, and of the remaining 160 samples, 74% balanced within 5% (n = 119 samples) used in the 1970–1980 archive data analysis (the remainder being excluded). Unfortunately, this archive data set lack water-point spatial coordinates, but were allotted to their respective 'water resource area' (WRA) surface-water catchment regions (Fig. 2), that approximately correspond to Malawian Districts allowing segregation of samples at WRA or approximate District level per their Fig. 2 spatial distribution (although assignment to geological – aquifer type was not possible). Additionally, 25 groundwater borehole sites were sampled in the Southern Region (specifically the LSB) by Bath (1980) during his 'Bath, 1980 survey' and shipped to the UK for lab analyses. Of the 25 samples, 2 samples had an ion balance over 5% and were excluded, with the remainder (n = 23) having a balance <5% and were used in the analysis herein and shown as a distinct survey in the results that follow.



Bath, (1980) – 1970-1980 Archive *WRAs in all 3 regions*
142 samples; 119 – MoAIWD archive (refined), 23 sampled
F^- Concentrations (mg/l):

• Low	(0 - <1.5)	104 samples
• S. Elevated	(1.5 - <2)	8 samples
• Elevated	(2 - <6)	14 samples
• Excessive	(6+)	16 samples

Mean – 2.2 mg/l ± 4.1

Kirkpatrick, (1969) *Locations in all 3 regions*
15 hot springs
F^- Concentrations (mg/L):

• Low	(0 - <1.5)	1 sample
• S. Elevated	(1.5 - <2)	0 samples
• Elevated	(2 - <6)	7 samples
• Excessive	(6+)	7 samples

Mean – 7.3 mg/l ± 5.5

Msonda et al, (2007) *Nathenje, Lilongwe*
176 boreholes; 2001 (wet and dry season), 2002 (wet season)
Dry season 2001 - 52.6% above WHO F^- guideline (1.5 mg/l)
Dry season 2002 - 50.8% above WHO F^- guideline (1.5 mg/l)
Wet season 2002 - 52.9% above WHO F^- guideline (1.5 mg/l)

Sajidu et al, (2008) *Southern Region*
49 boreholes
F^- Concentrations (mg/l):

• Low	(0 - <1.5)	27 samples
• S. Elevated	(1.5 - <2)	7 samples
• Elevated	(2 - <6)	11 samples
• Excessive	(6+)	4 samples

Mean – 2.0 mg/l ± 2.0

Sajidu et al, (2007) *Machinga District*
23 boreholes; 2001 (wet and dry season; 2004-2005)
F^- Concentrations, dry season (mg/l):

• Low	(0 - <1.5)	7 samples
• S. Elevated	(1.5 - <2)	1 sample
• Elevated	(2 - <6)	5 samples
• Excessive	(6+)	10 samples

Mean – 4.7 mg/l ± 3.0

Pritchard et al, (2008) *Southern Region*
24 shallow wells; 2001 (wet and dry season; 2008)
F^- Concentrations (mg/l):

• Low	(0 - <1.5)	15 samples
• S. Elevated	(1.5 - <2)	1 sample
• Elevated	(2 - <6)	7 samples
• Excessive	(6+)	1 sample

Mean – 2.0 mg/l ± 2.62

This study (2016 – 2018 Surveys)
52 sites: 9 hot springs; 5 springs; 37 boreholes (14 artesian); 1 river.

Lithology	***Low F^- (0 – <1.5 mg/l)***	***S. Elevated F^- (1.5 - <2 mg/l)***	***Elevated F^- (2 - <6 mg/l)***	***Excessive F^- (6+ mg/l)***
Superficial	22 sites	2 sites	2 sites	7 sites
Igneous (CAP)	2 sites	0	1 site	0
Basement	5 sites	2 sites	2 sites	2 sites
Karoo	1 site	0	0	0

Mean – 2.2 mg/l ± 2.6

Mapoma et al, (2017) *Karonga*
26 boreholes
1 sample above WHO guideline for F^-
Mean – 0.7 mg/l ± 0.4

1980-2014 Archive (MoAIWD)
Southern Region,
1,034 (refined) samples
Mean – 0.8 mg/l ± 0.5

Malawi Hydrogeology Atlas 2018 (MoAIWD)
Southern region samples only (others omitted),
37 boreholes
All samples > 6 mg/l F^-

Figure. 2. Location and summary statistics of literature, archive and our 2016–2018 surveys of fluoride occurrence in Malawi's groundwater (with geological distribution shown)

Regarding data set (iii), we have augmented our primary archive MoAIWD dataset with fluoride data drawn from work by the MoAIWD now recently released (internally) within its ‘Hydrogeological Atlas for Malawi’ in 2018 (Malawi Government, 2018), a compilation of hydrogeological and hydrochemical records. The ‘Atlas’ presents Water Resource Area (WRA) regional maps of records that includes fluoride data simply differentiated above, or below Malawi's 6 mg/l guideline. The Atlas accesses a similar data archive used to our own, but also includes some more modern data up until 2017 and potentially other archive data where further attempts have been made to locate the coordinates of samples. Rather than draw all data from the Atlas, we draw off site sample locations with fluoride >6 mg/l as the priority data points to consider (particularly recognising these occurrences were not evident in our 1980–2014 archive). These number 37 fluoride samples. Extraction of the fluoride data herein may not include all fluoride data held by the MoAIWD, but this intensive data mining effort is expected to include the vast majority of data and certainly be representative at the geographical scales considered.

2.3 Review of fluorosis occurrence literature

In-keeping with SDGs and human health concerns posed by groundwater fluoride, cursory review of the published literature was undertaken to provide contextual evaluation of fluorosis incidence in Malawi. No attempt was made to collate health facility records.

2.4 Recent groundwater quality surveys by CJF

We augmented the collated archive dataset with fluoride data collected during CJF field surveys of rural hand-pumped borehole supplies from groundwater in Southern Malawi. This includes targeted sampling of hydrothermal groundwater including springs, the latter appearing not to have received focused attention in the literature since the early work of Kirkpatrick (1969). In June 2016 a survey was undertaken sampling 16 groundwater supplies in the dry season (Fraser, 2016), located in the Shire Basin superficial deposits aquifer, including near the Mwanza and Zomba main rift faults (Fig. 1), and included hydrothermal sites. Known and suspected hot springs and high-temperature boreholes were specifically targeted in our follow-up 2018 survey. 15 sites (10 springs, 2 boreholes and 3 artesian boreholes) were chosen near large rift faults and CAP intrusions in Blantyre, Chikwawa, Machinga, Ntechu and Zomba Districts (Robinson, 2018). These sites span a range of dominant lithologies:

superficial sediments of the rift valley underlain by Karoo sequences (4 sites), fractured Karoo sedimentary rocks (1), fractured Basement (8) and CAP igneous rocks (2).

Samples in 2018 were shipped to Scotland for analysis at the University of Strathclyde using ion chromatography (Metrohm 850 Professional IC). Samples in 2016 were collected in collaboration with the Malawi Bureau of Standards (MBS) and analysed in the field using a Thermo Scientific Orion Ion Selective Electrode. Supporting major and minor ions were also measured in the laboratory, and temperature, pH, EC and TDS (total dissolved solids) in the field where possible.

3 Results and Discussion

3.1 Overview of literature studies

At least 15 journal or formal report publications have presented fluoride occurrence data. Of these, four were reviews of general hydrogeology or groundwater quality presenting aspects of data from other previous studies (BGS, 2004; Chavula, 2012; Mapoma and Xie, 2014; UN, 1989). Of the remaining eleven publications, discussion of fluoride results was often limited, with notable exception of Bath (1980). We summarise these studies in Fig. 2, indicating their approximate geographic coverage and key fluoride data findings. We conveniently classify fluoride concentrations into four categories based around the WHO guideline values as outlined in Table 1.

Table 1. Summary of classifications for fluoride concentrations used in this study.

Classification	Fluoride Concentration (mg/l)
Low	0 - <1.5
Slightly Elevated (S. Elevated)	1.5 - <2
Elevated	2 - <6
Excessive	6 +

The earliest study presenting groundwater fluoride data is that of Kirkpatrick (1969) and would represent an early fluoride survey globally. Fluoride data collected by Kirkpatrick (1969) show excessive fluoride is strongly linked to “thermal springs” sources. Their hot-spring data (n = 15) display groundwater temperatures mostly between 32 °C and 54 °C with fluoride from 3 to 12 mg/l; however, their two very elevated temperature springs sampled at 65 °C to 78 °C likewise displayed very elevated fluoride at 17 mg/l and 20 mg/l respectively (we later plot their fluoride – temperature data alongside our own data); Both Kirkpatrick (1969) and later Bath

(1980) comment on this data, particularly at Nkhotakota where the spring(s) have been used for urban supply and where "cases of dental fluorosis have been identified".

The British Geological Survey (BGS) Report by Bath (1980) entitled 'Hydrochemistry in groundwater development: Report on an advisory visit to Malawi' provides the most insight and extracts an early archive data. It is discussed as a standalone section following.

Other studies present original data into local fluoride occurrence (Fig. 2), potentially driven by health concerns and-or fluoride treatment considerations. These identified problem areas in Nathenje, Machinga, Chikwawa and Nsanje (Fig. 2), and included assessing health risks to pupils at schools (Msonda, 2003; Sajidu et al., 2007; Sibale et al., 1998). A further two studies present data, but primarily examine removal of fluoride from groundwater (Masamba et al., 2005; Sajidu et al., 2008) and the final study presents fluoride data in a general water quality assessment of three areas in the Southern Region (Pritchard et al., 2008). Generally, our review found that previous work revealed that slightly elevated to elevated fluoride occurs in the superficial sediments of the rift valley and near Lake Chilwa in Southern Malawi. Excessive concentrations tend to occur where there is known hydrothermal activity, and or near major faults. With the exception of Kirkpatrick (1969), Mapoma et al. (2017) and Pritchard et al. (2008) the studies fail to report measurement of sampled groundwater temperatures and hence definitive relationships to hydrothermal groundwater contributions were not shown by these authors, nor were other controlling processes on fluoride occurrence explored in detail. Some cases of elevated fluoride have been recorded in the Central and Northern Regions (Bath, 1980; Kirkpatrick, 1969; Msonda, 2003; Msonda et al., 2007) and more recently by Mapoma et al. (2017). Most occurrence identified though is within Southern Malawi, albeit recognising much less data are available for the former regions.

Mapoma et al. (2017) represents the only relatively recent published fluoride data. Their analysis on fluoride occurrence is limited, suggesting dissolution of fluorite and fluoride-bearing lithologies via silicate weathering of Basement rock is the main control. All their samples have low fluoride concentrations with the exception of one location showing slightly elevated fluoride. They do not provide spatial coordinates. Pritchard et al. (2008) present shallow well, wet and dry season fluoride data for Balaka, Chikwawa and Zomba Districts. Only data from Chikwawa District had suitable corresponding temperature data and have been included in our later fluoride-temperature analysis. They state that Balaka and Chikwawa are problem areas for elevated and excessive fluoride, with limited exploration of fluoride source, suggesting that fluoride-bearing minerals and evaporative concentration are probable causes.

3.2 Bath (1980) survey and 1970–1980 Geological Survey (Malawi) archive

Fluoride data from the Bath (1980) report (including: 1970–1980 archive plus Bath (1980) survey data) on a box plot by WRA indicates WRAs 1F, 1G and 1H (Thyolo, Nsanje and Chikwawa Districts - all located in the Southern Region) contain excessive, albeit variable fluoride (Fig. SM1 – in the Supplementary materials (SM)). Recognising that sample numbers are variable, for example: 1H (n = 39); 1E (n = 1), overall, the dataset (n = 142) contains 73.2% low fluoride, 5.6% slightly elevated, 9.9% elevated, and 11.3% excessive fluoride with a mean of 2.16 ± 4.07 mg/l and median of 0.8 and 25th and 75th percentiles of 0.4 and 1.5 mg/l respectively. 94% of all elevated and excessive concentrations (n = 15) are located in the Southern Region.

The study by Bath (1980) allowed some insight into fluorite precipitation control upon fluoride in groundwater when elevated calcium was present, as well as elevated temperatures influence indicative of hydrothermal contributions to borehole groundwater. These data from Bath (1980) are incorporated within the data analysis sections that follow. Some further key points made by Bath (1980) relating to the c. 1970–80 archive include:

- On occurrence: high fluoride concentrations, many >2 mg/l and a few around 10 mg/l are reported for the clay-sand superficial and weathered gneiss aquifers in the LSB; “anomalous” (meaning high) fluoride attributed to hydrothermal mineralisation (e.g. 8 mg/l around Nantana, Namamblo Fault system), recognising the general need to better identify deep-seated groundwater flow components to surface; and, low (<1 mg/l) fluoride in some weathered gneiss catchments contrasting with the LSB raises (if analytical data are correct) the question as to whether different pre-cursor lithologies for the gneisses in different locations account for fluoride variations;
- The reliability of fluoride concentrations reported “are somewhat suspect”, due to some typographical errors (e.g. omitted decimal points), reliability of the colourimetric method historically used, sometimes very poor ion balances, and notably the lack of an inverse correlation between high fluoride and low calcium for some samples expected from fluorite equilibrium control (see later);

- A recommendation that the possibility of elevated fluoride requires confirmation via new (in 1980) specific ion electrode analysis;
- Regarding fluoride sources and elevated concentrations, possibilities muted requiring proving were: breakdown of hornblende amphibole and biotite constituent phases of gneisses containing fluoride replacing –OH in the crystal lattice; same sources responsible for high salinity in the Karoo (and Laputa) sediments and the need to examine chloride – fluoride correlations; complexing of fluoride in saline solutions allowing fluorite effective solubility to increase with salinity;
- Prime targets for suspected high fluoride are those groundwaters of low calcium, i.e. Na-HCO3 and NaCl type composition.

Bath (1980) concludes “Further investigations of the magnitude of the fluoride problem are obviously required in view of the paucity of reliable data presently available”. We return to the progress made on this recommendation in our conclusion.

3.3 MoAIWD 1980–2014 archive data

The MoAIWD 1980–2014 archive fluoride dataset with spatial coordinates and ion balances within 5% (n = 1034) and additional Atlas MoAIWD (2018) archive data (n = 37) is presented for the Southern Region in Fig. 3. Groundwater supplies with fluoride meeting the current WHO 1.5 mg/l guideline are geographically widespread across all lithologies indicating low fluoride groundwater is often locally present, or available in the near vicinity. ‘Troublesome’ slightly elevated concentrations (1.5–<2 mg/l) though can also be quite widespread and are particularly prevalent across the more northern part of Southern Malawi. This location corresponds to areas where the rift valley floor is not submerged beneath Lake Malawi and instead forms plains on land. Prevalence of slightly elevated fluoride tends to occur on the fringes of superficial sediments of the rift valley and along the strike of main rift faults in Basement rock. Elevated fluoride at 2–<6 mg/l almost exclusively occurs in the superficial sediments of the rift valley, and most apparent in the most southern section of SB and, or in proximity to large rift faults with occurrences distributed throughout Southern Malawi. Excessive fluoride (>6 mg/l) is found around the Blantyre area – Zomba fault in the Basement uplands between the northern and southern portions of the rift valley (Fig. 1) and within the rift valley southern portion - LSB (Fig. 3). The (geological) controls upon the spatial occurrence of fluoride are discussed later for the entirety of fluoride data assembled.

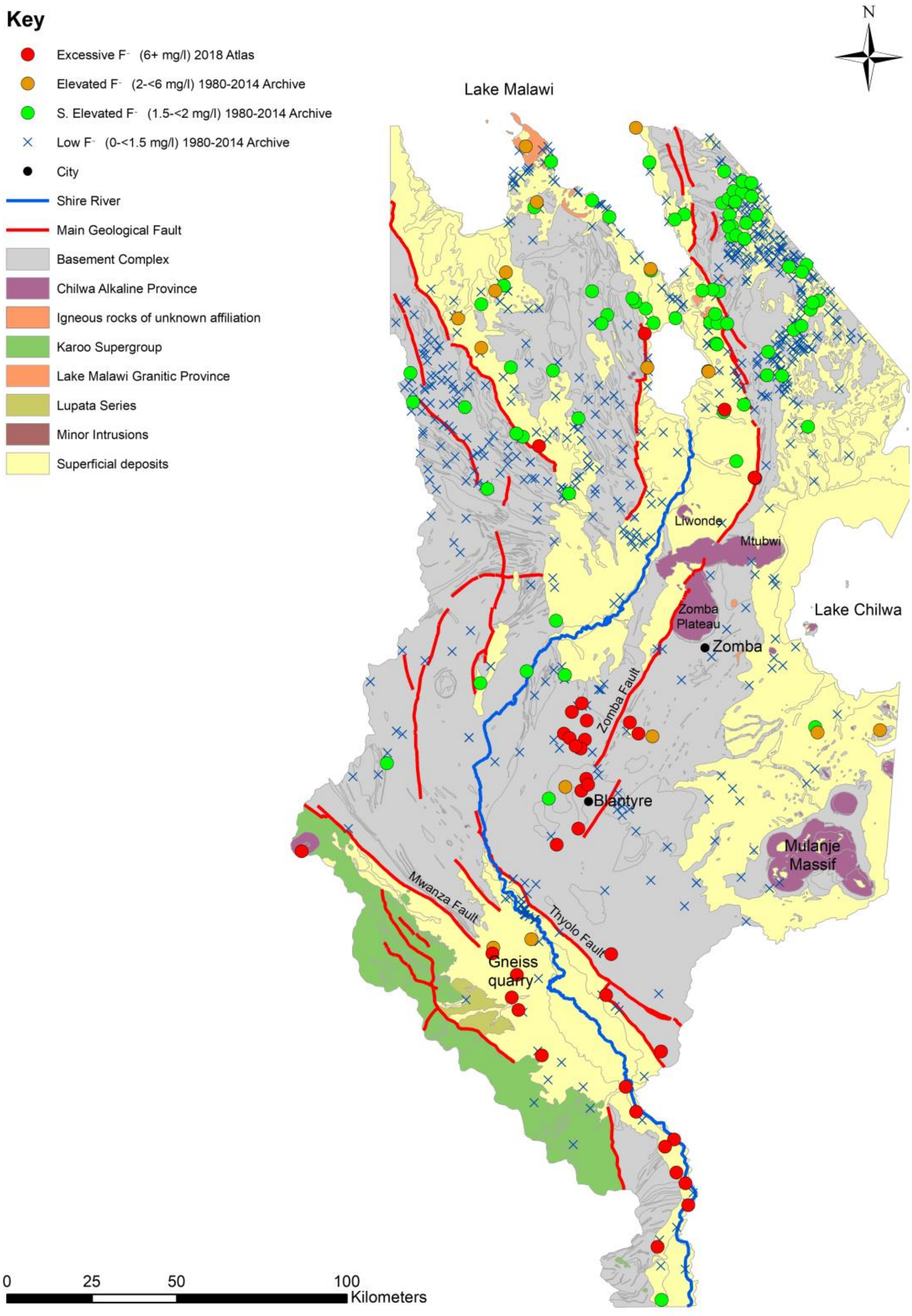


Figure. 3. Groundwater fluoride occurrence in Southern Malawi based on data extracted from the MoAIWD's 1980–2014 archive (*n* = 1034 samples), with additional data extracted from the MoAIWD (2019) Atlas (*n* = 37).

The MoAIWD archive data, whilst fragmented, does provide some opportunity to assess hydrochemical controls. For example, under fluorite precipitation control, an inverse relationship between fluoride and calcium is expected, low fluoride being thermodynamically predicted when calcium activities increase. This relationship is generally observed for both archive data sets and the Bath, 1980 survey data in Fig. 4, but with the 1970–80 archive data having excessive fluoride (6–31 mg/l) also displaying anomalously elevated calcium (c. 40–135 mg/l). Bath (1980) highlights this anomaly stating that a solution with 40 mg/l calcium should only in fact sustain 3 mg/l fluoride where there is solubility thermodynamic control by fluorite (CaF2) equilibration (see later figures for quantification of this equilibration control across the concentration range). Although salinity related complexing of fluoride could be influential, there are reservations expressed by Bath (1980) over both the colorimetric chemical analysis methods used historically for that archive and poor ion balances in some samples (where sufficient major ion data allowed balance calculation) and hence it is conceivable analytical errors may exist in both fluoride and calcium archive concentration data.

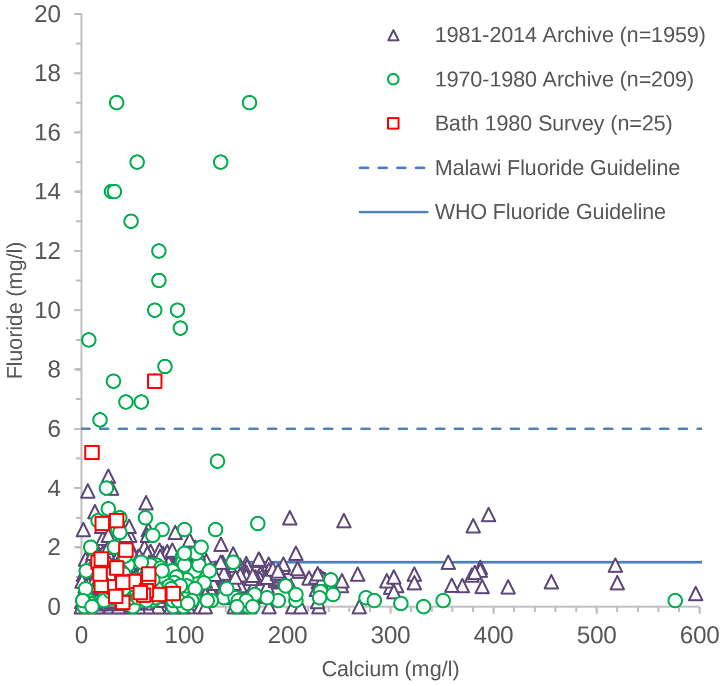


Figure. 4. Plot of fluoride versus calcium for all historical data passing QA/QC checks (y-axis truncated, one 1970–1980 archive data point not visible: fluoride = 31 mg/l, calcium = 108 mg/l).

3.4 CJF Programme data 2016–18 survey results

3.4.1 Groundwater temperature influence

Groundwater temperature data collected in our 2016 and 2018 surveys are shown to be important and confirm that increased fluoride occurs with increased groundwater temperature. This is evident in our data in Fig. 5 plotted together with all historical fluoride data. Excessive fluoride over 6 mg/l in the Southern Region was only found at elevated temperature, over 32 °C, with the exception of two locations, one is notably the only locality not directly related to the rift valley (Kirkpatrick, 1969), and the other is located in a shallow well in the superficial sediments of the rift valley (Pritchard et al., 2008), therefore vulnerable to surface processes and not necessarily representative of hydrothermal groundwater. By way of comparison, groundwater temperatures in Malawi are not significantly impacted by deep geothermal sources and appear typically around 20–30 °C (e.g. unpublished data (n = 284) for the Lake Chilwa catchment exhibit a mean groundwater temperature of 26.4 ± 1.9 °C and a range of 21.1–32.1 °C). Importantly, all of the >6 mg/l fluoride and >32 °C temperatures related to 'hot spring' samples (Fig. 5 filled symbols); none of the boreholes sampled with temperature data contained excessive fluoride, nor temperatures exceeding 32 °C. Boreholes with 'troublesome' fluoride concentrations between the present and former WHO (current Malawi) guidelines at 1.5–6 mg/l display groundwater temperatures that largely group in the range 26–31 °C, very similar to the temperature range displayed by the bulk of <1.5 mg/l fluoride data. Thermal springs sampled by Kirkpatrick (1969) had some 'troublesome' fluoride concentrations above 32 °C but none below the WHO guideline. Some of the lowest fluoride samples were from groundwater with the lowest temperatures (Fig. 5). Kirkpatrick (1969) data were plotted with Southern Region samples separate from other regions due to differing (hydro) geological conditions (Fig. 5).

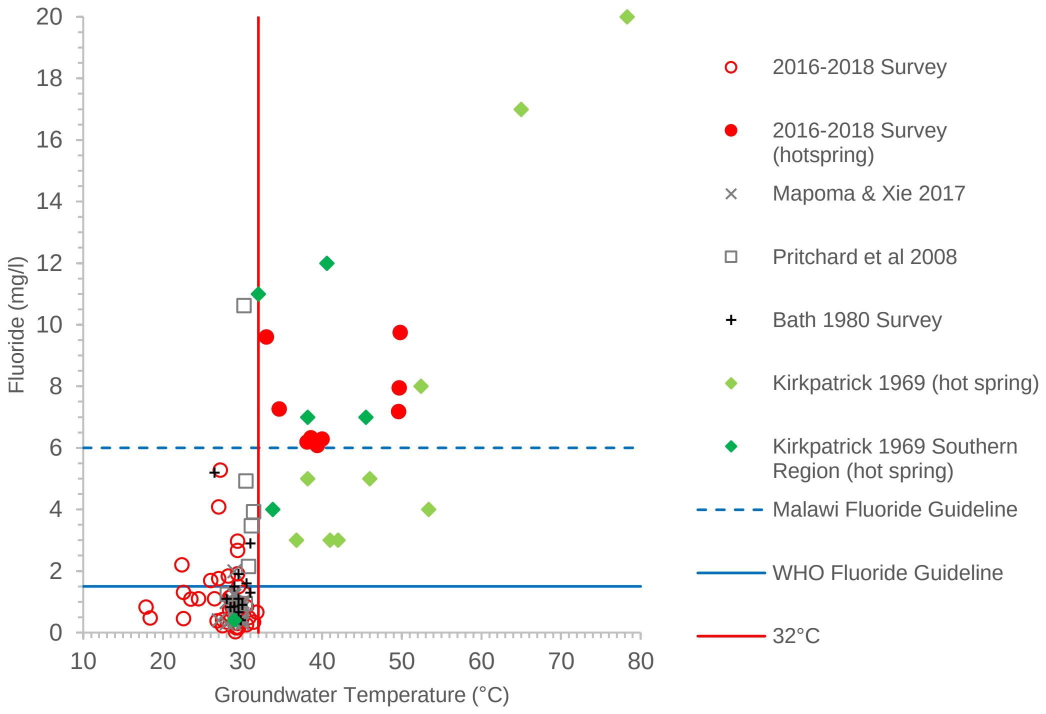


Figure. 5. Plot of groundwater fluoride versus groundwater temperature of all data collected in our 2016–18 surveys and historical data. Filled symbols correspond to spring samples, otherwise all other data relate to borehole samples.

From a policy and management perspective the Fig. 5 data suggest that elevated temperatures (>32 °C) alone may be used as a screening tool to indicate excessive fluoride above the former WHO (current Malawi) guideline in the Southern Region. However, it would not be possible to identify risks from groundwater concentrations in the 1.5–6 mg/l fluoride by using temperature as a proxy indicator. A key issue is whether the fluoride concentrations detected in this range are arising from geochemical reactions such as Na/Ca ion exchange and concurrent calcite and fluorite equilibrium in alluvial aquifers, or as hydrothermal groundwater components contributing to the borehole flows with dilution of both fluoride and temperature by mixing with shallower groundwater of lower fluoride and temperature, or if the fluoride is of other provenance. Detailed geochemical study and modelling is advised to underpin a revised policy/limit for fluoride in Malawi but is out with the scope of this publication. Overall, Fig. 5 does very much point to the control of increased hydrothermal groundwater contents upon increased fluoride risk, and also the risk posed by hot springs being used in water supply where deep-seated hydrothermal flows form a significant proportion of those discharges.

3.4.2 Hydrochemical observations

Our scope is not to consider detailed modelling of hydrochemical controls upon groundwater fluoride occurrence, but to present key policy relevant observations of our 2016–18 survey data together with relevant historical data. In summary, the geochemical data are consistent with a reaction scheme of proton loss through primary silicate dissolution of (sodium) alumino-silicates (e.g. Na-feldspar), leading to dissociation of bicarbonate and increased carbonate and acidity favouring calcite precipitation with sodium for calcium Na/Ca ion exchange resulting in removal of calcium from water and increased potential for fluorite to dissolve with resulting groundwater fluoride increase (Nordstrom and Jenne, 1977). Increased fluoride displays a somewhat scattered relationship with increasing pH (Fig. 6). Excessive fluoride within our hot-spring samples and in the literature study samples of Sajidu et al., 2007, Sajidu et al., 2008 and Kirkpatrick (1969) display pH towards the higher range from around 7.2 up to 9.6 with values over pH 8.9 only found in samples with excessive fluoride in the Southern Region. Dissolution of alumino-silicates (weathering) we assume is responsible for increases in pH and alkalinity. pH values in the range 7.6–8.6 are shown to be most favorable to fluorite dissolution (Saxena and Ahmed, 2001), therefore, samples in Fig. 6 may relate to lithologies or sediments where fluorite is able to dissolve. Samples taken by Sajidu et al., 2007, Sajidu et al., 2008 are from either Basement rock or rift valley basin locations in the Southern Region (Fig. 2). Their 2007 samples particularly lie close to known locations of hot springs at Liwonde and on the Zomba escarpment/plateau. Samples with higher fluoride concentrations and pH values in Fig. 6 may perhaps relate to other factors including; increased groundwater temperature which also favours increased solubility of fluorite (Edmunds and Smedley, 2013) and increased residence time. Groundwater with fluoride in the ‘troublesome’ 1.5–6 mg/l range is not easily diagnostic from its intermediate pH of 7 to 8.5 (perhaps excepting samples towards 8–8.5) in that this range is commonly found in samples with fluoride both above and below these concentrations. Very low fluoride though, below 0.5 mg/l, is frequently, but not always, characterised by low pH, c. 5.8–6.6.

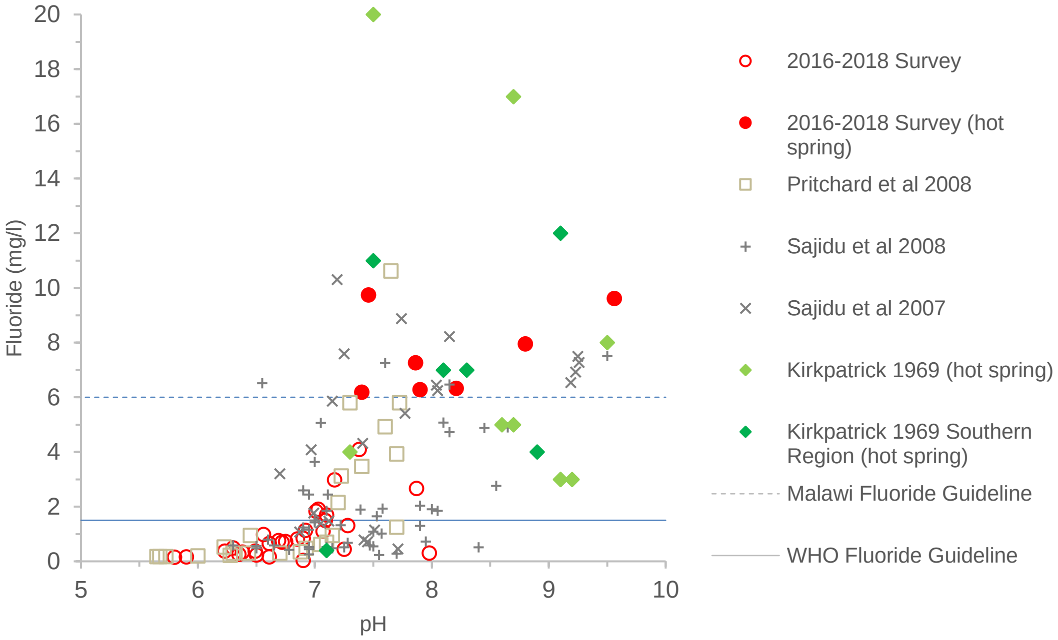


Figure. 6. Plot of groundwater fluoride versus pH of data collected in our 2016–18 surveys and available literature data in Malawi. Filled symbols correspond to hot spring samples, otherwise all other data relate to borehole samples.

Our 2016–2018 survey data provides good opportunity to revisit the fluoride – calcium relationship and fluorite solubility control, our data are shown in Fig. 7 superimposed upon the archive data previously presented in Fig. 4. Our 2016–2018 data, similar to the archive data display greatest fluoride concentrations with low calcium and where calcium concentrations are elevated fluoride is low. The data are banded where possible to display the possible groundwater temperature control, warmer colours corresponding to increased temperatures (temperatures were not available for archive data plotted in grey). A somewhat scattered relationship is observed with all temperature ranges with the exception of >35 °C, where all samples plot with excessive fluoride and low calcium (<40 mg/l). These also all relate to hot spring samples.

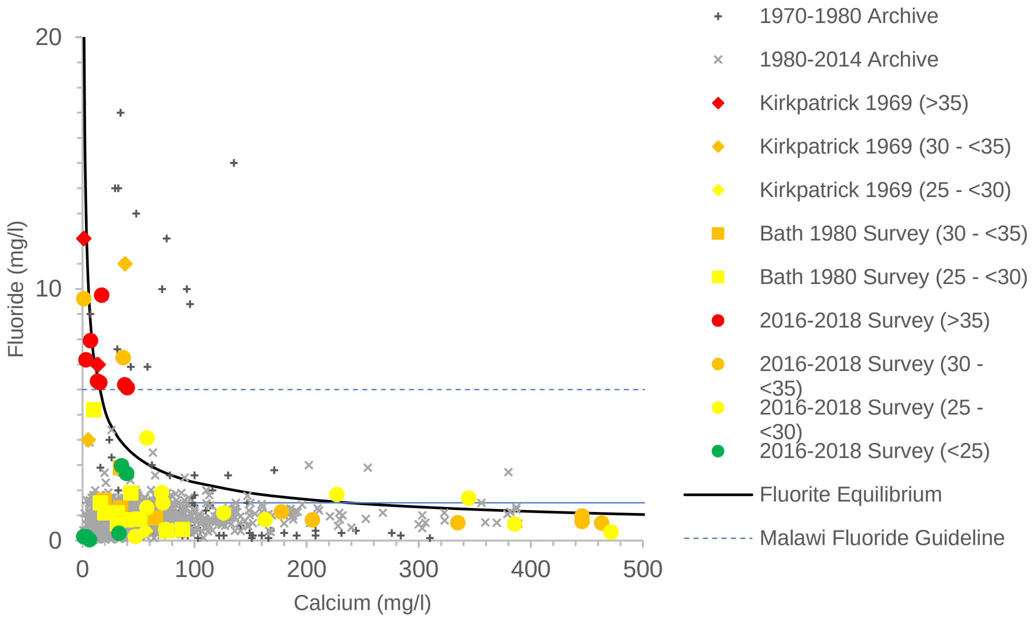


Figure. 7. Plot of groundwater fluoride versus Ca of data collected in our 2016–18 surveys and available literature study data in Malawi. Coloured symbols correspond to temperature ranges, grey symbols correspond to samples where temperature data was not available.

The equilibrium curve indicates the concentrations of calcium and fluorite at which fluorite (CaF_2) saturation would be predicted to occur is also shown in Fig. 7 (based on an equilibrium constant of 3.70 × 10^{-11} (Chemistry LibreTexts, 2017)). The data as a whole generally follow the hyperbolic trend confirming the significance of fluorite saturation control. Most data plot below the equilibrium curve indicating samples are mostly undersaturated with respect to fluorite (CaF_2). Where data are plotting above the equilibrium line indicating an apparent over-saturation, those samples from our 2016–18 survey data are not unduly over that line and still reasonably follow the hyperbolic trend. It is only the 1970–80 archive data with markedly high fluoride concentrations that plot substantially above the equilibrium line.

The same data are plotted in Fig. 8 to more quantitatively indicate the degree to which apparent saturation is exceeded. The envelope of saturation indices (SI) for fluorite calculated display an initial rapid increase in values up to c. 3 mg/l fluoride reaching a SI around zero (i.e. saturated equilibrium value) and thereafter a more gradual rise with data in the 1970–80 archive trending up to apparent saturations for the higher fluoride concentrations. Otherwise, the remaining data, i.e. our 2016–18 survey and the Kirkpatrick (1969), trend up to SI values of around 1. A detailed geochemical study is needed across Malawi given the data displays progressive trends, those breaching of the equilibrium curve may relate to analytical errors in the data, particularly the 1970–1980 archive dataset. Concerns over some of these data were expressed by Bath (1980), noting the use of less preferred analytical methods, some ion balance issues, typographical errors (e.g. omitted decimal points) and a less obvious inverse relationship of fluoride with calcium displayed. We concur that those archive data attract the most caution and potential qualification in the data interpretation.

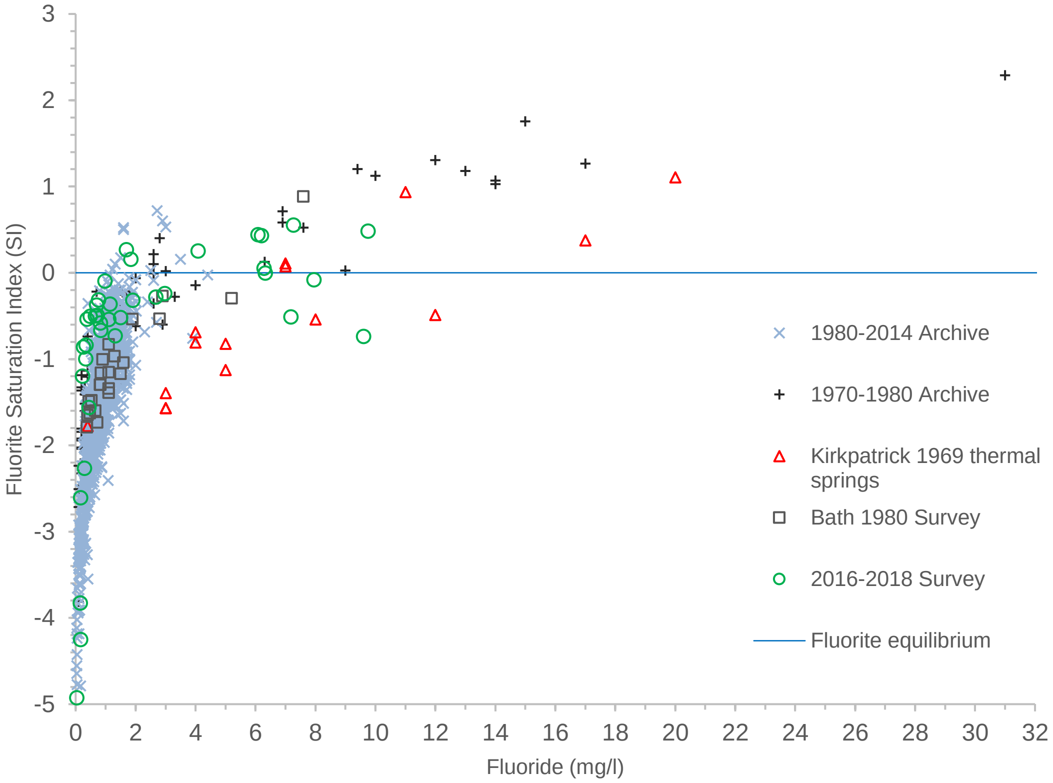


Figure. 8. Plot of groundwater fluoride versus saturation indices for fluorite which have been plotted per study for simplicity.

Groundwater from a hot spring with low salinity may be attractive to drink, especially in Southern Malawi where saline groundwater used for drinking is a concern (Monjerezi et al., 2011; Monjerezi and Ngongondo, 2012; Rivett et al., 2018a). From a policy and management perspective, this is problematic as once cooled, hot spring water may be pleasant to drink but would hide other naturally occurring health risks which are tasteless. Rivett et al. (2018b) found arsenic was elevated on the hot spring 2016–2018 survey sites. Our analysis of the fluoride data indicates that these sites also host the most excessive fluoride concentrations. These hot spring sites, if used regularly for drinking, pose significant health risks which may be not be known to those at risk. The findings do point to the policy and management opportunity of good measurements at the well head; temperature, pH, arsenic and fluoride may all be, or should be recorded at site and together would point to the health risks at site without resorting to off-site analysis at a laboratory.

3.5 Geological controls upon fluoride spatial distributions – all data

Geological controls upon the spatial distribution of all fluoride data with quantified concentration data with coordinates obtained from the archive literature (incl. >6 mg/l data points from the MoAIWD (2018) atlas) and 2016–18 CJF surveys is illustrated in Fig. 9 for Southern Malawi (*n* = 1143). It is notable that low fluoride groundwater supply can be extensively obtained across Malawi, and importantly in proximity to areas containing higher concentrations indicating concentrations can be locally heterogeneous. Some areas, notably eastwards from Blantyre in both Basement and superficial deposits removed from the rift valley, are extensively low fluoride. However, most areas regionally exhibit some fluoride occurrence above the 1.5 mg/l current WHO guideline. Slightly elevated fluoride occurs in Basement rock around the margins of the rift valley superficial aquifers (confined by rift faults); they are most apparent regionally across the northern part of the Fig. 9 study area to the south of Lake Malawi. The area is moderately faulted with a complex mix of Basement rock and superficial aquifer occurrences oriented north south.

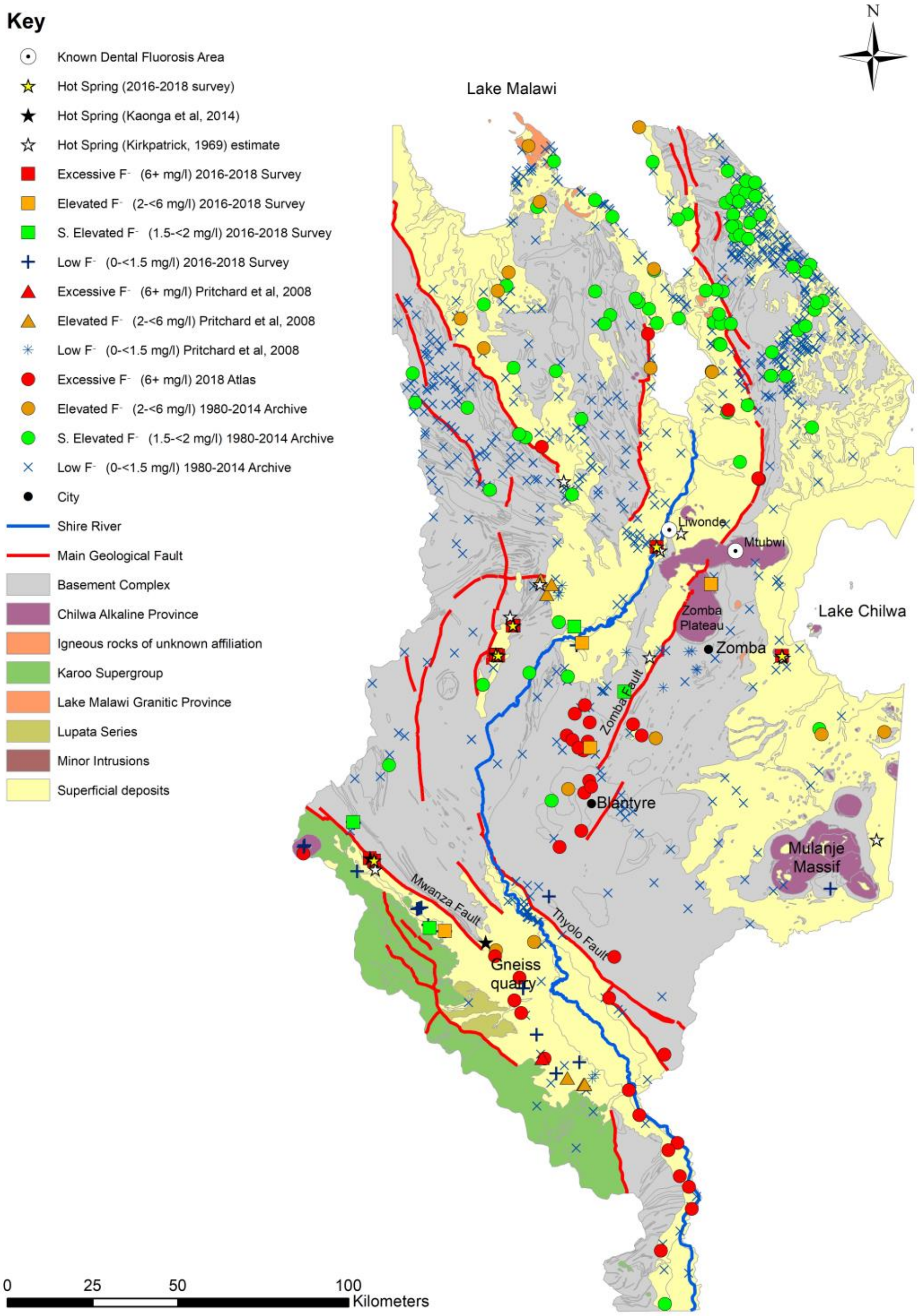


Figure. 9. Groundwater fluoride occurrence in Southern Malawi based on Fig. 3, with the addition of our 2016–2018 survey samples (*n* = 48) and hot spring locations (*n* = 9), Kirkpatrick (1969) "thermal spring" samples (*n* = 15), Pritchard et al. (2008) shallow well samples (*n* = 24) and Kaonga et al. (2014) hot spring locations which differ from those identified by Kirkpatrick (1969) (*n* = 2).

Considering higher concentrations, elevated fluoride occurs almost exclusively within the rift valley deposits, with only four exceptions in Basement rock, one on a contact between Basement rock and the Zomba Plateau intrusion and one in superficial sediments on the Eastern flank of the Mulanje Massif (Fig. 9). Elevated and excessive fluoride tends to occur in a north-south Z-shaped band of the rift valley with some occurrences somewhat south of Lake Malawi in the alluvial superficial deposits, but most occurrences in the Basement rock around Blantyre - southern extreme of the Zomba fault, or else occur towards the margins of the superficial deposits in the Lower Shire Basin nearing the contacts with the Basement complex or Karoo or Lupata series.

Of the excessive fluoride concentrations measured by our 2016–2018 survey, seven of nine are located at hot springs, with the remaining two at boreholes located in very close proximity to a hot spring and potentially receiving components of the deep groundwater flow system contributing to those springs. Similarly, excessive fluoride concentrations measured by Kirkpatrick (1969) derive from thermal springs. Excessive fluoride samples reported by MoAIWD (2019) appear to follow the strike of main rift faults, either on faults or adjacent to them in the rift valley, as do those of Pritchard et al. (2008). The cluster of excessive concentrations north of Blantyre is likely connected to the rift faults at that location. The Zomba Fault, for instance, is an extensional normal fault associated with the EARS and is a prime candidate for structural facilitation of deep groundwater flows to surface. Excessive concentrations also manifest in a line where the Mwanza fault may be buried beneath rift valley sediments in the west of the LSB inferring the fault may continue for some distance under the sediments. The association of excessive fluoride with geothermal waters and predominantly springs shows the significant control of geological structure; fluoride risk appears highest where structure permits deep-seated groundwater flows to reach (near) surface.

Hydrochemical controls may be expected to further influence the local – regional fluoride distributions and the variation in fluoride detailed occurrence in Fig. 9. Generalisations to consider include groundwater flows generally south/eastwards towards the lowland Shire River with ion exchange of calcium for sodium, creating more NaHCO3 and NaCl dominant water types of higher TDS (Monjerezi et al., 2011; Rivett et al., 2018a). Given the dependence of fluoride on calcium (fluorite dissolution/precipitation), its exchange removal may facilitate increased groundwater fluoride as older rift valley groundwater approaches the river – lowland discharge areas. Shallow groundwater here is vulnerable to phreatic evaporation during the dry season, further concentrating any fluoride present. Such processes could account for elevated fluoride in the nearer river, rift valley sediments. Towards margins of the rift valley sediments where minimum ion exchange for sodium has occurred, groundwater saturated with calcium may potentially have lowered fluoride via fluorite precipitation.

3.6 Summary statistics of fluoride occurrence – all data

Summary fluoride data statistics for Southern, Central, Northern and all Malawi for all quantified concentrations obtained are provided in Table 2 (this includes CJF and literature data, including data where regional location, but not exact coordinates are known). The percentage of data within the Regions is dominated by Southern at 94.1% compared to just 0.7% for Central and 5.1% for Northern. Whilst there is occurrence of some elevated (n = 8) concentrations and excessive (n = 4) concentrations in the latter two regions, the low sample numbers preclude conclusions being drawn on these regions, albeit pointing to the need for further fluoride survey data. Statistics for Southern Malawi (n = 1285) are more meaningful and indicate some 83% of samples were low, below the 1.5 mg/l WHO limit. Hence for the vast majority of water supply boreholes fluoride appears an insignificant issue. Combining slightly elevated and elevated fluoride occurrences encompassing the 'troublesome' 1.5–6 mg/l range between current WHO and current Malawi guidelines, around 14% of sampled groundwater supplies fall in this category. Excessive fluoride, above the current Malawi guideline occurs in a little over 3% of sampled groundwaters. Hence overall, generally fluoride in groundwater appears not to be an issue for the great majority of groundwater supplies, but certainly not all.

Table 2. Summary of all fluoride concentration data obtained.

Malawi Region	n	mean	25th Percentile	Median	75th Percentile	Fluoride (mg/l)			
						Low (0-<1.5)	Slightly Elevated (1.5 – <2)	Elevated (2 – <6)	Excessive (6 +)
Northern	70	1.13	0.3	0.45	0.9	85.71%	1.43%	11.43%	1.43%
Central	10	3.6	0.3	0.5	0.6	70%	0%	0%	30%
Southern	1285	1.22	0.5	0.81	1.23	82.88%	9.26%	4.51%	3.35%
All	1365	1.23	0.48	0.8	1.22	82.93%	8.79%	4.84%	3.44%

3.7 Fluorosis occurrence

There are some evidences in the literature of localised occurrence of dental fluorosis; where locations of incidences are sufficiently known, these are marked on Fig. 9. Historical incidences are evident, for instance Bath (1980) comments on

Kirkpatrick (1969) data stating; "this has been of particular concern at Nkhotakota where the spring has been used for urban supply and where cases of dental fluorosis have been identified". Msonda (2003) in a study in the Nsanje District found 'a positive correlation between prevalence of dental fluorosis in children and fluoride concentrations in groundwater. Sajidu et al. (2007) published dental fluorosis data for four schools in Machinga District documenting dental fluorosis in school pupils aged 8–9 from four schools: Liwonde LEA, Mtubwi FP, Mombe FP and Mmanga FP in the Southern Region. Mmanga FP school was reported to have minimal dental fluorosis cases, 13.2% of pupils showing symptoms. The other three schools had much higher incidence, with Mtubwi FP school being the highest at 52.6% of pupils. Locations of the two worst-affected schools are plotted in Fig. 9 and are proximal to some of the groundwater points - hot springs with the most excessive fluoride. Mtubwi FP School is located on the aforementioned Zomba fault escarpment on a large nepheline-syenite CAP intrusion and Liwonde LEA School is located west of the escarpment on superficial sediments in the centre of the rift valley.

Additional to the above studies that documented dental fluorosis, three more reported locations as having known or visible signs of the condition. Sibale et al. (1998) reported on Nsanje that "visible signs of dental fluorosis are common in this district" (Sibale et al., 1998). Other locations reported as having cases of fluorosis were Liwonde, Machinga and Nathenje (Sajidu et al., 2007, Sajidu et al., 2008; Msonda, 2003). This study confirms that of the areas mentioned in the literature as having dental fluorosis; Nsanje, Liwonde, Ulongwe, Mtubwi and Machinga, which are located in the Southern Region (Fig. 2) are vulnerable, as each have numerous locations nearby where elevated and excessive fluoride has been measured (Fig. 9).

It is unknown how many people in Malawi are affected by fluorosis, but this study has shown that there is a potential for fluorosis not only in the Southern Region, but within other regions of Malawi, particularly where there is rift activity. Affected numbers could well be in the tens or hundreds of thousands. The Malawi Gov't standard is one rural water point for each 250 persons; for the data in Table 2 it suggests for just those measured water points in this paper there are 282,999 persons using water supplies with fluoride above the WHO drinking water guideline, but without proper investigation the total remains speculative. Whilst fluorosis incidence may currently be overlooked in their wider and more pressing health concerns, such as HIV, malaria etc., developing countries with fluoritic groundwater will come under increasing pressure to address fluorosis incidence in the wake of the recent UN Joint Monitoring Programme

(JMP) classification as a main chemical contaminant of concern. Whilst fluorosis may not be a direct cause of death, potential secondary causes of death, such as untreated infection from damaged teeth or bones caused by fluorosis, remain unknown and of concern.

Further research into the prevalence of dental fluorosis in Malawi, particularly in the Southern Region is recommended as it may provide an additional proxy for locating fluoride hotspots. Dental fluorosis locations plotted onto geology correlates with excessive fluoride areas (Fig. 9). Correlations between elevated fluoride and dental fluorosis have been reported in Malawi literature (Msonda, 2003; Sajidu et al., 2007), although these studies are very localised and sparse. Whilst they present a clear relationship between fluoride chemistry and human health, they illustrate the need for further investigation.

3.8 Considerations from the wider East African Rift System

Elevated fluoride is documented throughout the EARS extent beyond Malawi. Concentrations of 10 mg/l are common in Ethiopia and are greatest near the rift where they can be 200–300 mg/l (Chavula, 2012). Both Kenya and Tanzania have reports of elevated concentrations which also tend to be highest at or near the rift (Ghiglieri et al., 2012; Nair et al., 1984). Rift-related alkaline intrusions are a recognised fluoride source throughout the EARS. They have been shown to produce significant fluoride concentrations in the Kenya rift valley which forms the lower section of the eastern branch of the EARS (Fig. 1) (Nair et al., 1984). Such intrusions occur across both branches of the EARS and have also been shown to contribute significant fluoride concentrations in Tanzania on the western branch (Ghiglieri et al., 2012). Although the western branch discharges an order of magnitude less heat than the more volcanically active eastern branch (Hochstein, 2005), significant hydrothermal systems are still in place.

Malawi hosts such lithologies which occur in the form of CAP intrusions in the Southern Region. Data here, however, are insufficient to draw conclusions around CAP intrusions as a fluoride source in the study area. Our 2016–18 survey only sampled two excessive fluoride locations proximal to a CAP lithology, both at the contact between the Zomba Plateau intrusion and the host Basement complex. These locations likely receive significant hydrothermal contributions related to the Zomba fault which may mask specific fluoride signatures caused by interaction with the intrusions. Kirkpatrick (1969) sampled one location on the eastern flank of the Mulanje Massif which is the only location in the Southern Region with elevated fluoride proximal to a CAP intrusion but not close to a rift fault (Fig. 9). This location appears as anomaly in plots of fluoride versus groundwater temperature and pH (Fig. 5, Fig. 6 respectively) which may indicate a more accurate chemical signature from interaction with CAP intrusions. Further sampling is recommended to examine the hydrochemistry around Malawi's CAP intrusions.

Nair et al. (1984) observed elevated fluoride groundwater in Kenya's Rift Valley caused by precipitation and dissolution of fluorite in limestones surrounding igneous rocks associated with the initial phases of rifting. It is therefore recommended that fluorite occurrence close to CAP intrusions and carbonatites are examined in Southern Malawi. Carter and Bennett (1973) reported significant fluorite occurrences around carbonatite cores in the Southern Region, particularly around Chilwa Island where the mineral runs in bands up to 50 m long. This would be a good starting point for geochemical investigation.

Bath (1980) proposes that hydrothermal mineralisation along major fault systems may be a source of fluoride. This may be particularly true in the LSB which forms the southern section of the Malawi Rift. Fluorite associated with low temperature hydrothermal systems will precipitate in veins during a cooling period following intrusion (Ackerman, 2005; Magotra et al., 2017). A post-emplacement cooling period led to the formation of fluorite-cemented breccia pipes in the Gallinas Mountains of New Mexico, USA. (William-Jones et al., 2000), the Southern Malawi context for this environment being the post CAP intrusion cooling period in the Lower Cretaceous. Emplacement of alkaline intrusions is, therefore, recognised as proxy locations for fluorite. Weathering of this material, accumulating in rift valley aquifers may account for some elevated fluoride we see in our 2016–18 survey samples and also both archive datasets. Detrital fluorite within sedimentary lithotypes was identified as a source of fluoride further north in the EARS on the NE slope of Mount Meru, Tanzania, proving at least that the process is present within the system, albeit further north where there is still active volcanism (Ghiglieri et al., 2012).

Elevated fluoride does not appear to be homogeneous within the rift valley in the study area. Our study revealed a biotite gneiss quarry located south of Chikwawa within rift valley sediments of the LSB, along the strike of the Mwanza fault (Fig. 9). The quarry was covered by less than a metre of alluvium, indicating that sediments are often not as deep as expected within the basin, at least in the LSB. Back-tilted, extensional block-faulting occurring beneath rift valley sediments may partition sections of basin sediments. This process has been shown to occur further north in Egypt's Suez rift valley (Withjack et al., 2002) so it is reasonable to infer that a similar structure may be present beneath the rift valley sediments of the study area. This coupled with evaporative concentration may create isolated, structurally controlled shallow aquifer units with locally variable fluoride concentrations.

4 Policy and management implications

The study gives rise to policy and management implications for fluoride in water supplies across Malawi. These are simply listed below with brief elaboration, but with the perception there is commonality of issues to parts of the wider developing world:

- Retention of national guidelines at the former WHO guideline rather than adopting the lower current WHO drinking water guideline is likely to come under increasing scrutiny, especially if concentrations in the 1.5–6 mg/l are shown prevalent, and more so if cases of (dental) fluorosis become apparent. Proving the typically more diffuse provenance of such concentrations is perceived onerous compared to more elevated concentration, hot-spot occurrence.
- Documentation of the fluoride problem in Malawi is of a fairly moderate standard, especially considering its potential rift valley related vulnerability, occurrences of elevated fluoride and some fluorosis cases have been long known; there is need to better spatially assess and monitor trends in identified localities of concern with increased monitoring and data sharing by sectors, e.g. NGOs at water-point commissioning, the Ministry via groundwater quality networks that require sustainable revenue to resource.
- Chemical analysis laboratory facilities in Malawi require significant investment and modernisation; colorimetric – wet chemistry methods have remained common to date in Ministry laboratories that have lacked modern analysis equipment or resource to keep operative. Equipping laboratories with modern techniques such as ion chromatography would provide more robust data sets and would allow for less uncertainty when modelling hydrochemistry. A more systematic approach to groundwater monitoring and data collection and analysis is necessary for Malawi, particularly in the current SDG climate.

- Diagnosis of dental fluorosis is likely limited for the aforementioned reasons (e.g. few dentists); there is need to more fully document its prevalence and linking of cases to water supplies and to raise community awareness. This could be achieved by appointing more local dentists nationally who can educate on the effects of fluorosis whilst gathering data and documenting cases.
- Our evidences are that fluoride (and arsenic – Rivett et al., 2018a, Rivett et al., 2018b) can be elevated in groundwater that is of low, and acceptable salinity; in that high salinity taste often acts as a deterrent to drinking water in the absence of analysis, this 'safeguard' is potentially removed.
- Data from this study confirms there is significant opportunity to screen health risks at the well-head without resort to sophisticated laboratories given investment in field probes or test kits to measure fluoride, arsenic, and indicator metrics of elevated temperature and pH.
- Rift structure controls: there is a need to better understand the controls of locality variation within the rift valley system upon the occurrence of fluoride at all scales; whilst the mapping of 'hot-springs' is easily undertaken the mapping of geological vulnerability due to faulting intensities – geological conditions should be increased to aid (hydro)geological conceptualisation of occurrences.
- Hydrochemical controls: there are needs for the increased use of field measurements (minor/major ions and isotopes), laboratory (batch) experiments and geochemical modelling to better understand the hydrochemical controls on fluoride occurrence, with local sensitivities expected.
- Human vulnerability to fluoride from groundwater must be assessed in terms of area. Once sources are identified, an assessment of vulnerability of the immediate and surrounding area should be quantified with respect to population density and distance from source. This will increase the ability to manage risk from fluoride going forward. This may be achieved plotting water point and population data into GIS and calculating (or estimating) numbers of people potentially affected by each waterpoint. This would be very useful for informing policy makers.
- Management response to fluoride problem areas needs to be developed to understand the scales and nature of response required and the availability of

options to ameliorate problems; e.g. is the problem fixed by a new borehole nearby, or are larger projects required with remote water (pipeline) import.

5 Conclusions

This study found that limited research has been undertaken to understanding the specific processes controlling fluoride provenance in Malawi's groundwater. Our conclusion from review of the literature and archive data on fluoride in Malawi's groundwater, is the conclusion by Bath (1980) that “Further investigations of the magnitude of the fluoride problem are obviously required in view of the paucity of reliable data presently available” still, some forty years later, has some validity. Whilst it is recognised advance has been made in terms of documenting fluoride occurrence and fluorosis, the advance in knowledge base has been modest. Comparatively few dedicated studies exist and those that have taken place have been small and locally focused, with the extent of the problem at all scales up to national level only moderately documented. There has been significant shortfall in the resourcing of groundwater quality monitoring networks and establishing laboratories with modern facilities that allow assessment of the fluoride problem with confidence. There is reasonably sufficient data to believe that fluoride is less pervasive or acute problem in Malawi than in other parts of East African Rift System but it is clear that fluoride in groundwater supplies is an issue to be addressed under Sustainable Development Goal 6 for Malawi. This study gives rise to a range of identified implications in Malawi for fluoride assessment, policy changes and management, with some anticipated to have wider validity across the developing world.

The former WHO 6 mg/l guideline for drinking water is still applied in Malawi, recognising that the 1970–80 archive data in particular are subject to analytical uncertainties and there remains a need to ground prove such concentrations. Our recent CJF survey work corroborates the importance of hydrothermal groundwater with data suggesting groundwater temperatures over 32 °C are likely diagnostic of significant fluorosis health risks. These concentrations tend to occur where there is known hydrothermal activity, or near major faults.

Concentrations at 1.5–6 mg/l, above current, but below the former WHO (current Malawi) guidelines, may pose a more challenging policy and management strategy. Groundwater within this concentration range appears widespread throughout Southern Malawi, perhaps related to rift valley structures and areas of known or suspecting faulting. The geological provenance of such fluoride needs to be better understood, as do the probable control of fluorite causing elevated fluoride risks in low calcium, high pH conditions as more conclusively shown herein from our recent surveys, but recognising the potential significance of calcium-sodium ion exchange and salinity complexing increasing fluoride. There a virtual absence of research geared to understanding the specific processes controlling fluoride provenance in Malawi.

Our expectation is that in the drive for SDGs (specifically SDG 6.1), concentrations in the 'troublesome 1.5–6 mg/l fluoride window' will come under increased scrutiny not only in Malawi, but in the wider developing world, especially with increasing capacity and attention to documenting fluorosis incidence. Whilst priority clearly should be given to cases where concentrations exceed 6 mg/l, our perception is that these are relatively easily identified, and it is the 'troublesome' concentration window where assessment and management efforts need to be intensified.

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Author Contributions

Conceptualization, M.J.A.; methodology, M.J.A.; software, M.J.A.; validation, M.J.A., M.O.R., H.R., A.F., A.M.M., P.P., P.M., and R.M.K.; formal analysis, M.J.A.; investigation, M.J.A.; resources, M.J.A., R.M.K.; data curation, M.J.A.; writing—original draft preparation, M.J.A.; writing—review and editing, M.J.A., M.O.R., H.R., A.F., A.M.M., P.P., P.M., and R.M.K.; visualization, M.J.A.; supervision, M.O.R., and R.M.K.; project administration, R.M.K.; funding acquisition, R.M.K. All authors have read and agreed to the published version of the manuscript.

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4.3 Supplementary Material

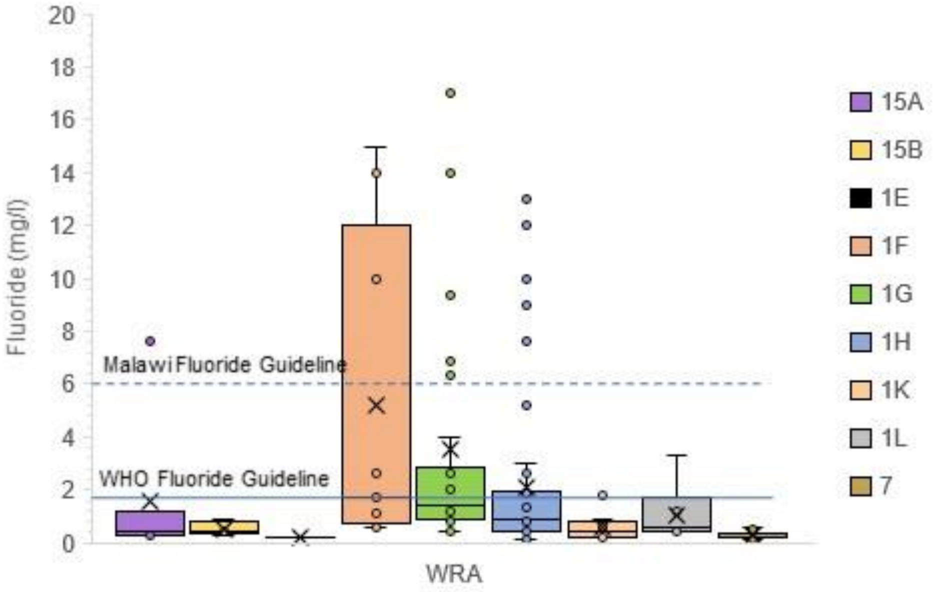

Figure. SM1. Boxplot of Bath (1980) groundwater fluoride data set (*n* = 142 samples, incl. the 1970–1980 archive (*n* = 119) and Bath, 1980 survey (*n* = 23) with a breakdown to WRA level (Fig. 2).

4.4 Summary and context

This chapter was written to fulfil RQ. 1: What is the current understanding/knowledge gaps with respect to groundwater fluoride in Malawi? The first objective (RO. 1.1) of this peer-reviewed paper was to collate all available literature and data pertaining to fluoride in Malawi. This was achieved by reviewing literature and collecting data from papers and from the Government of Malawi's archives. Individual studies with published data were useful for investigating fluoride occurrence on local scales, however, this study combined all data into one data set which could be analysed for fluoride nationally which was the first time such a collation had been attampted at that scale in Malawi. Key knowledge gaps identified were:

- No national-scale documentation of groundwater fluoride occurrence
- National groundwater data was not available
- No understanding of geological control on groundwater fluoride from various key geogenic sources (lithological, hydrothermal)
- No understanding of hydrochemical control on groundwater fluoride
- No knowledge of fluoride occurrence relative to other EARS countries
- No understanding of health links (fluorosis)
- No prediction method for groundwater vulnerability to geogenic fluoride, either published or within the government

The second objective (RO. 1.2) of this chapter was to augment archive data with recent groundwater data and conduct preliminary geological and geochemical analyses to investigate main sources and controls on fluoride occurrence in Malawi's groundwater. Fluoride correlation with calcium confirmed the presence of fluorite (CaF_2) equilibriation processes and a correlation with groundwater temperature and pH confirmed the influence of hydrothermal processes on elevated fluoride in Malawi's rit valley. Diffuse "troublesome" groundwater fluoride concentrations in the range 1.5 – 6 mg/L (between WHO and current Malawi guideline standards for fluoide in drinking water) were shown to be significantly more extensive and associated with shallow rock weathering of lithological sources which presents a key management challenge for Malawi's efforts to manage its groundwater assets for fluoride. A fundamental lack of data pertaining to the effect on human health from groundwater fluoride was additionally highlighted.

The findings of this study correlate with literature from other parts of the world which recognise that groundwater fluoride results from two main source types: deep hydrothermal and shallow rock weathering, both of which are active processes in Malawi. The study also highlights the difference in fluoride in drinking water guidelines in Malawi, compared to the globally recognised WHO guidelines. These findings have implications for Malawian drinking water standards which will require review within SDG 6. The next chapter develops a method for predicting groundwater fluoride from lithological sources using geological and groundwater geochemical data. Key issues addressed are: an investigation into the relationship between “troublesome” groundwater fluoride concentrations (1.5 – 6 mg/L) and shallow rock weathering of various lithological fluoride sources; quantification of the risk to human health from groundwater fluoride and further review of current Malawian and WHO drinking water standards.

This chapter fulfilled RQ. 1: What is the current understanding/knowledge gaps with respect to groundwater fluoride in Malawi? The next chapter addresses RQ. 2: Can groundwater fluoride risk be mapped using geology and limited groundwater data?, and RQ. 3: What is the direct link between geogenic groundwater fluoride and human health risk in Malawi and is the current fluoride standard for drinking water aligned with health risks?

Chapter 5 DEVELOPMENT OF GROUNDWATER FLUORIDE PREDICTION METHOD

5.1 Introduction

The previous chapter answered RQ. 1: What is the current understanding/knowledge gaps with respect to groundwater fluoride in Malawi? Two main sources of groundwater fluoride were identified with a focus on deep hydrothermal source. All current understanding and knowledge of fluoride occurrence in Malawi was presented. This chapter will address the diffuse “troublesome” fluoride concentrations in groundwater between the WHO and Malawian drinking water standards (1.5 – 6 mg/L) which occur from the most extensive groundwater fluoride source identified by the previous chapter: shallow weathering of lithological sources (basement rock). National management of groundwater fluoride for SDG6 will require a comprehensive understanding of all major sources and pathways, alongside an assessment of its effect on human health from fluorosis and a review of fluoride policy. For those reasons, this chapter will additionally address the human health link from groundwater fluoride occurrence and a further discussion of fluoride-relevant policy.

This chapter develops a method for predicting groundwater fluoride from lithological fluoride sources which is applicable in developing countries (limited data and resources). The chapter addresses RQ. 2: Can groundwater fluoride risk be mapped using geology and limited groundwater data? Since the JMP classification of fluoride as a priority chemical contaminant, countries globally must develop strategies to both manage current risk from fluoride and assess strategies for the future to ensure as little people as possible are affected by naturally occurring fluoride in drinking water. Detailed risk models can be developed in countries which possess extensive groundwater data however, some developing countries (such as Malawi) may not have access to data yet still must develop risk strategies for managing groundwater fluoride risk with the resources that are available to them. The first objective to address RQ. 2 was RO. 2.1: ‘Conduct a case study to investigate ‘source-extent’ relationship between geology and groundwater fluoride’. The second objective to address RQ. 2 was to use those results to address RO. 2.2: ‘Develop a method for predicting and mapping geology-based groundwater fluoride risk using groundwater data’. The method developed in RO. 2.2 had to have the ability to map groundwater fluoride risk from lithological sources which could be applied to any country using only geological data and limited groundwater data.

This chapter also addressed RQ. 3: What is the direct link between geogenic groundwater fluoride and human health risk in Malawi and is the current fluoride standard for drinking water aligned with health risks? Alongside assessing fluoride risk and managing existing groundwater resources, policy on fluoride standards will require review globally in the drive for SDG 6.1.1. Countries where fluoride standards do not align with health risks will need to review and adapt their standards to bring them in line with the WHO. The research question was addressed via the following research objectives: RO. 3.1: 'Quantify key link between geogenic fluoride and risk to human health via a human health risk assessment case study' used a case study to quantify the key link to human health risk from groundwater fluoride for the first time in Malawi; RO. 3.2: 'Investigate difference between current Malawi and global fluoride standards and advocate policy review via stepped progression for fluoride in drinking water in Malawi'. This chapter used a case study to review the drinking water standards in a country where the fluoride standard does not reflect health risks and is different from the WHO global drinking water guideline standard. The results of RO. 3.1 were thus presented as evidence to advocate a review of (Malawian) fluoride policy.

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5.2 Paper

Identifying groundwater fluoride source in a weathered basement aquifer in central Malawi: human health and policy implications

Marc J. Addison[1*], Michael O. Rivett[1], Peaches Phiri[2], Prince Mleta[2], Emma Mblame[2], Modesta Banda[2], Oliver Phiri[3], Wilson Lakudzala[3] and Robert M. Kalin[1]

[1] Department of Civil & Environmental Engineering, University of Strathclyde, Glasgow G1 1XJ, Scotland.
[2] The Ministry of Irrigation and Water Development, Lilongwe Headquarters, Private Bag 390, Lilongwe, Malawi.
[3] BAWI Consultants, Private Bag 15, Likuni, Lilongwe, Malawi.

* Correspondence: marc.addison@strath.ac.uk

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Abstract: Consumption of groundwater containing fluoride exceeding World Health Organization (WHO) 1.5 mg/L standard leaves people vulnerable to fluorosis: a vulnerability not well characterised in Malawi. To evaluate geogenic fluoride source and concentration, groundwater fluoride and geology was documented in central Malawi where groundwater supplies are mainly sourced from the weathered basement aquifer. Lithological composition was shown as the main control on fluoride occurrence. Augen gneiss of granitic composition posed the greatest geological fluoride risk. The weathered basement aquifer profile was the main factor controlling fluoride distributions. These results and fluoride-lithology statistical analysis allowed the development of a graded map of geological fluoride risk. A direct link to human health risk (dental fluorosis) from geological fluoride was quantified to support science-led policy change for fluoride in rural drinking water in Malawi. Hazard quotient (HQ) values were calculated and assigned to specific water points, depending on user age group; in this case, 74% of children under six were shown to be vulnerable to dental fluorosis. Results are contrary to current standard for fluoride in Malawi groundwater of 6 mg/L, highlighting the need for policy change. Detailed policy recommendations are presented based on the results of this study.

Keywords: fluoride; groundwater; Sustainable Development Goal 6; water quality; rural community water supply; weathered basement aquifer; hydrogeology; policy change

1 Introduction

The United Nations (UN)'s Joint Monitoring Programme (JMP) has classified fluoride as a Sustainable Development Goal 6 (SDG 6) chemical contaminant of concern for Water and Sanitation [1]. Whilst fluoride in small doses (0.5–1.5 mg/L) is beneficial, above this range the risks of worsening fluorosis conditions, dental–skeletal–crippling, increase [2]. Globally 200 million people may be at risk from fluoride consumption exceeding the 1.5 mg/L World Health Organization (WHO) standard [3,4]. During the Millennium Development Goal (MDG) period and continuing into the current SDG phase, community hand-pumped groundwater supplies have proliferated in low-income, developing countries. This has often occurred without systematic analysis of geo-hazards [5]. Research to investigate groundwater fluoride and associated health risks is required in such countries, including Malawi, where most rural communities fully rely on groundwater for their drinking-water supply [6]. Groundwater fluoride concentration data may often be sparse and assessment of health risks from natural, geogenic sources of fluoride is frequently non-existent. Science-based policy interventions to support the SDGs in such cases vitally require integrated consideration of geological, geographical, hydrochemical, and water-resource management factors together with risk analysis of human exposure to support regulatory control and provision of safe water supply.

Our recent review of groundwater fluoride in Malawi [7] confirms risks are much less well characterised than other fluoride 'hotspot' countries on the east African rift system (EARS), such as Kenya, Tanzania, and Ethiopia [7–11]. Systematic determination of fluoride risk has not occurred in this EARS periphery location and is despite some documented dental fluorosis in Malawi coinciding with increased groundwater fluoride [12–14]. Our interest in the Nathenje area, central Malawi was triggered by not only observations of dental fluorosis coinciding with somewhat elevated groundwater fluoride (<0.5–7.0 mg/L) [12,13], but also, our perception this fluoride occurrence appeared anomalous and perhaps unexpected given its plateau location removed from the main rift valley and a geological setting dominated by meta-sediments. Assessment of fluoride risk nationally requires such areas of less obvious risk (compared to say deep source hot springs) to be included. Factors controlling intermediate fluoride concentrations occurring mostly below the current (generous) Malawi drinking water standard of 6 mg/L, may well exceed the current WHO 1.5 mg/L standard. This concern motivates our study of the chosen area to inform the national strategy.

The nature of the geology present is expected to be a critical factor. Groundwater fluoride arises from two main geogenic source types: deep sourced hydrothermal inputs and/or shallow rock weathering [3,15,16]. Hydrothermal systems may contain elevated groundwater fluoride, occasionally exceeding 1000 mg/L [3]. Weathering of shallow rocks also contributes where groundwater flows through units rich in fluoride-bearing minerals. Alkaline igneous rocks are an important source of such minerals and globally recognised as a dominant groundwater fluoride source [2,17–19]. Fluoride is preferentially weathered from amphiboles (hornblende) and micas (biotite and muscovite) into groundwater. Apatites containing substituted fluoride are more soluble and an important source [3]. Example cases are reported in India, Ghana, Sri Lanka, and the USA [2,3]. In Sri Lanka, for instance, elevated fluoride occurs where granitic or biotite gneiss lithologies dominate and the nature of the underlying basement rock is the controlling factor on concentrations, with deeper boreholes generally containing higher fluoride [15]. Fluoride concentrations in crystalline basement rocks generally span <1 to 10 mg/L and hence may or may not pose problems [3]. Overall, the preponderance of international evidence confirms significant geological control on groundwater fluoride occurrence. This relationship provides the basis for our geological-based methodology. Whilst anthropogenic sources of fluoride exist, including industrial [20,21] and untreated sanitation [22] sources, these are currently insignificant in our rural study area and most of rural Malawi. Hence, an assumption of geological control on groundwater fluoride occurrence generally is reasonable.

Hence, our hypothesis is that the extent of fluoride occurrence in the weathered basement aquifers of Malawi is geologically controlled. Meaning, fluoride concentrations in groundwater predominantly reflect in-situ local geological composition. We test this hypothesis and investigate the link between fluoride occurrence and human health by integrating our results with health proxy indicators (dental fluorosis). Testing this hypothesis is pivotal to our overarching aim to provide an evidence-based framework that informs science-led policy review of groundwater fluoride risk management currently underway by the Government of Malawi, Ministry of Irrigation and Water Development (MoIWD). The ambition (and current Government planning strategy) is to mitigate risk to human health from groundwater fluoride by incrementally reducing the current Malawian drinking water standard for fluoride [23].

The framework to achieve this ambition is developed and demonstrated herein and comprises:

- Use of borehole water quality surveys to assess groundwater fluoride occurrence;
- Assessment of the hypothesised geological control on observed groundwater fluoride;
- Use of Government of Malawi survey results to assess health risks via proxy dental fluorosis indicators;
- Integrating these lines of evidence to investigate linkages between groundwater fluoride and health and develop risk factors for water points.

The study is the first in Malawi to integrate groundwater fluoride occurrence data with fluorosis health effects attributed to groundwater supply and consumption. The concurrent analysis of water source risks, geological sources and review of policy is multi-faceted and represents a paradigm shift in Malawi's approach in assessing fluoride problems by critically assessing the linkage between groundwater fluoride occurrence, health effect risks and proxy manifestation.

2 Study Area

2.1 Setting

Malawi is situated at the southern periphery of the EARS (Figure 1). In central and northern Malawi, it features as a deep freshwater lake, Lake Malawi [24]. In southern Malawi, the valley floor is exposed at the surface as a series of sedimentary basins [7]. The traditional authority (TA) Mazengera study area is in the district of Lilongwe, central Malawi (Figure 1). It lies on the eastern edge of the Kasungu-Lilongwe Plain, an elevated plateau composed of Lower Palaeozoic–Precambrian basement rock and colluvium of around 6000 km^2 with elevations varying from 1000–1800 m above sea-level (masl). Drainage in the study area generally flows northwest from the Nkhoma and Chilenje hills towards the Lilongwe River, and southeast towards the Linthipe River (Figure 1).

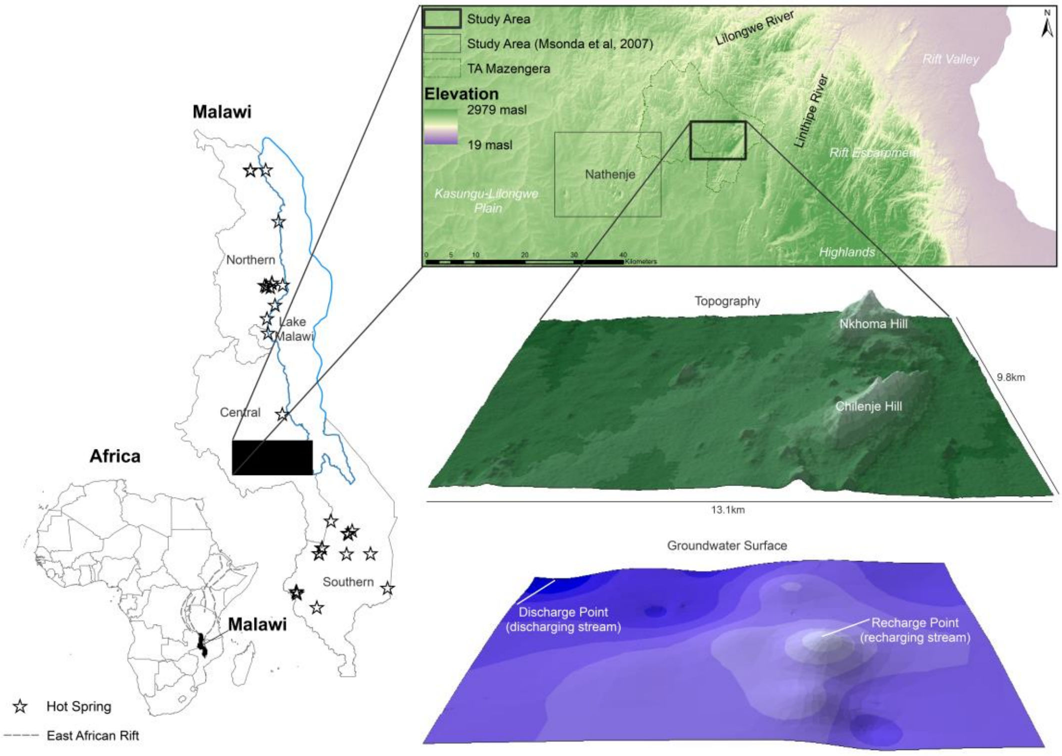


Figure 1. Location of study area within traditional authority (TA) Mazengera alongside Msonda et al. [13] study area at Nathenje area. The figure depicts Malawi's location within the east African rift system, marks the locations of all known hot springs and provides 3-D visualisation of the study area topography and drainage (2× vertical exaggeration), above a 3-D visualisation of groundwater surface indicating the main recharge and discharge points (5× vertical exaggeration).

Climate in the region is sub-tropical/semi-arid with distinct wet (November–April) and dry (May–October) seasons [25]. Monthly rainfall at the peak of the wet season (January) can reach an average of 222 mm, but falls to <1 mm at the dry season height (August). Mean annual precipitation averages 883 mm [26]. This type of climate is conducive to shallow groundwater fluoride enrichment that is found in a similar environment in northeast Sri Lanka. There, the semi-arid climate appears the main factor controlling enrichment due to a number of processes including low precipitation (recharge) and evaporative concentration [15]. Under semi-arid conditions, evapotranspiration at the surface where the water table is shallow may increase fluoride concentrations by a factor of 10–100 [3].

Fluoride occurrence in the study area had not been well characterised prior to this study. The Malawi Government internally released a 'Hydrogeology Atlas (2018)' containing six data points displayed simply as <6 mg/L fluoride [27]. Only one study has conducted fluoride research nearby [13] (Figure 1) which documented fluoride occurrence in the groundwater of Nathenje area, about 20 km southwest of our study area (Figure 1). They sampled 176 boreholes over two years (2001–2002) during both wet and dry seasons. Basement geology comprised an identical range of gneiss lithologies to our study area, however, their western section has considerable colluvium (superficial sediment) which is mostly absent in our case. Over 50% of their samples had fluoride concentrations exceeding the WHO 1.5 mg/L drinking water standard. Concentrations were slightly higher during the dry season, but with spatial trends of highs and lows in concentration comparable across the seasons. Concentrations increased east-northeast leading them to hypothesise high fluoride may be anticipated out with their study area in a geological trend in that direction, towards TA Mazengera, but do not elaborate on specific lithologies. They concluded that in-situ weathering of fluoride-bearing minerals in the basement rock (biotite and hornblende in weathered gneiss) is the probable contributing source of fluoride to groundwater.

Highest groundwater fluoride is typically associated with the rift valley hydrothermal processes and alkaline igneous intrusions [7,28]. Low Ca^{2+} groundwaters were identified as target waters for elevated fluoride (Na-HCO_3, Na-Cl-types) and the breakdown of biotite and hornblende (constituent phases of the basement gneisses of Malawi) is a probable source of fluoride, as fluoride can replace OH^- groups in the crystal lattices of those minerals [13,28]. Water-bearing minerals such as biotite and muscovite are particularly susceptible to hydroxide-replacement [10].

2.2 Geology and Hydrogeology

The study area is 13.1 km by 9.8 km and is located on a plateau some distance from the main rift valley (Figure 1) and is characterised by a distinct lack of major fault systems (Figure 2). The nearest large fracture is 10 km northeast and the nearest rift fault 30 km in the same direction. It is inferred that rift valley processes may exert minimal influence. Structural separation from the rift valley results in no hot spring activity within 70 km of the study area (Figure 1). The nearest is to the northeast at Chikwidzi on the rift escarpment near a large rift-margin normal-fault. The hot spring also represents the closest recorded >6 mg/L (Malawi standard) fluoride concentration [29].

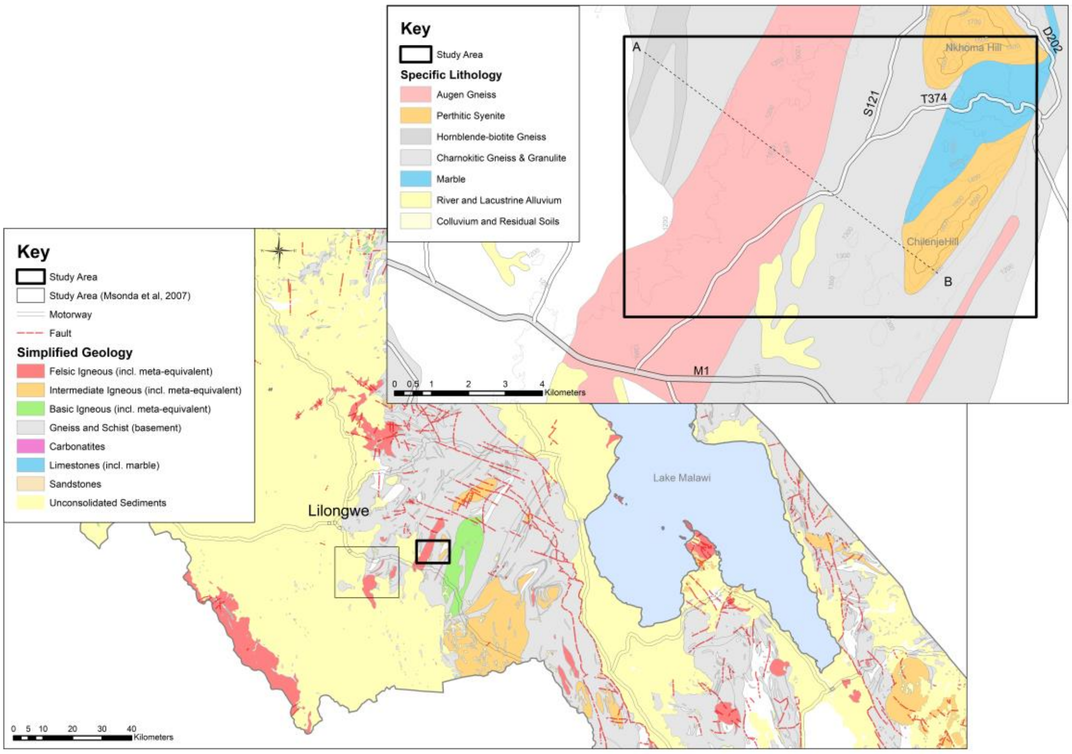
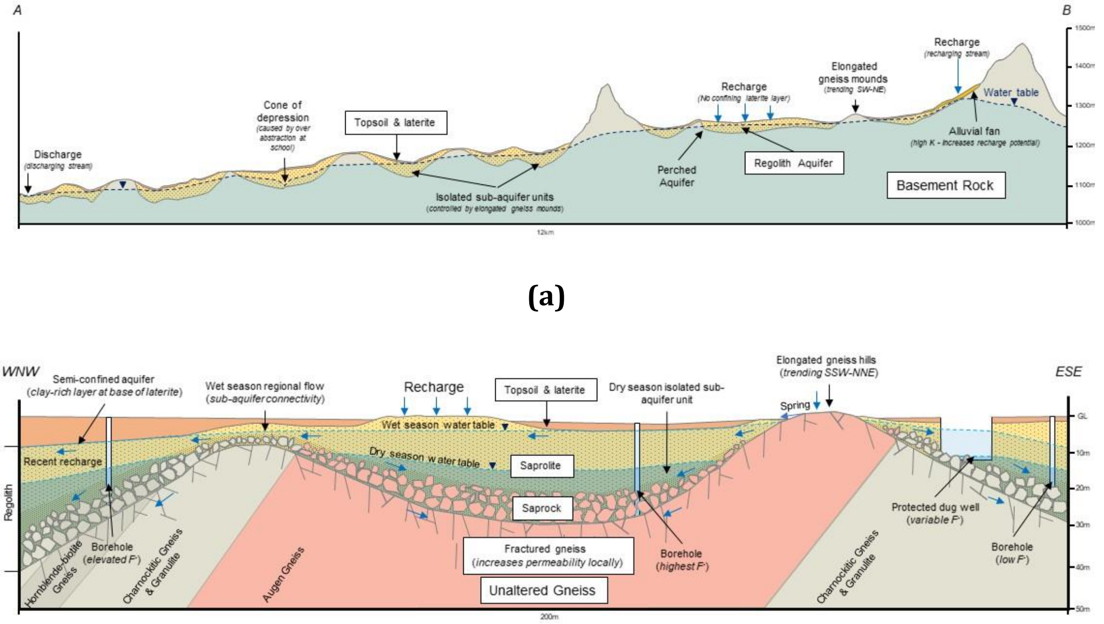


Figure 2. Regional geological map (simplified into lithological type–based on dominant composition) of central Malawi showing relative location of the study area to regional geological features. Map shows structural separation of the study area from the main rift valley (absence of faulting). Inset map shows the specific study area geology and the line of cross-section (A–B) from Figure 3.

The area comprises almost entirely weathered basement aquifer units [30]. Lithology is dominated by a mix of basement (meta-igneous and meta-sedimentary) rocks: augen gneiss (meta-granite), perthitic syenites, charnockitic gneiss and granulite, hornblende-biotite gneiss and calc-silicate marble. Gneissic foliations and lineations all strike southwest-northeast and dip 40–44° northwest. Hornblende-biotite gneiss occurs as a plunging syncline within charnockitic gneiss and granulite in the northwest of the study area (Figure 2). Nkhoma and Chilenje hills in the east are perthitic syenites which have been intruded into the host basement causing isolated uplift of marbles and steep topography. Small, isolated dambo wetland of river and lacustrine alluvium occur in the south. The western edge contains colluvium deposits which form part of the eastern edge of the superficial deposits' aquifer of the Kasungu-Lilongwe Plain (Figure 2) [31].

Hydrogeological conceptualisation of the wider catchment flow regime from the uplands to Lake Malawi has been described [25]. Catchments originate in the plateau area east of the rift valley and drain northeast towards Lake Malawi, cross cutting the rift escarpment (Figure 1). The study area lies on a small ridge between the catchments for the Lilongwe and Linthipe Rivers and on the divide between catchments, with northwest and southeast flow from the Nkhoma and Chilenje Hills high points. Groundwater levels based on 16 water points (8 boreholes, 4 natural springs and 4 hand dug shallow wells) were used to conceptualise the water table. For the purposes of this conceptual model, only the aquifer west of Chilenje Hill was considered as the hill represents a flow barrier. The primary recharge point is a stream flowing onto an alluvial fan at the base of the northwest slope of Chilenje Hill, natural discharge occurs at a stream in the extreme northwest (Figure 1). Temporal changes in water table elevation (limited by boreholes going dry) suggest seasonal swings may be large at up to 8 m and probably reflect low storage. Geophysical data [32] show that regolith aquifers in this area have uneven thickness, ranging from 0–60 m in depth and are often semi-isolated due to uneven bedrock surface caused by folding. Bedrock often breaches the surface as linear gneiss mounds which strike southwest-northeast, perpendicular to local groundwater flow (assumed from consistent decrease in groundwater elevation southeast-northwest from Chilenje Hill). Pumping tests conducted at five sites within the study area (separate from geochemical sampling sites) show that hydraulic conductivity is variable but low in these aquifers (K = 0.03–0.2 m/day) [33]. A cross-sectional aquifer profile was developed, based on available geophysical and local groundwater data, and is presented in Figure 3a.

The 'weathered basement' conceptual aquifer profile developed (Figure 3b) illustrates the key hydrogeological controls. A regolith aquifer containing saprock and saprolite layers of varying thickness is the main storage unit. Localised fracturing in underlying basement rock increases permeability and limited storage where present, however, the lateral extent of permeability remains unknown. Uneven bedrock surfaces create isolated sub-aquifer units which may become increasingly isolated during the dry season when groundwater levels are low. The aquifer exists under semi-confined conditions due to discontinuous clay layers at the base of the laterite layer. Boreholes drilled where there is clay often have resting water levels above the original water strike [34]. Recharge occurs at the base of the Nkhoma and Chilenje Hills (Figure 1), at alluvial fans, places where unaltered and fractured gneiss is exposed as gneiss mounds and at areas where topsoil/laterite is absent exposing saprolite [32] (Figure 3). Higher groundwater levels may facilitate increased sub-aquifer connectivity (flushing) during the wet season, down-hydraulic-gradient from the Nkhoma and Chilenje Hills in northwest and southeast directions, following decreasing altitude (Figure 3), however this is assumed to be minimal based on low hydraulic conductivities [33] and perpendicular flow barriers.



(a)

(b)

Figure 3. **(a)**—Aquifer cross-section (A–B) of study area showing decreasing altitude and groundwater levels southeast-northwest from recharge at high elevation to discharge at low elevation (vertically exaggerated), topography surface, aquifer depth and water table levels calculated from data. The figure shows semi-isolated nature of regolith aquifer units. **(b)**—Schematic hydrogeological conceptual model (not to scale).

Groundwater resource development is mainly boreholes accounting for 66% of water points (incl. surface water). Drilling may be with little geological or hydrogeological knowledge. Boreholes are drilled to an average depth of 47 m (range: 34–66 m) and cover all lithologies. A smaller proportion of hand dug shallow wells (3–10 m depth) exists (19% of water points), 81% of which are protected at the surface by hand-pumps. The unprotected wells have open sections and are often covered simply by a piece of wood. There are also some natural springs (2% of all water points) at the base of the hills. There is a partially functional piped water supply network in the area (12%) where water is transported from gravity-fed systems and a reticulated borehole, via pipes to various kiosks. Piped supplies were not sampled in this study.

3 Materials and Methods

3.1 Groundwater Survey

Groundwater samples (39) were collected to investigate the geochemical relationship between groundwater and local geology and to test our hypothesised geological control. These covered the three main lithological aquifer sources: augen gneiss, hornblende-biotite gneiss and charnockitic gneiss and granulite. They also covered the range of groundwater supply types: 34 boreholes, three hand dug shallow wells and two natural springs. They comprised 16% of all water points in the area and were evenly distributed. All sampled boreholes and shallow wells were located in regolith and both springs located in bedrock. Samples were collected in November 2019 (wet season) in 1 litre plastic bottles and stored away from light at 4 °C. Purging of boreholes fitted with Afridev hand-pumps was not necessary as all were regularly used prior to sampling, natural springs and shallow wells were sampled in situ. Samples were shipped to Scotland for analysis at the University of Strathclyde. Water temperature was measured at site, using portable measuring equipment. Electrical conductivity (EC), total dissolved solids (TDS) and pH were measured upon delivery at the laboratory using a Mettler Toledo meter (Model MPC 227). All samples were then filtered and anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) were analysed by ion chromatography (IC Metrohm, 850 Professional) and cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) analysed by a inductively coupled plasma optical emission spectrometer (ICP OES) (iCAP 6200, Thermo Scientific, Waltham, MA, USA). Total alkalinity ($CaCO_3$) was analysed by KONE Aquakem v. 7.2.AQ2 with results multiplied by a factor of 1.22 to estimate total alkalinity (HCO_3^-). In total, 35 of the samples ion-balanced within the conventionally accepted ±5% analysis uncertainty, the remaining four samples within ±10%. The latter were excluded from geochemical analyses but not excluded from fluoride spatial analyses, or analyses where fluoride is the only geochemical component (as fluoride contribution to total anions was <2% in all four samples, therefore, it is unlikely that fluoride would influence the overall ion balance).

3.2 Survey Data

A total of 6804 households in the TA Mazengera study area were visited by Government of Malawi enumerators as part of a wider SDG 6 survey. Dental fluorosis proxy indicator data from this survey was provided to link fluoride occurrence in the area to human health risks. The area reflects a typical low-income, rural population for central Malawi where most of the population gather their daily water from public water points. Only 9.6% of households surveyed had access to a public piped water supply. The survey data was comprised of anonymised questionnaire responses gathered from doorstep interviews with residents on their water use. One question concerned visible symptoms of dental fluorosis.

Survey results provide qualitative proxy information on the visible symptoms of dental fluorosis, but do not constitute a medical or human health survey and results are not definitive in case diagnosis. Results are hence indicative of the condition based on recording of visual symptoms (brown/black staining of the teeth). No inclusion or exclusion criteria were applied. It is recognised that there could be a misappropriation of potential fluorosis respondents who might have had other medically confirmed dental problems, or a history of tobacco (very low in Malawi) or kola use that could yield similar symptoms [35]. Such caveats are recognised.

3.3 Risk Evaluation

3.3.1 Mapping Risk

Demonstration of geological control on groundwater fluoride occurrence is significant as it would permit use of available geological maps to effectively map fluoride risk; i.e., certain lithologies would map as high risk, others intermediate and other low risk. Proving this hypothesis for the study area (ultimately shown herein) allowed a geological fluoride risk map to be developed for the study area based on statistical analysis of groundwater fluoride data with corresponding host lithology. An arbitrary grading system was developed to represent risk of groundwater with fluoride concentrations in excess of the WHO standard (1.5 mg/L) from each lithology in the study area: Grade 0 (unknown risk–no corresponding groundwater fluoride data); Grade 1 (<20% risk); and Grade 2 (>60% risk). Each lithology was represented on the map as a zone with its corresponding risk grade. The map was based solely on the influence of lithological composition to groundwater fluoride concentrations as it assumes very reasonably in the Malawian rural setting that anthropogenic fluoride inputs were insignificant. The map also assumes the local rock mapped has the dominant influence on its groundwater, rather than a neighboring geological unit from which it may have received some inflows. In addition, the evolution of groundwater hydrochemistry along a flow path within the mapped locality does not result in fluoride concentration changes sufficient to alter the host rock risk grading.

3.3.2 Human Health Risk Assessment

To support policy change on fluoride standards in rural drinking water in Malawi, a 'human health risk assessment' was undertaken on each of the water points sampled for geochemistry. The method was based upon the approach introduced by the United States Environmental Protection Agency (USEPA) as a tool to "assess the nature and possibility of adverse health effects in humans who consume highly contaminated water" [36,37]. Similar studies have been conducted since in India and Iran [36,38,39]. The method involves the calculation of a non-carcinogenic risk index, also known as a 'hazard quotient' (HQ) (dimensionless) detailed below [40,41] (in [38]): chronic daily intake (CDI) is calculated (1) [40,41] (in [38]) and defined by the following parameters:

$$CDI = \frac{C * DI * F * ED}{BW * AT} \tag{1}$$

C - Fluoride content in drinking water (mg/L)

DI - Daily Water Intake (l/day)

F - Exposure Frequency (days/year)

ED - Exposure Duration (years)

BW - Average Body Weight (kg)

AT - Averaging Time for non-carcinogens (days)

The HQ is then defined as follows (2) [40,41] (in [38]):

$$HQ = \frac{CDI}{RfD} \tag{2}$$

CDI - Chronic Daily Intake (mg/kg/day)

RfD - Oral Reference Dose (mg/kg/day)

The HQ value indicates the "ratio of the potential exposure to a substance and the level at which no adverse effects are expected as a result of exposure. If HQ > 1, adverse effects are possible" [39]. HQ represents an indication of potential risk from fluoride at any water point. Three risk categories were applied: children (aged 6 years old), children (aged 12 years old) and adults (>19 years old) (adapted from Qasemi et al. [38]). The values used for Equations (1) and (2) were from previous studies [38,39] (Table 1). BW (body weight) and DI (daily water intake) values were based on averages for the age groups chosen and broadly represent the study area population. Once calculated, HQ values were further analysed to explore statistical relationships with geology. This was achieved by comparing calculated proportions of HQ values > 1 for each lithology.

Table 1. Values used to calculate the hazard quotient (HQ) for the study area water points per age group (adapted from: [38,39]). 'C' values are not included as they represent individual fluoride concentrations for each water point and vary from water point to water point.

Risk Exposure Factors	**Values for Age Groups**			**Units**
	Adults (>19 Years Old)	Children (12 Years Old)	Children (6 Years Old)	
C				(mg/L)
DI	2	1.7	1	(l/day)
F	365	365	365	(days/year)
ED	19	12	6	(years)
BW	70	40	15	(kg)
AT	6935	4380	2190	(days)
RfD	0.06	0.06	0.06	(mg/kg/day)

4 Results

4.1 Hydrochemical Observations

Groundwater in the study area is exclusively Ca-Mg-HCO_3 type. Hydrochemical data (HCO_3^-, Ca^{2+}, Na^+, Mg^{2+}, F^- and pH) were plotted with TDS alongside a TDS map (Figure 4). Groundwater is least mineralised around the Nkhoma and Chilenje Hills. Two natural springs were sampled at the base of the southeast slope of Chilenje Hill. These springs contained the least mineralised groundwater. Increasing fluoride concentrations follow a southeast-northwest trend, with the highest fluoride at locations with the highest HCO_3^-, Na^+ and Mg^{2+}. Low TDS samples from Augen gneiss display notably higher (an order of magnitude) Na^+, Mg^{2+} and F^- signatures than low TDS samples from charnockitic gneiss and granulite. Concentrations then increase with TDS following a similar trend in both lithologies. Geochemical data can be viewed in Table S2 in the supplementary materials.

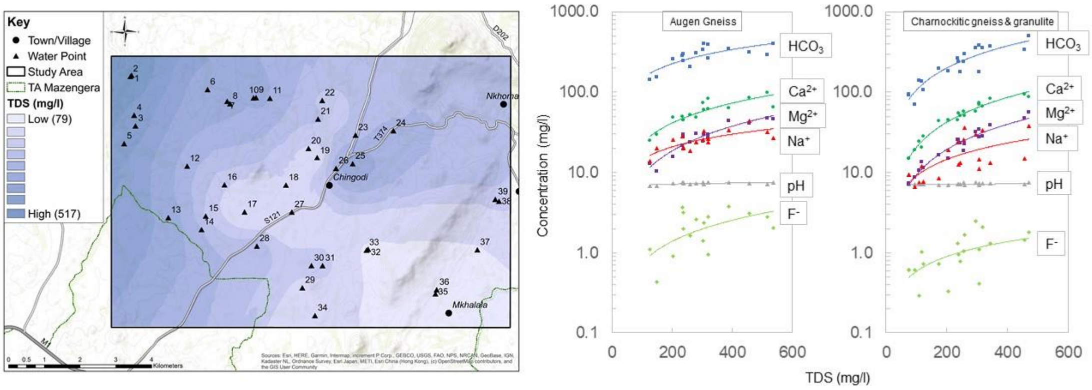


Figure 4. Total dissolved solids **(**TDS) map of the study area with log plots of relevant hydrochemical concentrations vs. TDS. Map shows TDS values increasing northwest in the direction of decreasing altitude. Graphs show increasing trends in relevant ions with increasing TDS (as seen on the map).

Correlation is not observed between fluoride concentrations and temperature data that span 21–27 °C (groundwater temperatures in Malawi not influenced by geothermal sources are typically around 20–30 °C [7]). Temperatures appear to increase northwest with elevation decline (Figure 1) corresponding to where the water table may be shallow and more vulnerable to surface temperature fluctuations.

Fluoride was plotted with Ca^{2+} alongside fluorite (CaF_2) equilibrium (Figure 5). For water with TDS above 200 mg/L, a few water samples approach fluorite saturation but this may be a common ion effect with calcite. Low TDS samples (least mineralised–recent recharge) all plot well below equilibrium displaying both low Ca^{2+} and low fluoride (Figure 5); all are located near the foot of the Nkhoma and Chilenje Hills (Figure 1).

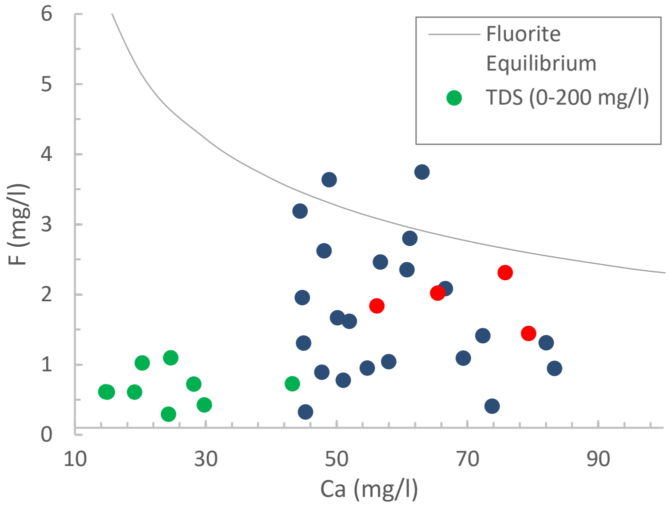


Figure 5. Plot of calcium versus fluoride showing equilibrium for the mineral fluorite (CaF_2). The fluorite equilibrium curve was calculated from {F} = $(K_{eq}/\{Ca\})^{0.5}$ that assumes equality of the ion activity product (IAP) with the equilibrium constant (K_{eq}) (3.7×10^{-11}).

A Gibbs diagram plot confirms rock weathering is the dominant process controlling groundwater composition (Figure 6). Just a slight incline towards evaporation suggests minimal evaporation influence on shallow groundwater geochemistry in this system.

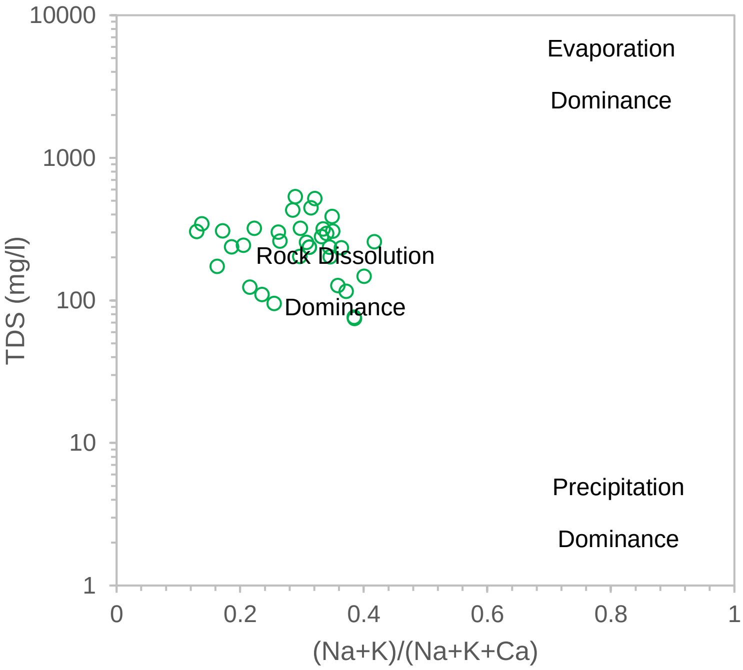
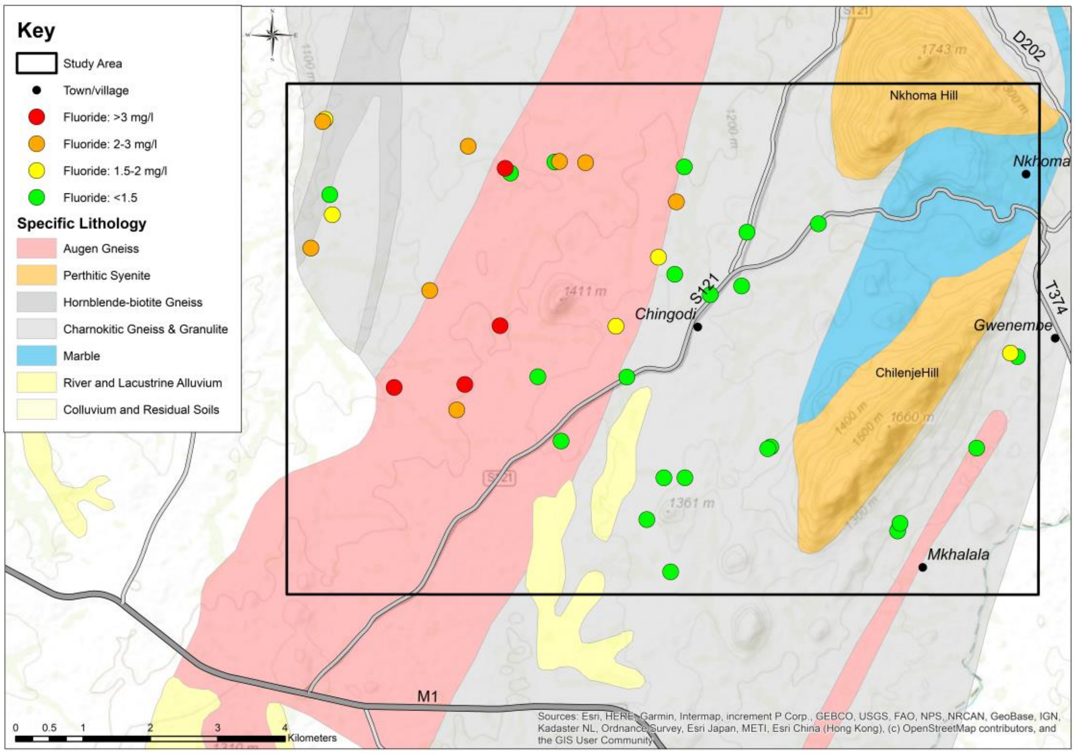


Figure 6. Gibbs diagram of study area groundwater samples showing dominance of rock dissolution. Calculations are shown on axes.

4.2 Geological Controls on Fluoride Occurrence

Fluoride concentrations were lowest in the southeast where the dominant lithology is charnockitic gneiss and granulite, becoming progressively more elevated northwest where the highest fluoride concentrations were located within alkaline meta-igneous rocks (augen gneiss). This lithology contains all fluoride concentrations >3 mg/L. Concentrations then decrease slightly further northwest where the dominant lithology returns to Charnockitic gneiss and granulite, with interbedded hornblende-biotite gneiss (Figure 7). No data were available for perthitic syenite, calc-silicate marble or superficial deposits so their (fluoride) hydrochemical profile remains unknown.



Sources: Esri, HERE, Garmin, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), (c) OpenStreetMap contributors, and the GIS User Community

Figure 7. Map showing fluoride data in the study area plotted onto local geology.

A box and whisker plot to investigate the specific lithology-fluoride relationships (Figure 8) shows Charnockitic gneiss and granulite producing the lowest groundwater fluoride with only 20% of samples exceeding the WHO standard for fluoride in drinking water of 1.5 mg/L. A total of 10% of groundwater samples in this lithology exceeded 2 mg/L and none exceeded 3 mg/L. Augen gneiss (alkaline composition) on the other hand had 69% of samples exceeding the WHO standard. This lithology also possesses the highest fluoride concentrations with 56% of samples exceeding 2 mg/L and 25% exceeding 3 mg/L (Table S1–Supplementary Materials). Hornblende-biotite gneiss sits between those lithologies with respect to fluoride concentrations. Low sample numbers for this lithology prevent definitive conclusions, although the expectation would not differ much from those measured values as it contains more fluoride-bearing minerals (relatively) than charnockitic gneiss (biotite and hornblende) and less sodium than the augen gneiss (contains an abundance of Na-plagioclase megacrysts) (Figure 4) which makes it a fluoride source candidate. It has been provisionally included in the (later) risk map for this reason, recognising the need for greater sample numbers.

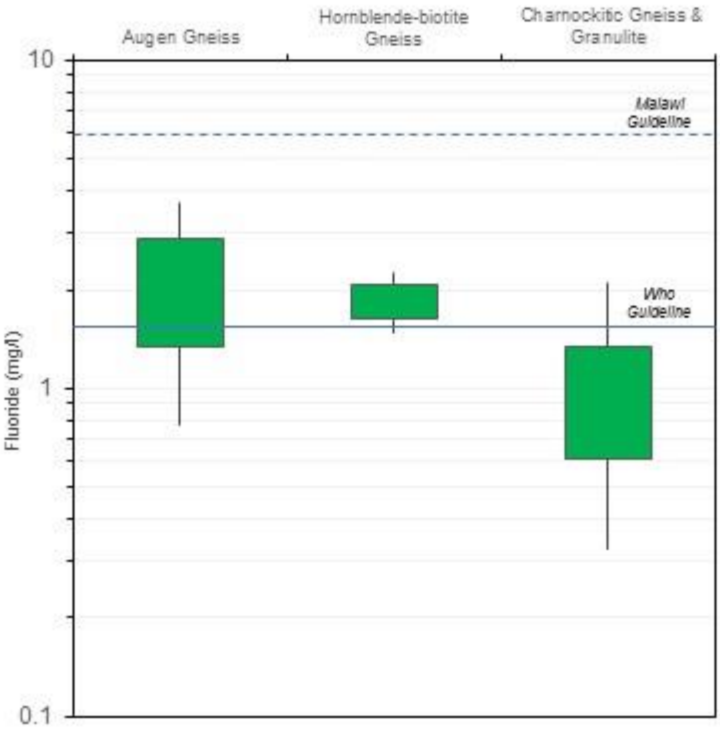


Figure 8. Box and whisker plot of fluoride concentrations (5th, 25th, 75th and 95th percentiles) in the various lithological units (augen gneiss (*n* = 16), hornblende–-biotite Gneiss (*n* = 3) and charnockitic gneiss and granulite (*n* = 20)).

4.3 Dental Fluorosis Indicators

Survey responses provide a preliminary indication of dental fluorosis prevalence and are categorised in Table 2 with corresponding host lithologies (only responses within lithologies with groundwater fluoride data are included). Statistically, charnockitic gneiss and granulite had the lowest percentage of “yes” responses at 22% (6% below the average; *n* = 1022). Augen gneiss hosts the highest percentage of “yes” responses at 41% (13% above the average; *n* = 853) (Table 2). These results concur with our hydrochemical and geological data, illustrating that groundwater within augen gneiss is the most vulnerable to fluoride, followed by hornblende-biotite gneiss (again, recognising relative low sample numbers for this lithology; *n*–134) and finally charnockitic gneiss and granulite. This is an important result substantiating our hypothesis.

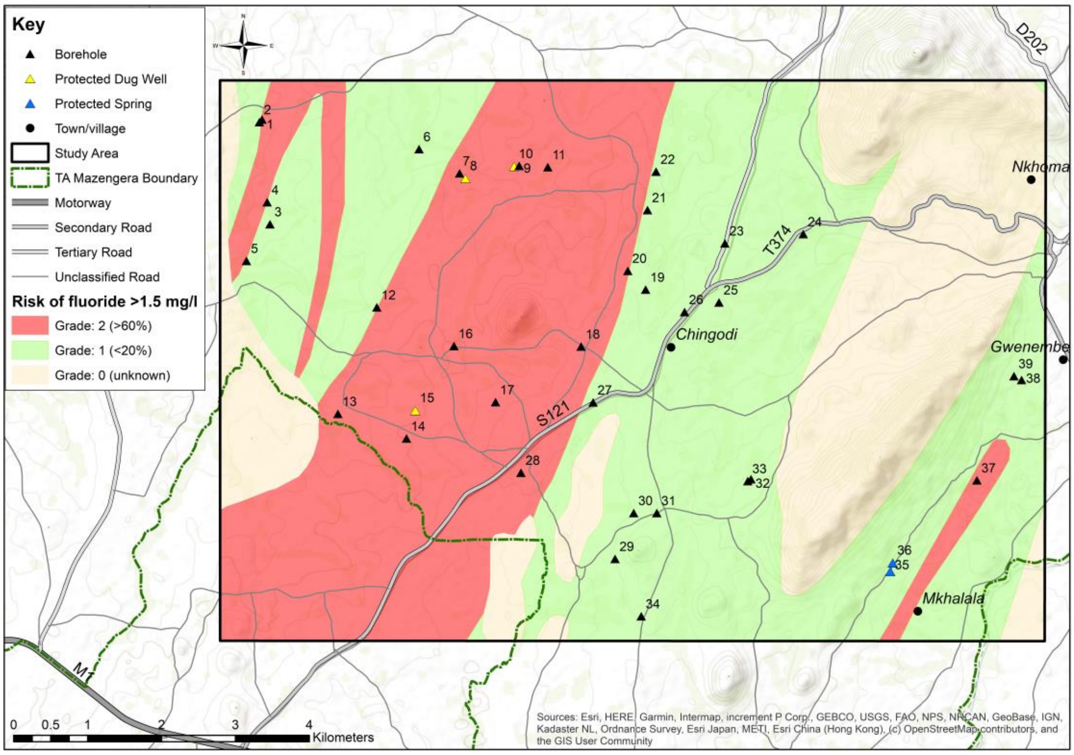
Table 2. Summary statistics of dental fluorosis indicator data and corresponding geology.

Question Asked	**Lithology**			**Total**
“Does anyone in your household suffer from brown-black staining of the teeth?”	Augen gneiss	Hornblende-biotite gneiss	Charnockitic gneiss and granulite	
Total responses	2070	134	4600	6804
“Yes” responses	853	54	1022	1929
% yes	41%	40%	22%	28%

4.4 Risk Evaluation

4.4.1 Risk Map

Statistical analysis of fluoride-lithology data may be hence used to map geological fluoride risk zones (Figure 9). Both augen gneiss and hornblende-biotite gneiss lithologies host >60% risk (68.8% and 66.7% respectively) of producing drinking water in excess of the WHO standard (1.5 mg/L) and are thus mapped as Grade 2 (highest risk). Statistically, charnockitic gneiss and granulite displayed the least risk (<20%) and were mapped as Grade 1. The blank areas were mapped as Grade 0 as no hydrochemical data were available with which to perform statistical analyses. Red zones (Grade 2), therefore, represent areas where there is >60% risk of abstracted groundwater used for supply producing enough fluoride to cause dental fluorosis (assuming regular consumption from the same water point). Such geology-based risk maps, calibrated to fluoride occurrence, may provide the foundation for the development of risk maps in other areas of similar mapped geologies for which groundwater fluoride data may not exist. With increased groundwater fluoride occurrence data coverage of the presently Grade 0 (unknown) areas it is anticipated greater resolution of the grading system may be possible with increased numbers of grades to characterise the system.



Sources: Esri, HERE, Garmin, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), (c) OpenStreetMap contributors, and the GIS User Community

Figure 9. Geological fluoride risk map showing lithologies with risk of groundwater fluoride concentrations > 1.5 mg/L as graded zones. Blank zones (Grade 0) reflect areas where geological data are available but corresponding hydrochemical data are not. Sampled water points are shown with their corresponding sample numbers.

4.4.2 Human Health Risk Assessment

74% (*n* = 29) of sampled water points had HQ values > 1 for children under the age of 6, indicating possible and increasing risk of dental fluorosis from exposure to fluoride in drinking water from those groundwater points (Table 3). 44% (*n* = 17) of water points had HQ values > 1 for children under the age of 12 and 28% (*n* = 11) had HQ values > 1 for adults over 19 years old. The latter also included all children under 12 years old. 26% (*n* = 10) had HQ values <1 for all age groups and appear safe for anyone to drink from. Water Point 13, which displayed the highest HQ value (4.11), also displayed the highest fluoride concentration in the study area (3.75 mg/L) (Table 3).

Table 3. Calculated HQ values for each age group and each water point from the study area. HQ values > 1 shown in bold.

Sample Number	**Water Point Type**	**Fluoride (mg/L)**	**Hazard Quotient (HQ)**		
			Adults (>19 years old)	**Children (12 years old)**	**Children (6 years old)**
1	Borehole	1.84	0.86	**1.28**	**2.00**
2	Borehole	2.02	0.95	**1.42**	**2.22**
3	Borehole	1.78	0.86	**1.28**	**2.00**
4	Borehole	1.45	0.67	0.99	**1.56**
5	Borehole	2.31	**1.10**	**1.63**	**2.56**
6	Borehole	2.08	**1.00**	**1.49**	**2.33**
7	Borehole	3.04	**1.43**	**2.13**	**3.33**
8	Protected dug well	1.41	0.67	0.99	**1.56**
9	Borehole	2.80	**1.33**	**1.98**	**3.11**
10	Protected dug well	0.89	0.43	0.64	**1.00**
11	Borehole	2.80	**1.33**	**1.98**	**3.11**
12	Borehole	2.46	**1.19**	**1.77**	**2.78**
13	Borehole	3.75	**1.76**	**2.62**	**4.11**
14	Borehole	2.36	**1.14**	**1.70**	**2.67**
15	Protected dug well	3.64	**1.71**	**2.55**	**4.00**
16	Borehole	3.19	**1.52**	**2.27**	**3.56**
17	Borehole	0.43	0.19	0.28	0.44
18	Borehole	1.62	0.76	**1.13**	**1.78**
19	Borehole	1.03	0.48	0.71	**1.11**
20	Borehole	1.96	0.95	**1.42**	**2.22**
21	Borehole	2.62	**1.24**	**1.84**	**2.89**
22	Borehole	1.31	0.62	0.92	**1.44**
23	Borehole	0.78	0.38	0.57	0.89
24	Borehole	1.09	0.52	0.78	**1.22**
25	Borehole	1.42	0.67	0.99	**1.56**
26	Borehole	1.31	0.62	0.92	**1.44**
27	Borehole	0.29	0.14	0.21	0.33
28	Borehole	0.95	0.43	0.64	**1.00**
29	Borehole	0.33	0.14	0.21	0.33
30	Borehole	0.95	0.48	0.71	**1.11**
31	Borehole	0.41	0.19	0.28	0.44
32	Borehole	0.61	0.29	0.43	0.67
33	Borehole	0.73	0.33	0.50	0.78
34	Borehole	0.73	0.33	0.50	0.78
35	Protected spring	0.61	0.29	0.43	0.67
36	Protected spring	0.61	0.29	0.43	0.67
37	Borehole	1.10	0.52	0.78	**1.22**
38	Borehole	1.05	0.48	0.71	**1.11**
39	Borehole	1.67	0.81	**1.20**	**1.89**

Statistical analysis of HQ values with corresponding host lithology (Table 4) demonstrated that for all age groups, augen gneiss carries the most groundwater fluoride risk. For children under the age of 6: 94% of water points in this lithology displayed HQ values > 1. Statistically, hornblende-biotite gneiss appeared to be highest risk lithology for that age group (100% of HQ values >1) but again, low sample numbers (*n* = 3) prevents definitive conclusion. The lithology with least fluoride risk was charnockitic gneiss and granulite with only 55% of water points displaying HQ values > 1. For children under the age of 12: water points within augen gneiss, again, were the most vulnerable with 69% displaying HQ values > 1. 67% of water points within hornblende-biotite gneiss have HQ values >1 and only 20% for charnockitic gneiss and granulite. The same trend was observed in adults over the age of 19 (Table 4). These results again support augen gneiss as the dominant source of groundwater fluoride, therefore posing the highest dental fluorosis risk.

Table 4. Summary statistics for HQ values > 1 per lithology. Values are percentages of sampled water points with an HQ value >1 for each lithology.

Lithology	***n***	**Hazard Quotient (HQ) = > 1**		
		Adults (>19 years old)	Children (12 years old)	Children (6 years old)
Augen gneiss	16	50.00%	68.75%	93.75%
Hornblende-biotite gneiss	3	33.33%	66.66%	100.00%
Charnockitic gneiss and granulite	20	10.00%	20.00%	55.00%
All	39	28.21%	43.59%	74.36%

5 Discussion

5.1 Geological Fluoride

Augen gneiss poses the highest potential for elevated groundwater fluoride, ascribed to its granitic-type (alkaline) composition. The augen gneiss is a metamorphosed granite and hosts an abundance of fluoride-bearing minerals such as hornblende, biotite (and accessory apatite) along with characteristic Na-feldspar mega-crysts which are an additional source of sodium (recognised to be conducive to fluoride enrichment). Solubility of fluoride-bearing minerals is generally low. One dimensional reactive-transport equations have shown long residence times are required to produce appreciable concentrations of fluoride in groundwater from silicate rocks, however, higher reactive surface area can significantly increase the rate at which concentrations accumulate [42]; meaning, weathered basement aquifers will have significantly increased fluoride mobilisation potential. Samples represent recent recharge (low mineralisation) and it is likely that increased reactive surface area of the weathered basement aquifer (Saprock, saprolite and fractured gneiss) is a key control on the release of fluoride and may account for observed concentrations. Our geological, geochemical and hydrogeological data support this hypothesis.

Fluorite solubility is usually expected to control fluoride concentrations in groundwater leading to a proportional relationship between F^- and Ca^{2+} ions in solution. Clay minerals and fine sands are moderate adsorbents for fluoride [3], while clay minerals can also be a source of Na^+ for ion exchange with Ca^{2+}, furthering the potential for fluoride enrichment [3,7]. Water type, therefore, plays an important role in fluoride concentration. Lowest fluoride is expected in recharging water, naturally increasing with groundwater evolution through: Ca-$CaCO_3$ (recharge); Ca-Mg-HCO_3; Na-HCO_3; Na-Cl (endmember) [3,28]. While elevated fluoride is expected in geochemically evolved waters, it is commonly found in Ca-Mg-HCO_3-type where there are basement lithologies [39]. This corresponds with our study area where the dominant water type is Ca-Mg-HCO_3 and basement lithologies dominate. Figure 4 shows that Mg^{2+} increases northwest. The loss of Ca^{2+} for Mg^{2+} may facilitate the increasing fluoride trend seen in that direction as there is less Ca^{2+} available to precipitate fluorite (CaF_2). Groundwater samples from augen gneiss plot closest to equilibrium in Figure 5, indicating that equilibration of fluorite (ultimately controlled by equilibration of calcite) is an active process in those samples.

Regional groundwater flow (northwest) is unlikely to be the dominant process producing the hydrochemical trends in that direction (Figure 4). This is due to the shallow, uneven and seasonally isolated nature of the hydrogeological profile (Figure 3) and low hydraulic conductivity values in those aquifers. Local groundwater flow may, however, have increased influence (albeit minimal) during the wet season where there is higher potential for sub-aquifer connectivity via an elevated water table (Figure 3). The surface of unaltered gneiss beneath the study area is locally uneven, with regolith aquifer thickness ranging from 0–60 m below the surface. Elongated gneiss mounds striking southwest-northeast often breach the surface exposing the uneven nature of the bedrock. These may be potential barriers to groundwater flow. The shallow and uneven nature of the regolith controlled by bedrock surface creates (locally) low sub-aquifer connectivity. These results may reflect a slight dry season-wet season shift in groundwater processes where mostly isolated in-situ weathering of basement rock dominates, with the wet season rains allowing a limited degree of sub-aquifer connectivity, flushing groundwater down-hydraulic gradient from the Nkhoma and Chilenje Hills. This slight seasonal shift in processes was assumed from the available data (locally uneven aquifer thickness and a dry season decrease in groundwater levels) as there were no dry season data to compare. Over time, this may allow some down-hydraulic-gradient geochemical groundwater evolution (i.e., transient development of solute concentrations: Figure 4) to occur in that direction, however, the process would be extremely slow and have a relatively insignificant effect on local groundwater hydrochemistry when compared to in-situ weathering. Augen gneiss hosts the lowest hydraulic conductivities (K = 0.003–0.046 m/day) and the outcrop strikes perpendicular to hydraulic gradient, therefore, may act as a boundary to local groundwater flow over lithological boundaries.

Figure 6 confirms rock weathering as the dominant control on fluoride concentrations, with little evaporation or precipitation influence on the hydrochemistry. This supports our hypothesised geological control on groundwater fluoride and significance of in-situ weathering of the underlying geology. Both meta-sedimentary gneiss lithologies play an important role in the concentrations of fluoride that fall within the expected range for rock types [3]. The augen gneiss (alkaline igneous) produced the highest concentrations and is the primary source lithology for fluoride. A geochemical signature for augen gneiss and charnockitic gneiss and granulite appears to be reflected (Figure 4), where low TDS waters (proxy for minimal phreatic influence) from augen gneiss host an order of magnitude higher Na^+ and F^- concentrations than those low TDS waters from charnockitic gneiss and granulite, which may indicate relative parent rock compositional differences (in the absence of rock-powder analyses). These results support the literature consensus that granitic-type rocks host the highest potential for elevated groundwater fluoride [2,15,43]. Augen gneiss outcrops across central Malawi (Figure 2) and may represent a key zone of (dental) fluorosis risk. Hornblende-biotite gneiss on the other hand requires further sampling to be confident in categorising it as a high-risk lithology.

The data support our hypothesis that geology is the dominant control on fluoride occurrence in groundwater in weathered basement aquifers. Weathering of aquifer rock mobilises fluoride into solution, but generally low aquifer transmissivity ensure that fluoride is not transported far from source within the weathered basement profile. This facilitated the development of a map of geological fluoride risk ‘zones’ (Figure 9). The inherent lack of groundwater fluoride (and other) data for most water points in the study area (and many in Malawi) justifies the need for a preliminary screening approach which can identify high risk zones in the absence of observed groundwater fluoride measurements. User-level risk maps based on Figure 9 could be utilized by local communities to determine if their available, or proposed water points may be at risk from groundwater fluoride. This would be especially useful for users near a zone border who may decide to travel further for water (to a water point within a low-risk zone) to dilute overall fluoride intake. Graded zoning of geological fluoride risk will also prove useful for groundwater development programmes (Government or non-governmental organisations—NGOs) when drilling new boreholes and should be integrated into any subsequent planning strategies. Making informed decisions that avoid drilling in high-risk areas may provide a significant contribution to reducing (dental) fluorosis risk.

5.2 Human Health Risk

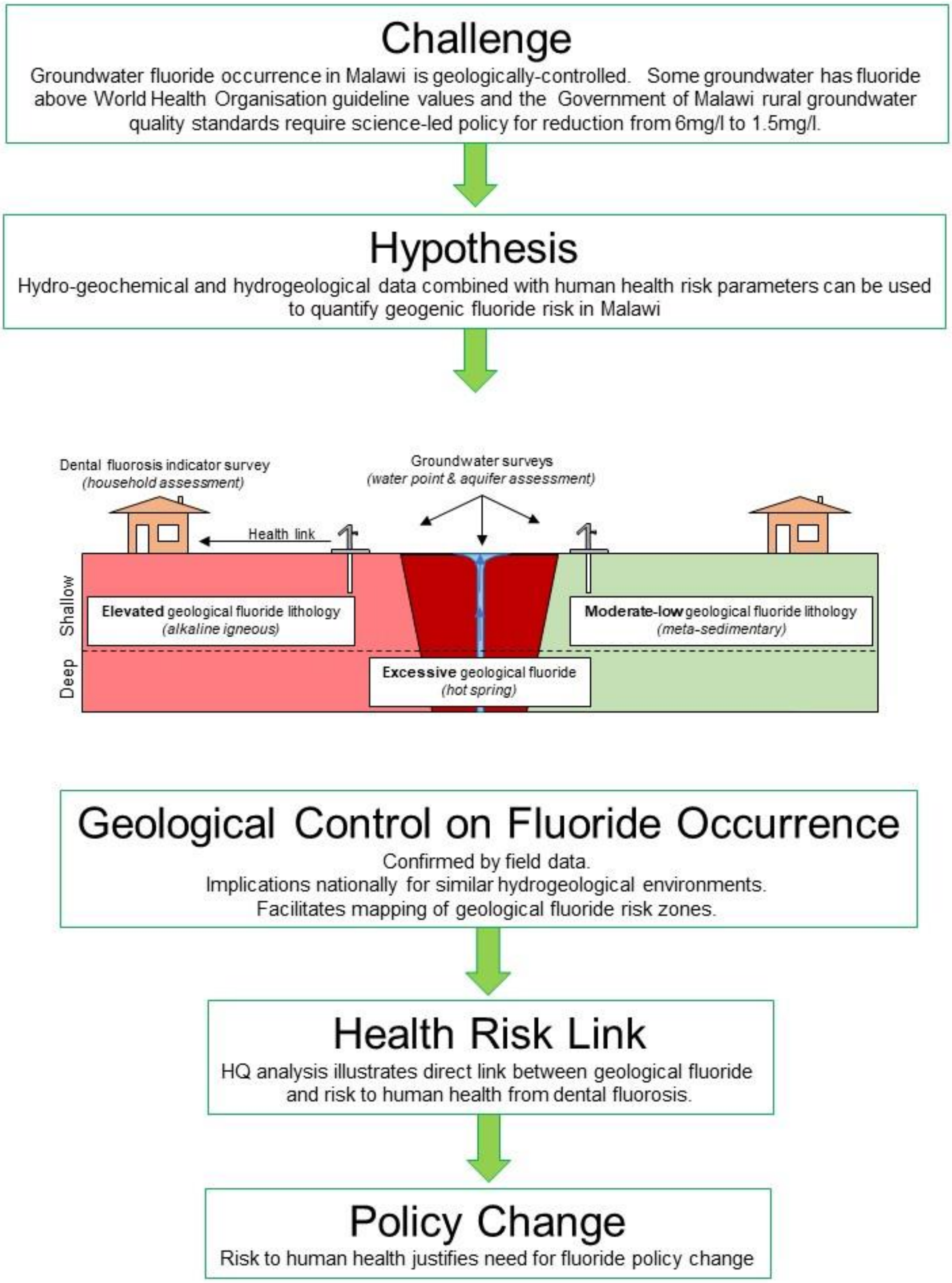
Our overarching goal is to inform science-led policy change in Malawi to assist the attainment of SDG targets. For a reduction in drinking water fluoride standard from 6 mg/L to 1.5 mg/L to be achieved, a direct link (risk) to human health from geologically controlled fluoride must be identified and quantified. The calculation of HQ values was completed for each water point sampled. HQ values provide a specific risk factor for each water point, per age group (Table 3) and support other data, identifying augen gneiss as the highest geological fluoride risk lithology (Table 4). HQ values expose the risk from drinking groundwater abstracted directly from high risk lithologies and provide the justification required to advocate policy change. When the HQ values from our sampled water points were compared to the fluoride map contained within the Malawi Hydrogeology Atlas [27], the difference in apparent risk was startling. Malawi's continued use of its 6 mg/L standard implies that the area is safe from dental fluorosis and (ground) water points within are safe to drink (limited to six water points). The HQ values for the same area are contrary, with 74% of water points considered unsafe for children aged 6 years old or under to drink, and 44% of water points unsafe for children under 12 (Table 3).

HQ values have additional value as a means of local risk reduction in the interim. HQ values could be utilised in practice to cycle water use between low and high-risk water points to dilute overall fluoride consumption. For example: anyone over the age of 12 should be safe from developing dental fluorosis by drinking water consistently from water point 30 (F^- = 0.95 mg/L), but a 6-year-old is vulnerable. Water Point 31 (F^- = 0.33 mg/L), however, is safe for anyone to drink (Table 3). By cycling water intake for children aged 6 years and under (also pregnant and breastfeeding women) between

Water Points 30 and 31 (50/50), the overall risk for those vulnerable at Water Point 30 is reduced by half, potentially preventing the development of dental fluorosis in those children. If this method can be applied by users at as many of the vulnerable water points as is possible (recognising variable distances between water points), the incidences of dental fluorosis in the study area could be vastly reduced, preventing potentially thousands of people from developing the condition. This method may prove fruitful in the short term via simple planning and informed decision making at user level.

6 Policy and Management Implications with Recommendations

This study began with a challenge: Malawian standard for fluoride in rural (mainly groundwater) drinking water is out of date (currently 6 mg/L) and sufficient understanding of fluoride in over 120,000 rural water supplies must be considered within the SDG 6 timeframe. This research was undertaken to support policy change (Figure 10). A science-based understanding of fluoride occurrence in Malawi combining hydro-geochemical, hydrogeological and human health proxy indicator data was used to quantify the geogenic fluoride risk in a case study area where a weathered basement aquifer dominates groundwater quality. We conducted groundwater surveys to assess groundwater fluoride occurrence, household surveys to assess the extent of the human health impact (dental fluorosis) and water point assessments via geospatial geogenic calculations to quantify the risk to human health from naturally occurring fluoride. The outcomes of this research, specifically the direct health link and potential for geological fluoride risk mapping, has instigated a need within the Malawian Government to review a change in the standard and policy for fluoride in rural water supplies, as scaling of the research outcomes can support new standards in line with WHO. We are now working closely with the MoIWD in Malawi to plan a review and assessment of fluoride risks and implementation of an incremental reduction of the fluoride standard, based on the fluoride risk levels identified (Figure 10).



Challenge

Groundwater fluoride occurrence in Malawi is geologically-controlled. Some groundwater has fluoride above World Health Organisation guideline values and the Government of Malawi rural groundwater quality standards require science-led policy for reduction from 6mg/l to 1.5mg/l.

Hypothesis

Hydro-geochemical and hydrogeological data combined with human health risk parameters can be used to quantify geogenic fluoride risk in Malawi

Geological Control on Fluoride Occurrence

Confirmed by field data.
Implications nationally for similar hydrogeological environments.
Facilitates mapping of geological fluoride risk zones.

Health Risk Link

HQ analysis illustrates direct link between geological fluoride and risk to human health from dental fluorosis.

Policy Change

Risk to human health justifies need for fluoride policy change

Figure 10. Integrated conceptual model of groundwater fluoride occurrence and health risk linkage leading to advocated groundwater fluoride policy change in Malawi.

This SDG framed research provides tangible and reasonable recommendations which can be implemented within Malawi, including:

- High-level policy change and SDG targets are required for national assessment. Simply changing the fluoride standard from 6 mg/L to 1.5 mg/L is unrealistic and expensive. We propose an incremental decrease in the fluoride standard over time. The 1st stage would be a reduction to 4 mg/L by 2024, instigating an assessment of "excessive fluoride" (hot springs) and "elevated geological fluoride" water points, removing the risk of skeletal fluorosis. Stage 2 would be a reduction to 2 mg/L by 2028, instigating an assessment of "moderate-low geological fluoride" water points and removing the worst of dental fluorosis risk. The final stage would be a reduction to 1.5 mg/L by 2030, bringing their standard in line with the WHO and removing the remaining risk of dental fluorosis from all water points. An evaluation of individual water points in each stage will identify those most harmful and replacement water supplies must be acquired, highlighting the need for incremental change.
- National geological fluoride risk maps should be developed for Malawi. Statistical analyses of fluoride–lithology relationships where fluoride data exist may be translated into risk maps (similar to Figure 9). For areas where fluoride data do not exist, preliminary risk estimates to be later proven may be extrapolated from existing fluoride–lithology data, justified by literature and applied to similar lithologies on a national scale. Risk maps would ultimately be controlled by a synergy of compositional geology and (fluoride) hydrochemistry in non-rift valley zones, and structural geology, compositional geology, hydrothermal processes, and hydrochemistry in rift valley zones. More complex risk models require extensive data sets which Malawi does not currently possess, therefore, mapping geological risk (i.e., fluoride sources) may be the most achievable method of tackling fluoride occurrence at a national scale. National mapping would allow the Government of Malawi and non-governmental organisations (NGOs) active in the water sector in Malawi to integrate fluoride contamination risk into their groundwater resource development strategies.
- Hazard quotient (HQ) values should be shared locally with water point users. It may prove a simple but effective way to inform local people about

the potential dangers of each water point and allow them to make informed decisions about water consumption on their own. Decommissioning water points based on elevated fluoride is an expensive venture as a replacement water supply must be provided. In a country with water scarcity problems and low-income, this is a considerable investment planning issue. Revision of rural water quality standards that allow 'yes/no' information on water quality at the water point and information on the negative health effects of fluoride ingestion may prove much more realistic across the country.

- A wider study of varied lithologies should be sampled in the same manner for hydrochemistry to determine their fluoride–lithology relationships. Both perthitic syenite and limestone (marble in this case) lithologies have been linked to high fluoride and are present in the study area but do not currently have corresponding hydrochemical data. National coverage of lithology types is required.
- Collaboration with dental studies in Malawi would be beneficial to corroborating occurrences of fluoride with definitive and documented incidences of dental fluorosis. This will be achieved by working together at the planning stage to ensure both disciplines are conducting their respective research in the same geographical areas. Sharing of data afterwards and working together on cross-discipline publications would ensure the impact of the research to a wider audience of both scientists and policy makers.
- An investigation into piped water supply networks should be undertaken. Piped groundwater from reticulated wells (high-yielding boreholes) drilled to support a network of pipes, powered by solar panels, to numerous kiosks where users can collect groundwater from the same source should be evaluated for fluoride. If a reticulated well is drilled into augen gneiss where fluoride potential concentrations are high, a larger number of people across a wider area will be at risk. The MoIWD or local government (or NGOs) should test for fluoride at kiosks and if found, water cycling with nearby, low fluoride water points should be advised in the first instance. If such methods are not possible at kiosks, those kiosks should be decommissioned, and replacement water supplies installed. If elevated fluoride is found in numerous kiosks fed from the same well, decommissioning of the full system and replacement of the water supply is

advised. Future plans for similar piped supplies should incorporate some level of fluoride risk assessment as described by this study. Simply avoiding target (high geological fluoride risk) lithologies may be enough and should be implemented.

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Conflicts of Interest

The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

Ethical Statement

Regarding the use of the Government of Malawi dental fluorosis indicator data, a number of household, functionality, and water quality surveys were carried out in traditional authority Mazengera by Government and private enumerators over the period of the 2019–2020 financial year. Survey responses were anonymous, and all subjects gave their informed consent for inclusion before they participated in the study which complied fully with the Ethical Guidelines of the Malawi Government. All enumerators were professionally trained on the Malawi Government's ethical guidelines which they ably followed in the field during the surveys.

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5.3 Supplementary Material

Table SM1. Summary statistics for fluoride data in the study area.

Lithology	*n*	Mean	25th Percentile	Median	75th Percentile	Fluoride (mg/l)			
						0 - 1.5	**1.5 - 2**	**2 - 3**	**3 - 4**
Augen Gneiss	16	2.16	1.34	2.19	2.86	31.25%	12.50%	31.25%	25.00%
hornblende-biotite Gneiss	3	1.87	1.64	1.84	2.08	33.33%	33.33%	33.33%	0.00%
Charnockitic Gneiss and Granulite	20	1.06	0.61	0.99	1.34	80.00%	10.00%	10.00%	0.00%
All	39	1.58	0.84	1.41	2.2	56.41%	12.82%	20.51%	10.26%

Table SM2. Geochemical data from TA Mazengera samples.

Sample	**Type**	**Latitude**	**Longitude**	**pH**	**EC (µS/cm)**	**TDS (mg/l)**	**F (mg/l)**	**Cl (mg/l)**	**NO2 (mg/l)**	**Br (mg/l)**	**NO3 (mg/l)**	**PO4 (mg/l)**	**SO42 (mg/l)**	**Ca (mg/l)**	**Mg (mg/l)**	**Na (mg/l)**	**K (mg/l)**	**Total Alkalinity CaCO3 (mg/l)**
1	BH	-14.03288	34.01013	7.37	1036	518	1.84	1.24	0.03	0.03	9.35	0.06	73.74	56.12	40.52	26.50	4.38	288.74
2	BH	-14.03319	34.00981	7.54	1067	536	2.02	1.08	0.03	0.03	7.31	0.05	69.90	65.43	45.82	26.56	3.39	327.88
3	BH	-14.04563	34.01110	7.4	946	471	1.78	6.90	0.03	0.03	48.23	0.03	137.12	87.59	56.02	37.55	3.42	403.34
4	BH	-14.04295	34.01076	7.38	860	431	1.45	3.81	0.03	0.03	21.62	0.03	99.12	79.35	49.46	31.61	2.32	374.72
5	BH	-14.05009	34.00824	7.52	893	446	2.31	4.34	0.03	0.03	34.08	0.03	110.53	75.75	59.68	34.74	2.63	381.96
6	BH	-14.03649	34.02924	7.35	635	317	2.08	14.84	0.03	0.03	26.72	0.03	12.97	66.60	28.21	33.39	1.65	290.92
7	BH	-14.03943	34.03418	7.25	909	458	3.04	47.60	0.03	0.17	208.95	0.06	24.25	84.43	40.13	44.06	1.70	257.23
8	SW	-14.04006	34.03488	7.47	603	302	1.41	16.17	0.07	0.03	9.64	0.03	13.04	72.34	24.36	25.62	0.84	272.16
9	BH	-14.03851	34.04143	7.13	1032	518	2.80	89.26	0.09	0.18	276.77	0.03	18.49	98.98	47.49	31.44	2.68	235.08
10	SW	-14.03859	34.04081	7.23	406	203	0.89	1.24	0.05	0.03	0.16	0.20	6.33	47.72	15.60	25.17	0.96	208.71
11	BH	-14.03867	34.04492	7.53	640	321	2.80	32.38	0.08	0.03	98.23	0.16	13.47	61.17	29.52	25.88	1.54	213.16
12	BH	-14.05575	34.02410	7.4	591	296	2.46	9.76	0.03	0.03	16.55	0.03	9.42	56.69	31.64	29.18	1.12	291.97
13	BH	-14.06871	34.01936	7.37	770	389	3.75	30.86	0.03	0.03	115.13	0.03	8.81	63.05	43.94	33.71	2.13	279.98
14	BH	-14.07172	34.02771	7.14	610	306	2.36	10.88	0.03	0.03	3.38	0.07	5.54	60.75	29.71	32.65	2.07	323.22
15	SW	-14.06831	34.02878	7.42	466	234	3.64	4.15	0.03	0.03	7.06	0.07	3.78	48.85	21.25	27.91	0.48	234.68
16	BH	-14.06046	34.03349	7.3	474	237	3.19	8.95	0.05	0.03	46.56	0.03	5.93	44.38	27.27	20.09	1.75	198.15
17	BH	-14.06728	34.03855	6.77	297	148	0.43	18.98	0.03	0.03	7.23	0.06	2.18	29.74	10.37	19.86	1.58	123.95
18	BH	-14.06052	34.04897	7.09	520	261	1.62	35.98	0.03	0.03	65.11	0.03	8.53	51.91	23.79	18.62	2.05	168.46

19	BH	-14.05359	34.05683	7.11	231	116	1.03	1.74	0.03	0.03	8.10	0.07	3.91	20.28	13.40	11.97	0.55	111.63
20	BH	-14.05130	34.05466	7.48	472	237	1.96	4.63	0.03	0.03	5.60	0.03	3.13	44.71	29.49	20.27	0.90	246.23
21	BH	-14.04390	34.05705	7.34	556	280	2.62	13.28	0.03	0.03	28.81	0.03	7.55	48.07	30.45	23.81	0.85	251.82
22	BH	-14.03923	34.05810	7.09	471	236	1.31	12.32	0.03	0.03	19.03	0.03	5.57	44.95	25.27	23.60	0.81	214.10
23	BH	-14.04796	34.06648	7.1	487	244	0.78	23.19	0.03	0.03	83.68	0.03	11.89	51.01	23.16	13.16	0.82	145.30
24	BH	-14.04683	34.07601	7.23	615	307	1.09	3.60	0.03	0.03	0.61	0.05	18.05	69.36	33.91	14.33	0.51	310.73
25	BH	-14.05515	34.06576	7.16	907	455	1.42	57.70	0.03	0.03	178.78	0.03	21.96	93.49	46.90	14.86	1.27	275.94
26	BH	-14.05632	34.06157	7.31	687	344	1.31	13.63	0.03	0.03	45.71	0.03	11.06	82.00	38.54	13.09	1.17	307.19
27	BH	-14.06732	34.05043	7.06	220	110	0.29	1.43	0.03	0.03	0.99	0.12	1.97	24.27	10.61	7.46	2.30	113.28
28	BH	-14.07588	34.04165	7.38	639	320	0.95	5.86	0.03	0.03	14.43	0.05	8.04	83.29	27.04	23.83	2.15	317.69
29	BH	-14.08637	34.05310	6.84	407	204	0.33	17.09	0.03	0.03	37.40	0.08	11.29	45.20	14.78	19.03	0.90	148.16
30	BH	-14.08078	34.05538	7.04	475	238	0.95	13.74	0.06	0.03	25.76	0.03	14.07	54.67	25.21	12.46	0.10	196.42
31	BH	-14.08079	34.05819	6.9	605	305	0.41	39.74	0.03	0.03	131.24	0.03	26.23	73.75	27.38	10.95	0.51	146.75
32	BH	-14.07666	34.06965	7.03	189.7	95.5	0.61	7.58	0.03	0.03	25.96	0.06	3.41	19.11	8.57	6.53	0.42	56.78
33	BH	-14.07690	34.06926	7.16	248	124	0.73	8.12	0.03	0.03	15.82	0.07	14.57	28.13	11.45	7.72	0.47	85.86
34	BH	-14.09336	34.05629	7	346	173	0.73	2.29	0.03	0.03	21.82	0.03	3.34	43.24	16.16	8.39	0.17	159.02
35	PS	-14.08790	34.08660	7.33	151.5	76.1	0.61	2.85	0.03	0.03	0.17	0.05	0.72	14.95	7.24	9.32	0.10	76.71
36	PS	-14.08687	34.08691	7.09	147.6	74.9	0.61	2.54	0.03	0.03	0.13	0.05	0.69	14.69	7.12	9.19	0.10	74.59
37	BH	-14.07681	34.09715	6.83	254	127	1.10	2.60	0.03	0.03	0.37	0.06	15.20	24.62	12.75	13.72	0.10	116.71
38	BH	-14.06459	34.10258	7.4	512	256	1.05	7.32	0.77	0.03	25.94	0.27	45.75	57.94	18.39	25.65	0.81	196.09
39	BH	-14.06412	34.10166	6.85	516	258	1.67	1.92	0.03	0.03	3.75	0.06	33.06	50.11	22.48	35.80	0.31	242.86

5.4 Summary and Context

This chapter addressed and fulfilled RQ. 2: ‘Can groundwater fluoride risk be mapped using geology and limited groundwater data?’ via a published paper in a peer-reviewed journal. The case study addressed RO. 2.1: ‘Conduct a case study to investigate ‘source-extent’ relationship between geology and groundwater fluoride.’. Fluoride-lithology relationships were investigated in Malawi’s most extensive aquifer type (weathered basement) and key geological fluoride sources were identified within specific lithology types: groundwater from alkaline igneous rocks (Augen gneiss in this case) presented significantly higher groundwater fluoride concentrations than groundwater from other rocks. The extent of influence from lithological source was also identified and found to be minimal, illustrating that interaction with lithological fluoride source is the dominant mechanism for groundwater fluoride occurrence, and that geochemistry of groundwater in the weathered basement aquifer reflects the composition of the host aquifer rock for any given water point. The case study addressed RO. 2.2: ‘Develop method for predicting and mapping geology-based groundwater fluoride risk using groundwater data.’. The results from the case study were used to develop an innovative method for predicting groundwater fluoride risk from lithological sources, where fluoride-lithology statistical relationships were calculated, and a prediction map of geology-based risk was developed based on those statistics. The method can be applied to any country with geological data and groundwater fluoride concentration data. Whilst the method can be successful with only limited or sparse groundwater data (containing only a fluoride concentration), the accuracy of the model is increased with increasing volume of fluoride data from which to calculate statistical relationships with host geology.

This chapter additionally answered and fulfilled RQ. 3: ‘What is the direct link between geogenic groundwater fluoride and human health risk in Malawi and is the current fluoride standard for drinking water aligned with health risks?’. The direct human health risk from groundwater fluoride was quantified via a human health risk assessment (USEPA, 2019) and the results were discussed to advocate Malawian groundwater policy reform. The findings from the case study highlighted significant challenges for Malawi if they are to achieve SDG 6.1 with respect to fluoride policy and standard. With the JMP classification of fluoride as a priority chemical contaminant and the SDG deadline approaching, such challenges must be overcome quickly. For a developing country such as Malawi where low income is a key challenge, new and innovative methods such as those developed in this chapter will be key to SDG 6 success. The groundwater fluoride prediction method developed in this chapter must be scaled nationally if the Government of Malawi is to use it as a prediction and asset management tool going forward. A more thorough investigation of current fluoride policy documents will also be required, along with realistic suggestions of how to redefine them to include fluoride contamination and potential mitigation methods. Those points are addressed in the next chapter.

Chapter 6 PREDICTING GROUNDWATER FLUORIDE NATIONALLY

6.1 Introduction

The previous chapter addressed and fulfilled RQ. 2: ‘Can groundwater fluoride risk be mapped using geology and limited groundwater data?’. A screening method for predicting groundwater fluoride risk from lithological sources in the most extensive aquifer type in Malawi was developed, using geological and groundwater fluoride data. The method was based on statistical relationships identified between groundwater fluoride and specific lithologies which were used to create a local-scale groundwater fluoride prediction map. This chapter addresses RQ. 4: ‘Can the groundwater fluoride prediction method developed be scaled nationally to cover all lithologies using existing data?’. The research question was answered via two primary research objectives. Digital geological data were not available for Malawi but were essential for analysing spatial relationships with fluoride and for calculating fluoride-lithology statistics required to upscale the geology-based prediction method nationally. RO. 4.1: ‘Create high resolution digitised map of Malawi’s geology’ was thus achieved by digitising the geology of Malawi at 1:250,000 scale, a significant task. RO. 4.2: ‘Scale methodology for mapping geological fluoride nationally using existing statistical ‘fluoride-lithology’ correlations where present, and extrapolations where data are absent.’ was achieved and is discussed in detail in the following section. The subsequent groundwater fluoride prediction map contained a risk factor hierarchy of classifications from low to excessive risk from groundwater fluoride. The map was a synthesis of ‘site-specific’ groundwater fluoride risk from hot springs, ‘generic’ groundwater fluoride risk from lithological sources and estimations of the number of water points and water point users at risk from each risk zone.

The previous chapter addressed RQ. 3: ‘What is the direct link between geogenic groundwater fluoride and human health risk in Malawi and is the current fluoride standard for drinking water aligned with health risks?’. The direct human health link was quantified using a case study and a preliminary investigation of national and global policy and standards for fluoride in drinking water was conducted. This chapter will further address RQ. 3 by providing a more thorough investigation of fluoride-relevant policy in Malawi.

RO. 3.2: ‘Investigate difference between current Malawi and global fluoride standards and advocate policy review via stepped progression for fluoride in drinking water in Malawi.’ was achieved via an interrogation of Malawi’s fluoride-relevant groundwater policy documents. Malawi’s continued use of its 6 mg/L standard for fluoride in drinking water from groundwater sources is outdated and leaves people vulnerable to fluorosis. Realistic recommendations are presented on update for the specific fluoride-relevant sections of Malawi’s policy documents and advocation of national groundwater policy reform via stepped progression is discussed.

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6.2 Paper

Predicting Groundwater Vulnerability to Geogenic Fluoride Risk: A Screening Method for Malawi and an Opportunity for National Policy Redefinition

Marc J. Addison [1,*], Michael O. Rivett [1], Peaches Phiri [2], Prince Mleta [2], Emma Mblame [2], Gift Wanangwa [2] and Robert M. Kalin [1]

[1] Department of Civil & Environmental Engineering, University of Strathclyde, Glasgow G1 1XJ, Scotland; marc.addison@strath.ac.uk (M.J.A); michael.rivett@strath.ac.uk (M.O.R.); robert.kalin@strath.ac.uk (R.M.K.)

[2] The Ministry of Forestry and Natural Resources, Lilongwe Headquarters, Private Bag 390, Lilongwe, Malawi; peachesphiri@gmail.com (P.P.); princemleta@gmail.com (P.M.); emmambalame@gmail.com (E.M.); gjwanangwa@gmail.com (G.W.)

* Correspondence: marc.addison@strath.ac.uk

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Abstract: Fluoride concentrations in Malawi's groundwater are primarily controlled by geogenic sources that are highly variable and may cause a heterogeneous fluoride occurrence and local-to-regional variations in fluorosis health risks posed. Our aim was to address the challenge of developing a national solution to predicting groundwater vulnerability to geogenic fluoride risk in the country of Malawi where incidences of fluorosis are reported and typical developing world problems of limited data and resources abound. Previously there have only been sporadic, local-scale studies linking fluoride occurrence with health risks in Malawi with no attempts to tackle the issue nationally. We hence develop a screening method for predicting groundwater vulnerability to geogenic fluoride in the form of detailed risk maps developed from statistical relationships shown between groundwater fluoride occurrence and known geogenic fluoride sources. The approach provides for dynamic update and informed acquisition of new data and hence on-going improving capacity to manage fluoride risks in Malawi. Our screening method provides a technical basis for redefining national fluoride policy to ensure commensurate management of health risks posed. Specifically, the approach provides a pathway for stepped progression from the current 6 mg/L Malawian standard for fluoride in drinking water to adoption of the World Health Organisation 1.5 mg/L guideline standard.

Keywords: fluoride; groundwater; risk management; environmental management; SDG 6; rural community water supply; policy change

1. Introduction

Over 82% of Malawi's burgeoning 17.5 million population live in rural areas that are heavily dependent upon groundwater for drinking water supply [1]. Our comprehensive mapping of rural water supplies in Malawi indicate international aid programmes have drilled nearly 60,000 boreholes and wells, most without prior hydrogeological knowledge or assessment of potential geo-hazards, with 24.5% resulting in poor performance and another 14.1% resulting in failure and abandonment [2–4]. The proportion suffering from poor water quality is unknown, however issues with iron, salinity, fluoride, and others are widespread [3,5–8]. Considering the reliance on groundwater in Malawi, significant focus is needed to mitigate risks of geogenic fluoride and to sustainably assess and manage existing supplies. Geogenic fluoride has been identified by the United Nations (UN)'s Joint Monitoring Programme (JMP) as a global-level priority contaminant under Sustainable Development Goal (SDG) 6.1 [9].

Concentrations of fluoride in the range 0.5–1.5 mg/L are beneficial to health in promoting the development of strong bones and teeth. Hence fluoride is often added to drinking water supplies and dental products where supplies fall below these concentrations. Drinking water fluoride concentrations exceeding 1.5 mg/L increases the risk of fluorosis with severity of the condition increasing from dental to skeletal to crippling with greater exposure [10], with children more vulnerable [11]. The World Health Organisation (WHO) recommends 1.5 mg/L for fluoride in drinking water to set a global guideline standard which is aligned with health risks [12]. The current Malawian standard for fluoride in drinking water from boreholes and wells is higher at 6 mg/L [13]. In the drive for SDG 6.1 and in response to the JMP classification of fluoride as a priority chemical contaminant globally, Malawi must review and redefine their fluoride standard and set targets that bring groundwater policy in line with known health risks, whilst assessing and managing existing groundwater supplies.

Endemic fluorosis occurs globally in distinct provinces; including the East African Rift System (EARS) [14] of which Malawi is part [5]. Groundwater fluoride and associated occurrence of fluorosis is well-documented in many EARS countries [15–17]. However, there has been only limited research in Malawi where there have been a few documented localities of increased dental fluorosis tentatively linked to increased fluoride based on quite sparse data [18–20]. There has been no published assessment of the fluorosis condition nationally and possible linkage to groundwater-derived drinking water supplies.

Fluorine is a naturally-occurring element making up 0.06–0.09% of the Earth's crust [21]. This occurrence gives rise to geogenic sources of fluoride to groundwater arising from water-rock interactions [5,6,14,18,22]. Alkaline igneous rocks are recognised as a major source of groundwater fluoride due to relatively high concentrations of fluoride-bearing minerals compared to other rock types [6,10,23–25]. Higher ratios of fluoride-bearing minerals in rocks result in higher fluoride concentrations in groundwaters and this is reflected in global data (Figure 1). In Malawi, hot springs and alkaline igneous rocks have been identified as significant sources of groundwater fluoride [5,6]. Anthropogenic activities such as the use of fertilisers, large-scale brick-making or industrial processes (aluminium and cement plants) can additionally contribute to fluoride concentrations to groundwater [11,14,26], however, these inputs in groundwater are considered negligible when compared to geogenic sources.

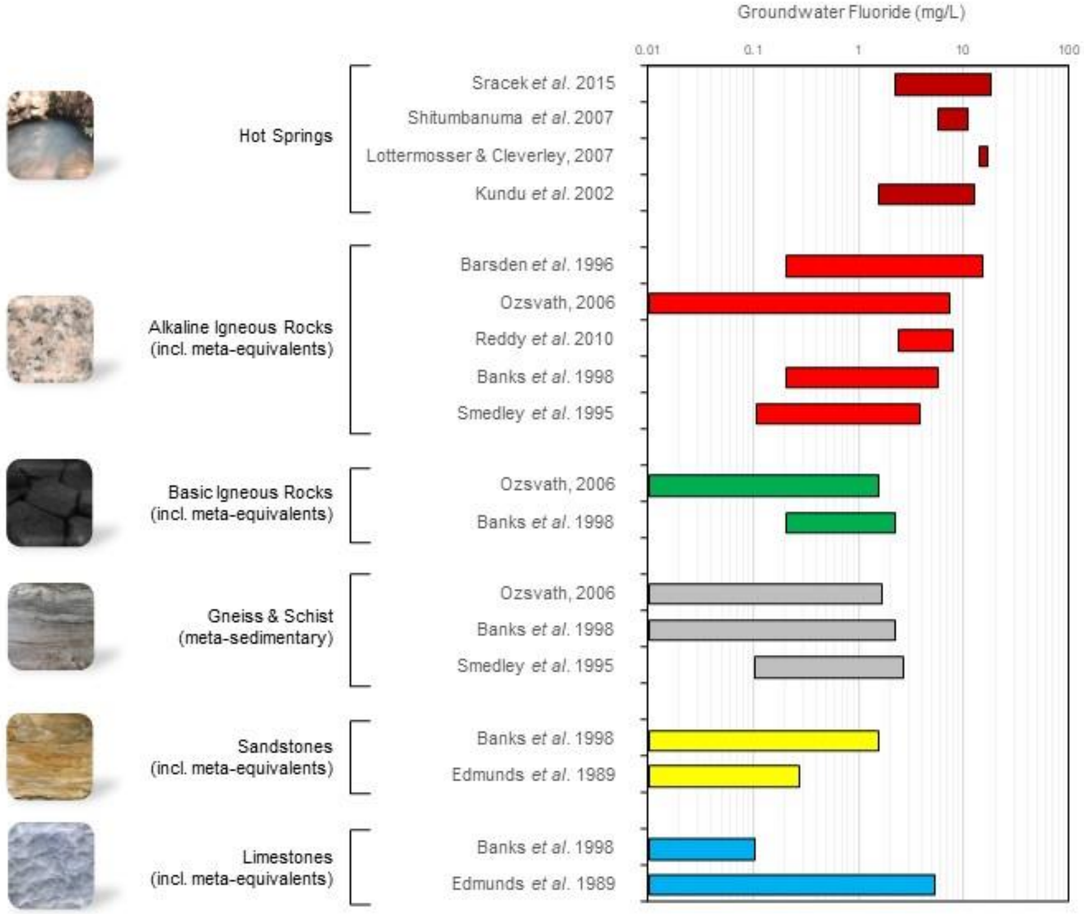


Figure 1. Summary of global data for groundwater fluoride concentration ranges and geogenic source. Hot springs represent deep hydrothermal

groundwater fluoride source, all others represent shallow rock weathering groundwater fluoride source, sorted per lithology type (References for data: [10,27–35]; hot spring photo source: [36]).

Whilst some geostatistical models have been developed to predict occurrence of groundwater fluoride risks nationally, for instance in India [37] and globally [38], this has not been specifically attempted for Malawi. Fluoride occurrence in Malawi's groundwater is moderately, but not comprehensively documented; the national dataset available have been recently collated for the first time by ourselves [5] and underpins our approach herein. Two distinct source types are evident: shallow weathering of aquifer rocks of diffuse occurrence; and highly localised hydrothermal inputs from hot springs along rift faults. Our approach herein is further underpinned by relationships found in our recent Central Malawi study setting where we mapped geogenic fluoride risk using statistical relationships identified between groundwater fluoride concentrations and aquifer lithology [6]. Zones of generic geogenic fluoride risk could be mapped, based on the statistical likelihood of a lithology producing groundwater with fluoride concentrations exceeding the WHO standard of 1.5 mg/L. Whilst the method developed used fluoride concentration data with corresponding lithological data, we [6] proposed the method could be extended to cover lithologies without corresponding fluoride concentration data where extrapolations on likely fluoride content may be reasonably made based on the wider international geogenic source literature.

This study expands upon this previous work to investigate existing fluoride-lithology statistical relationships over a wider range of lithologies occurring nationally, and to extrapolate likely fluoride content of rocks where fluoride data were absent. This allowed geological-based mapping of generic geogenic fluoride risk nationally even where groundwater fluoride concentration data are absent. It is recognised though within the Rift Valley setting, structural geological control in the form of faulting may additionally control the occurrence of particularly elevated fluoride due to the provision of pathways to surface of deep-seated hydrothermal, fluoride-rich groundwaters. It is hence proposed hot spring data may be additionally collated to proxy map 'hot-spot' site-specific groundwater vulnerability to geogenic fluoride from known hydrothermal sources.

Our goal was hence to develop a geological-based screening method for predicting groundwater vulnerability to geogenic fluoride risk in Malawi nationally, with local-to-regional granularity assessment of risks posed. The methodology aimed to not only make optimal use of existing, often sparse data, but also to direct future acquisition of data enabling on-going improvement in fluoride risk management capacity. The screening method proposed takes the form of detailed geogenic risk maps identifying site-specific 'hot-spot' risks signified by known hot spring occurrences overlying a more regional zonation of generic groundwater fluoride risk developed from statistical relationships between groundwater fluoride occurrence and lithological fluoride sources identified within the mapped geology. Combining such risk maps with our wider research programme's detailed water point mapping across the whole of Malawi may then allow estimation of the numbers of people at risk of fluorosis from every functioning water point, nationally. The above ambitions were substantially achieved. The screening method developed provides the first comprehensive mapping of data-informed vulnerability of Malawi's groundwater resource to geogenic fluoride and attendant increased risks of fluorosis. The approach informs national policy development through primarily providing a data-informed, risk-based pathway for stepped progression from the current 6 mg/L fluoride Malawian drinking water standard to adoption of the current WHO standard of 1.5 mg/L.

2. Material and Methods

Multiple data sets have been synthesised by us to develop the overall method of predicting and mapping groundwater vulnerability to geogenic fluoride. The approach involved five stages of development which are summarised in Table 1 and discussed in detail below. Some fluoride sources were excluded from this study as they likely have a negligible effect on groundwater fluoride concentrations in Malawi. For example, anthropogenic source via fertilisers high in fluoride can be a viable source of groundwater fluoride where present. A proxy for measurement is a correlation between nitrate (NO_3^-) and fluoride (F^-) [11], however, no correlation was found in our data and fluoride input from this source was excluded. Fluoride from precipitation has been shown to have mean concentrations in rainfall (in the absence of volcanic emissions and marine aerosols) of one to two orders of magnitude less than those in (Malawian) groundwater (median range: 0.03–0.22 mg/L), the higher end of the range caused by proximity to large-scale aluminium and cement plants which are absent in Malawi [14,26]. Atmospheric input from coal burning or brick making may increase fluoride levels in precipitation, however, in the absence of large-scale industrial processes (e.g., India; China), concentrations will remain within the same precipitation range [14], thus, precipitation as a source was not considered due to Malawi's predominantly rural, low industry landscape. Surface water fluoride was excluded as concentrations are generally higher than in precipitation, but still within the μg/L range [14]. Additionally, most rivers are were found to be ‘gaining’ rivers in Malawi, therefore any fluoride in river water likely has a groundwater origin [39–41]. Seasonal effects on fluoride were excluded due to a negligible effect in Malawi, where minor seasonal variations have comparable spatial trends across the seasons (wet and dry) [18]. Geochemical studies suggest that rock-silicate weathering (of aquifer material) is the dominant source of groundwater fluoride [6,11] and was the focus of this study.

Table 1. Summary of methodology development, per stage, with a short description of the objectives of each stage.

Methodology Development		
Stage 1	Groundwater Fluoride Data Collation	Collate master data set of groundwater fluoride concentrations and hot springs for Malawi
Stage 2	Geological Data Collation and Digitisation	Produce Digital Geological Map of Malawi for use in statistical and spatial analyses with groundwater data
Stage 3	Development of Statistical Relationships and Extrapolations	Determine geogenic fluoride risk classifications by calculating fluoride-lithology statistical relationships and extrapolating where data are absent
Stage 4	Development of National Groundwater Risk Maps and Statistics	Produce national and catchment-level geogenic fluoride groundwater risk maps. Estimate number of water points and people at risk from groundwater fluoride.
Stage 5	Policy Review and Implications	Investigate the Malawian standard documents for fluoride in drinking water relative to the WHO and SDGs

2.1 Stage 1: Groundwater Fluoride Data Collation

A master data set of groundwater fluoride concentrations for Malawi was collated (n = 1126) so that statistical and spatial correlations with geology could be determined. The collation was achieved and discussed within our earlier published works: In brief summary, fluoride data from groundwater quality analyses across Malawi were compiled, and augmented by field work carried out by the Climate Justice Fund: Water

Futures Programme (CJF) for the period 2016–2018 [5]. Data were further augmented by our local study in Central Malawi [6]. Hot spring data were collated for this study ($n = 63$) from published literature [5,42–46] and data provided by the Malawi Ministry of Forestry and Natural Resources (formerly Ministry of Agriculture, Irrigation and Water Development). All data had previously been through QA/QC protocols. The resulting two collated data sets represented both known groundwater fluoride sources in Malawi: (i) A groundwater fluoride concentration data set to represent 'shallow rock weathering' source and for use in fluoride-lithology statistical analysis; (ii) A groundwater fluoride concentration data set from hot springs to represent 'deep hydrothermal' source and for use in fluoride-hot spring statistical analysis.

2.2 Stage 2: Geological Data Collation and Digitisation

Fluoride concentration data were spatially analysed with respect to geology to calculate fluoride-lithology statistical correlations. Digital geological data were not available for Malawi so had to be digitised from existing, non-digital geological maps [47]. Data from maps were enhanced with lithological and structural detail from geology bulletins and journal publications [48–51]. Lithological composition was found to be the main control on groundwater fluoride concentrations and extent in the weathered basement aquifer of Malawi [6], so was therefore assumed here as the main control from shallow rock weathering due to the presence or absence of fluoride-bearing minerals [6,10,23–25,52]. Each lithology in Malawi was digitised into a geological map per lithological group (shown later) which were determined based on dominant mineralogical composition. In order to view geology in the detail discussed within this study, the geological map was divided into 10 separate maps (Figures S1–S10–Supplementary Materials). Deeper hydrothermal groundwater from hot springs were mapped separately as highly localised, site-specific 'hot-spot' sources of particularly elevated fluoride.

2.3 Stage 3: Development of Statistical Relationships and Extrapolations

The method developed for mapping generic geogenic fluoride risk zones outlined by [5] is adapted and scaled nationally here to cover lithologies (zones) which had corresponding groundwater fluoride concentration data and extending to cover those which did not. The previous study calculated fluoride-lithology statistical correlations to develop a generic fluoride risk map covering three lithologies in TA Mazengera [5]. Similarly, the groundwater fluoride data set compiled for this study ($n = 1126$) was spatially joined with digitised geology in ArcGIS (10.6) and evaluated with corresponding geological attributes for analysis separately in Microsoft Excel (2010). The percentage of groundwater fluoride concentrations > 1.5 mg/L were calculated for 12 lithologies where corresponding groundwater fluoride data from the master groundwater data set occurred. Geogenic fluoride risk categories were then identified using the resulting fluoride-lithology relationships and classified based on the statistical likelihood of a lithology containing groundwater with fluoride concentrations > 1.5 mg/L. Hot springs were calculated separately, regardless of host lithology due to a different groundwater source system (deep hydrothermal). This allowed an accurate fluoride signature of each lithology to be calculated without external influence from a hydrothermal system which would interfere with the results.

For lithologies where corresponding groundwater fluoride data were absent, fluoride-lithology relationships were estimated where suitable extrapolations could be made on likely mineralogical content of rocks and thus, likely generic geogenic fluoride classification. Estimations and extrapolations were based on the observed relationships from this study and augmented by literature where necessary. The dominant mineralogy of each lithology was used to associate individual lithologies with the appropriate risk classification. Lithologies where no similar fluoride-lithology statistical relationships were available from which to extrapolate a classification, or where no suitable justification could be made, were classified simply as ‘Insufficient Data for classification’.

A total of 28 hot springs (those from the collated master hot spring data set that had corresponding groundwater fluoride concentration data) were used to determine a statistical relationship between hot springs and groundwater fluoride concentrations in order to determine a groundwater fluoride risk category for hot springs (i.e., statistical likelihood of a hot spring containing groundwater with fluoride concentrations > 1.5 mg/L). The risk category for hot springs was extrapolated to the remaining 35 hot springs which had no corresponding groundwater fluoride concentration data.

2.4 Stage 4: Development of National Groundwater Risk Maps and Statistics

A national map of geogenic groundwater risk for Malawi was developed (presented later). The map was built in ArcGIS to display zones of statistical geogenic fluoride groundwater risk from shallow rock weathering sources (generic) and deep hydrothermal sources (site-specific-hot springs). In Malawi, water resources are managed at (surface water) catchment-level, so smaller-scale maps were developed for each major catchment, or 'Water Resource Area' (WRA) (Figures S11–S27- Supplementary Materials), to facilitate groundwater resource development planning for fluoride by the Government. These maps also demonstrate the ability of our approach to be adapted to any scale.

National statistics were calculated using a master data set of water points. Efforts to develop a 'live' national Management Information System (MIS) in Malawi are ongoing and are core to the CJF aim of assisting the Government of Malawi to proactively manage its water supply infrastructure assets [2]. The mWater platform (www.mwater.co) (referred to simply as 'mWater') hosts the MIS and manages data for over 120,000 water points in Malawi, mapped and managed in a joint Government of Malawi and CJF venture. The ability to cross reference highly detailed, national water point data with geological data has proven to be a powerful tool as the data were used to identify specific water points which may be at risk from geogenic fluoride. The full water point data set was extracted from mWater and analysed spatially with geology to estimate the number of people at risk from increased groundwater fluoride concentrations from every water point. Each water point contains data on its functional status which are characterised as follows:

- Functional
- Partly functional but in need of repair
- Not functional
- No longer exists/abandoned

Only "functional" and "partly functional but in need of repair", direct groundwater abstraction sources were included (*n* = 49,730). 'not functional' water points (*n* = 4158) were calculated separately as they are continually repaired across the country, therefore, still represent a potential future risk if drawing groundwater from an elevated geogenic fluoride source (Figure 2).

Water point data from mWater (i.e., groundwater abstraction points) were divided per geogenic fluoride zone (defined previously from statistical correlations) so that the exact number of water points in each zone could be calculated. Each water point contained Government of Malawi survey data on the number of people who normally use it, which was used to estimate the number of people at risk from geogenic fluoride (chronic exposure to the same water point was assumed), thus fluorosis, using the geogenic fluoride risk classifications developed within this study. This was performed nationally and calculated statistics for water points and users at risk were presented on the final maps (national and catchment-level) as tables. An additional table of national statistics is presented per district to aid local government in policy review efforts. This study was solely concerned with fluorosis risk arising from chronic consumption of groundwater (home/village water supply) abstracted directly from a geogenic fluoride source. Fluoride exposure complexities arising from consumption of water from multiple sources was out with our scope, therefore, water points with >850 users were excluded as they likely represented heath centres or schools.

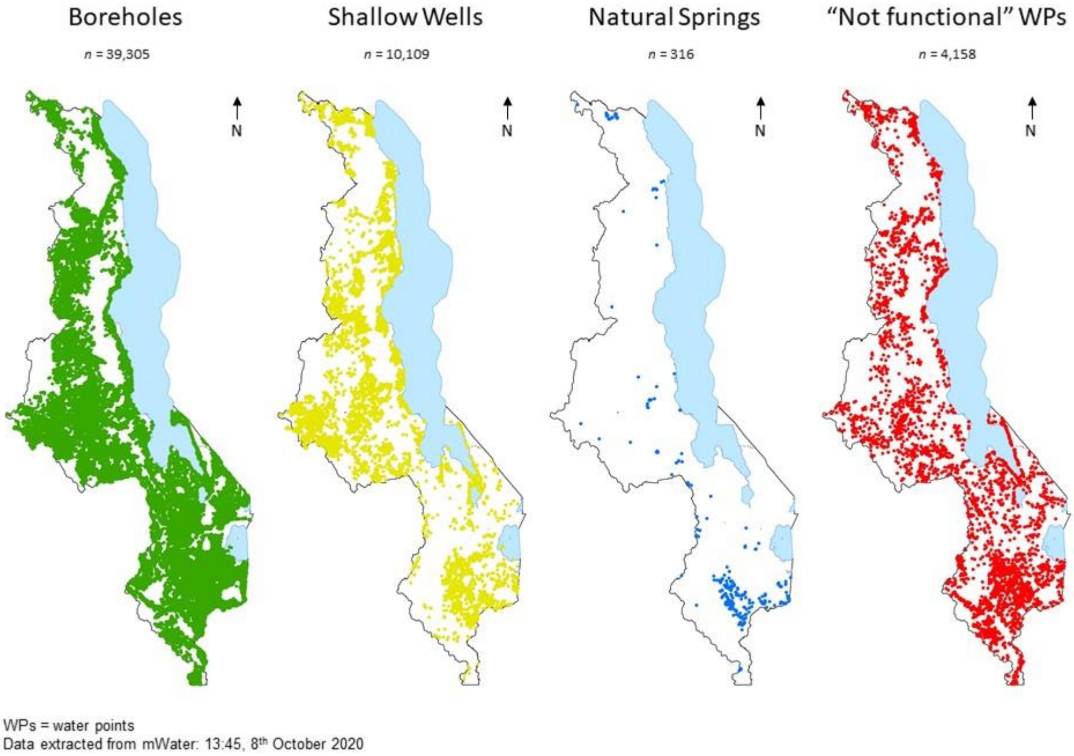


Figure 2. All water points included in this study. Only direct groundwater sources were considered (each water point type is represented separately). The data is representative of the time/date it was extracted from mWater (8 October 2020).

2.5 Stage 5: Policy Review and Implications

An assessment of the current Malawian standard documents related to fluoride in drinking water was undertaken. We present a discussion of the value of our screening method in directing the redefinition of Malawi's fluoride standard along with recommendations on how it may be revised within the context of the SDGs and health risks in Malawi.

3. Results

3.1 Groundwater Data

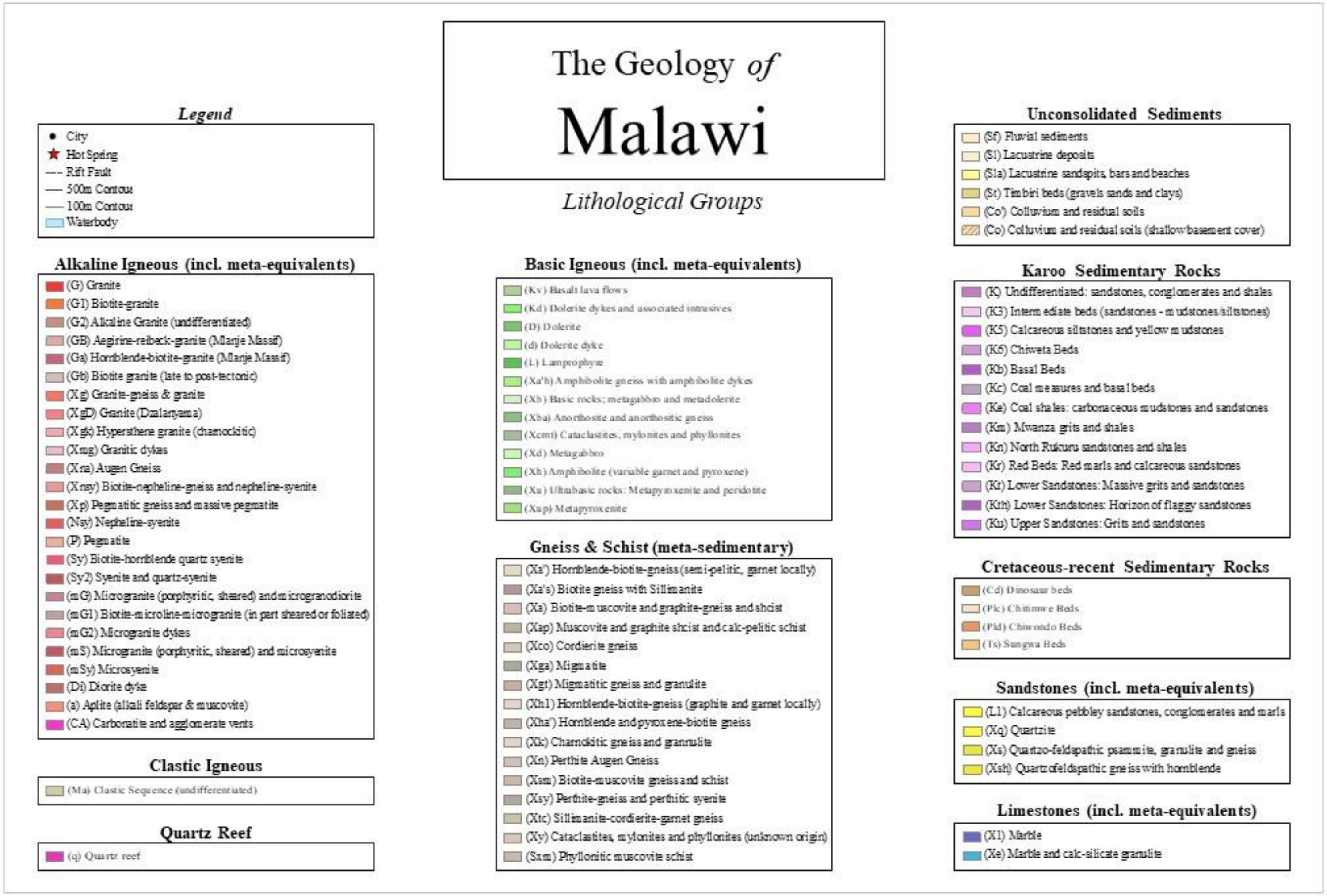
In total, 1126 groundwater fluoride concentrations from boreholes, shallow wells and natural springs were compiled, along with data for 28 hot springs. (Table 2). The separation of hot springs from other groundwater data allowed both groundwater fluoride source systems (shallow rock weathering vs. deep hydrothermal) to be analysed separately. The average fluoride concentration from the groundwater fluoride data set was 0.97 mg/L, with 87% of samples falling within the WHO standard for fluoride in drinking water of 1.5 mg/L. The remaining 13% had concentrations < 6 mg/L, with one outlier at 10.63 mg/L from a shallow well. Hot springs had significantly higher fluoride concentrations: all hot springs with corresponding fluoride concentration data (*n* = 28) exceeded the WHO standard, with an average of 6.38 mg/L.

Table 2. Summary of groundwater fluoride data collated for use in this study.

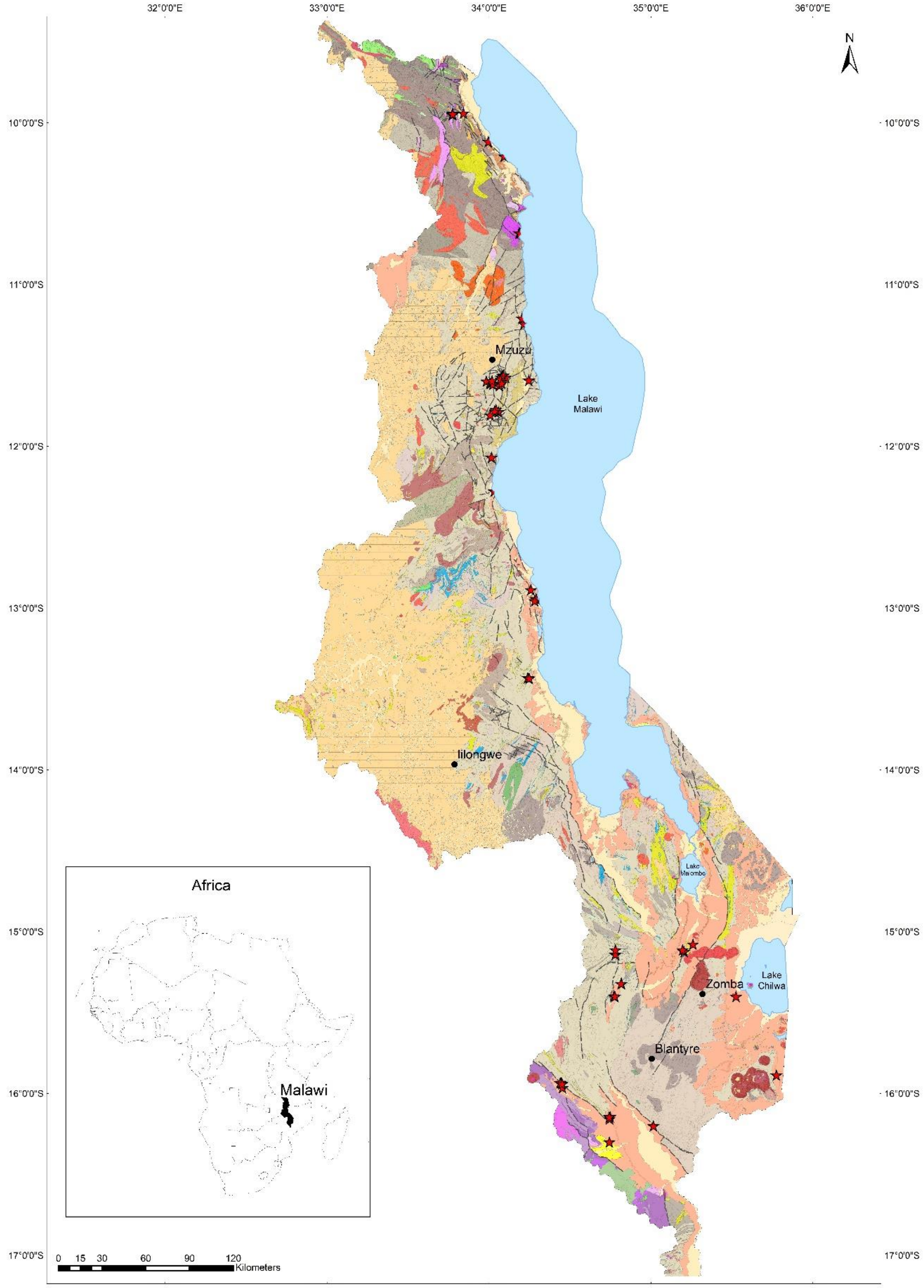
Data Set	***n***	**Fluoride Concentration (mg/L)**								
		<1.5	>1.5	1.5–6	>6	Min.	Max.	Mean	Median	Std. Dev.
Groundwater F^-	1126	86.77%	13.23%	13.14%	0.09%	0.02	10.63	0.97	0.80	0.95
Hot Springs	28	0.00%	100%	46.43%	53.57%	2.21	20	6.38	5.88	3.89

3.2 Geological Data

85 separate lithologies in Malawi were identified and digitised from existing geological maps (Figure 3b), which were sub-divided into 10 main lithological groups (Figure 3a). The geology of Malawi was additionally split into 10 separate maps (spatial cuts) so that detail at the relevant scales discussed in this study can be viewed with ease (Figures S1–S10–Supplementary Materials). The maps additionally display major faulting associated with rifting and the locations of all 63 known hot springs.


The Geology of
Malawi
Lithological Groups
Legend
● City
★ Hot Spring
--- Rift Fault
— 500m Contour
— 100m Contour
Waterbody
Alkaline Igneous (incl. meta-equivalents)
(G) Granite
(G1) Biotite-granite
(G2) Alkaline Granite (undifferentiated)
(GB) Aegirine-reibeck-granite (Mlanje Massif)
(Ga) Hornblende-biotite-granite (Mlanje Massif)
(Gb) Biotite granite (late to post-tectonic)
(Xg) Granite-gneiss & granite
(XgD) Granite (Dzalanyama)
(Xgk) Hypersthene granite (charnockitic)
(Xmg) Granitic dykes
(Xna) Augen Gneiss
(Xnsy) Biotite-nepheline-gneiss and nepheline-syenite
(Xp) Pegmatitic gneiss and massive pegmatite
(Nsy) Nepheline-syenite
(P) Pegmatite
(Sy) Biotite-hornblende quartz syenite
(Sy2) Syenite and quartz-syenite
(mG) Microgranite (porphyritic, sheared) and microgranodiorite
(mG1) Biotite-microline-microgranite (in part sheared or foliated)
(mG2) Microgranite dykes
(mS) Microgranite (porphyritic, sheared) and microsyenite
(mSy) Microsyenite
(Di) Diorite dyke
(a) Aplite (alkali feldspar & muscovite)
(CA) Carbonatite and agglomerate vents
Clastic Igneous
(Ma) Clastic Sequence (undifferentiated)
Quartz Reef
(q) Quartz reef
Basic Igneous (incl. meta-equivalents)
(Kv) Basalt lava flows
(Kd) Dolerite dykes and associated intrusives
(D) Dolerite
(d) Dolerite dyke
(L) Lamprophyre
(Xa'h) Amphibolite gneiss with amphibolite dykes
(Xb) Basic rocks; metagabbro and metadolerite
(Xba) Anorthosite and anorthositic gneiss
(Xcmt) Cataclastites, mylonites and phyllonites
(Xd) Metagabbro
(Xh) Amphibolite (variable garnet and pyroxene)
(Xu) Ultrabasic rocks: Metapyroxenite and peridotite
(Xup) Metapyroxenite
Gneiss & Schist (meta-sedimentary)
(Xa') Hornblende-biotite-gneiss (semi-pelitic, garnet locally)
(Xa's) Biotite gneiss with Sillimanite
(Xa) Biotite-muscovite and graphite-gneiss and shcist
(Xap) Muscovite and graphite shcist and calc-pelitic schist
(Xco) Cordierite gneiss
(Xga) Migmatite
(Xgt) Migmatitic gneiss and granulite
(Xh1) Hornblende-biotite-gneiss (graphite and garnet locally)
(Xha') Hornblende and pyroxene-biotite gneiss
(Xk) Charnockitic gneiss and granulite
(Xn) Perthite Augen Gneiss
(Xsm) Biotite-muscovite gneiss and schist
(Xsy) Perthite-gneiss and perthitic syenite
(Xtc) Sillimanite-cordierite-garnet gneiss
(Xy) Cataclastites, mylonites and phyllonites (unknown origin)
(Sxm) Phyllonitic muscovite schist
Unconsolidated Sediments
(Sf) Fluvial sediments
(Sl) Lacustrine deposits
(Sla) Lacustrine sandspits, bars and beaches
(St) Timbiri beds (gravels sands and clays)
(Co') Colluvium and residual soils
(Co) Colluvium and residual soils (shallow basement cover)
Karoo Sedimentary Rocks
(K) Undifferentiated: sandstones, conglomerates and shales
(K3) Intermediate beds (sandstones - mudstones/siltstones)
(K5) Calcareous siltstones and yellow mudstones
(K6) Chiweta Beds
(Kb) Basal Beds
(Kc) Coal measures and basal beds
(Ke) Coal shales: carbonaceous mudstones and sandstones
(Km) Mwanza grits and shales
(Kn) North Rukuru sandstones and shales
(Kr) Red Beds: Red marls and calcareous sandstones
(Kt) Lower Sandstones: Massive grits and sandstones
(Kth) Lower Sandstones: Horizon of flaggy sandstones
(Ku) Upper Sandstones: Grits and sandstones
Cretaceous-recent Sedimentary Rocks
(Cd) Dinosaur beds
(Plc) Chitimwe Beds
(Pld) Chiwondo Beds
(Ts) Sungwa Beds
Sandstones (incl. meta-equivalents)
(L1) Calcareous pebbley sandstones, conglomerates and marls
(Xq) Quartzite
(Xs) Quartzo-feldspathic psammite, granulite and gneiss
(Xsh) Quartzofeldspathic gneiss with hornblende
Limestones (incl. meta-equivalents)
(Xl) Marble
(Xe) Marble and calc-silicate granulite

(a)


32°0'0"E
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35°0'0"E
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N
10°0'0"S
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17°0'0"S
Mzuzu
Lake
Malawi
lilongwe
Lake
Malombo
Zomba
Lake
Chilwa
Blantyre
Africa
Malawi
0 15 30 60 90 120
Kilometers

(b)

Figure 3. (**a**) Map legend and geological key for all maps, lithology organised per lithological group. (**b**) Full geological map of Malawi (digitised after others: [47,51], with Malawi's location on the African continent inset. Map is divided into 10 separate maps with additional detail necessary to identify specific lithologies in the Supplementary Materials (Figures S1–S10).

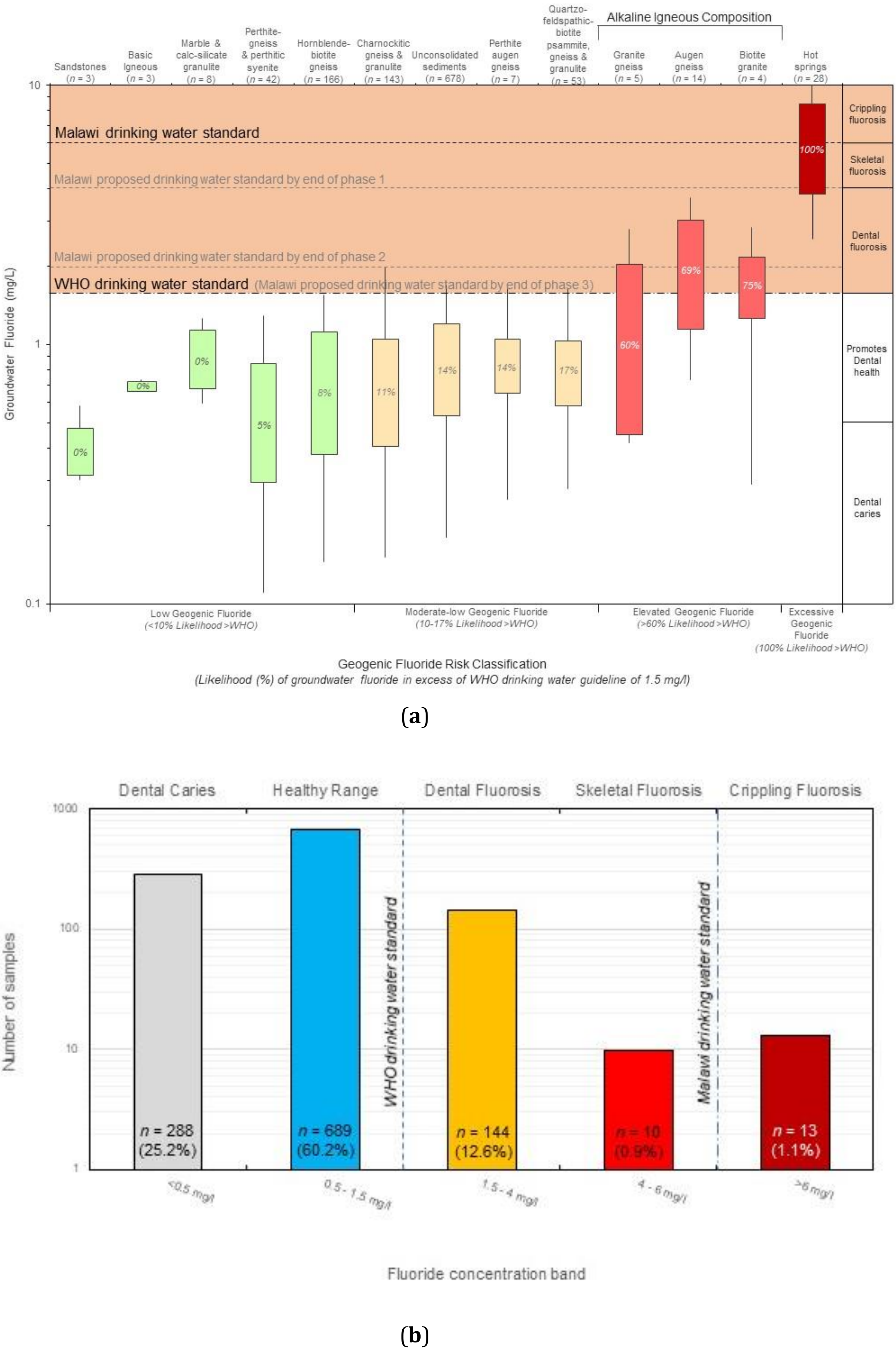
3.3 Statistical Relationships and Extrapolations

The results of spatial analysis of both groundwater data sets (groundwater fluoride and hot springs) allowed statistical relationships between fluoride concentrations in groundwater and aquifer lithology/hot springs to be classified. Six classifications were developed based on the statistical likelihood of encountering groundwater fluoride concentrations which exceed the WHO drinking water guideline standard of 1.5 mg/L (Table 3).

Table 3. Fluoride classifications and likelihood (%) of encountering groundwater fluoride > 1.5 mg/L. Hot springs represent site-specific groundwater fluoride sources; all other classifications represent generic sources.

Classification	Likelihood of Groundwater Fluoride > 1.5 mg/L
Excessive Geogenic Fluoride (hot spring)	100%
Elevated Geogenic Fluoride	>60%
Moderate-high Geogenic Fluoride	17–60%
Moderate-low Geogenic Fluoride	10–17%
Low Geogenic Fluoride	<10%
Insufficient Data for classification	Unknown

Water points from our groundwater data set occur within 12 of Malawi's 85 specific lithologies. The plot of 12 lithologies (plus hot springs) with georeferenced fluoride data confirms statistical risk categories can be assigned to lithologies where hydrochemical data for fluoride exist (Figure 4). Sample numbers vary for different lithologies (*n* = 3 to 678) (Figure 4), showing increased confidence for lithologies with higher sample numbers and decreasing confidence for those with lower sample numbers.


Sandstones (n = 3)
Basic Igneous (n = 3)
Marble & calc-silicate granulite (n = 8)
Perthite-gneiss & perthitic syenite (n = 42)
Hornblende-biotite gneiss (n = 166)
Charnockitic gneiss & granulite (n = 143)
Unconsolidated sediments (n = 678)
Perthite augen gneiss (n = 7)
Quartzo-feldspathic-biotite psammite, gneiss & granulite (n = 53)
Alkaline Igneous Composition
Granite gneiss (n = 5)
Augen gneiss (n = 14)
Biotite granite (n = 4)
Hot springs (n = 28)
10
1
0.1
Groundwater Fluoride (mg/L)
Malawi drinking water standard
Malawi proposed drinking water standard by end of phase 1
Malawi proposed drinking water standard by end of phase 2
WHO drinking water standard (Malawi proposed drinking water standard by end of phase 3)
0%
0%
0%
5%
8%
11%
14%
14%
17%
60%
69%
75%
100%
Crippling fluorosis
Skeletal fluorosis
Dental fluorosis
Promotes Dental health
Dental caries
Low Geogenic Fluoride (<10% Likelihood >WHO)
Moderate-low Geogenic Fluoride (10-17% Likelihood >WHO)
Elevated Geogenic Fluoride (>60% Likelihood >WHO)
Excessive Geogenic Fluoride (100% Likelihood >WHO)
Geogenic Fluoride Risk Classification
(Likelihood (%) of groundwater fluoride in excess of WHO drinking water guideline of 1.5 mg/l)
Dental Caries
Healthy Range
Dental Fluorosis
Skeletal Fluorosis
Crippling Fluorosis
1000
100
10
1
Number of samples
n = 288 (25.2%)
n = 689 (60.2%)
n = 144 (12.6%)
n = 10 (0.9%)
n = 13 (1.1%)
WHO drinking water standard
Malawi drinking water standard
<0.5 mg/l
0.5 - 1.5 mg/l
1.5 - 4 mg/l
4 - 6 mg/l
>6 mg/l
Fluoride concentration band

(**a**)

(**b**)

Figure 4. (**a**) Integrated graphic showing summarised statistical fluoride-lithology relationships for existing data. The percentage in each bar reflects the statistical likelihood of each source (lithology/hot spring) producing groundwater fluoride exceeding 1.5 mg/L. Sample numbers (*n*) are shown with lithology names. The figure shows the various health conditions associated with ingestion of fluoride and their corresponding fluoride concentration bands [10]. Horizontal lines display current and proposed fluoride drinking water standards. (**b**) Chart showing fluoride concentration bands and their respective proportion of the sample number from the data set. Y-axis has a logarithmic scale to expand data with low sample numbers.

The highest statistical likelihood of encountering groundwater fluoride > 1.5 mg/L is from hot springs with 100% (*n* = 28) possessing fluoride exceeding this limit. Hot springs displayed the highest fluoride concentrations (range: 2.2–20.0 mg/L) and were classified separately as 'Excessive Geogenic Fluoride'. All fluoride concentrations in the data set > 6 mg/L (except one outlier) are associated with a known hot spring (conduit for hydrothermal water). Lithologies of alkaline igneous composition display a statistical likelihood of encountering groundwater fluoride > 1.5 mg/L of 60–75%. All other lithologies displayed likelihoods of 17% or less, with a complete absence of any lithological groundwater fluoride source between 17% and 60% (Figure 4a). 60.2% of all samples (water points) produce groundwater fluoride concentrations within a healthy range which actively promotes the formation of strong teeth and bones in children (0.5–1.5 mg/L), 12.6% of samples produce groundwater fluoride concentrations high enough to cause dental fluorosis and 2% of samples produce concentrations high enough to cause skeletal and crippling fluorosis (Figure 4b).

Rocks of alkaline igneous composition displayed the highest generic statistical likelihood (>60%) of encountering groundwater fluoride > 1.5 mg/L (Figure 4a) and were classified as 'Elevated Geogenic Fluoride'. Granite gneiss, Augen gneiss (metamorphosed granite in this case) and Biotite granite have statistical likelihoods of 60%; 69% and 75% respectively. Even with low sample numbers for Granite gneiss and Biotite granite, these results are not surprising due to significantly higher ratios of fluoride-bearing minerals in granitoid rocks (Figure 1), relative to other rocks [6,10,23–25]. The 'Elevated Geogenic Fluoride' classification was thus extrapolated to the 19 remaining lithologies of alkaline igneous composition (Figure 3a).

Perthite-gneiss and perthitic syenite, present as extensive outcrops south east of Lilongwe at the Malawi/Mozambique border and around Blantyre (Figure 3), appear anomalous as "syenite" (alkaline igneous composition) should reflect a relatively high statistical likelihood of elevated groundwater fluoride. Our data show this lithology displaying only 5% likelihood (Figure 4a). The gneiss was originally meta-sedimentary which was intruded by syenite (unknown volume), then subsequently perthitised. Syenite was intruded along axial planes of refolded major F1 structures and has since been highly altered during at least two deformation stages [47]. This resulted in localised linear occurrences of syenite within the gneiss. Consistently low groundwater fluoride within this lithology (*n* = 42) may reflect locations where there is an absence or low volume of syenite. This lithology, originally classified as alkaline igneous [47], was subsequently reclassified to meta-sedimentary (in this study), based on these statistical and descriptive observations. Further field work is necessary to confirm the relative syenite/meta-sediments ratio, and locations of syenite bands for the outcrop, but a high ratio of low fluoride concentrations suggests that syenite volume is low in this lithology and its reclassification is valid.

The 'Moderate-high Geogenic Fluoride' range (17–60% likelihood of encountering groundwater fluoride > 1.5 mg/L) (Figure. 4a) was defined by the lower limit of 'Elevated Geogenic Fluoride' and upper limit of 'Moderate-low Geogenic Fluoride' and is characterised by complete lack of lithological sources in Malawi.

Lithologies with 10–17% likelihood of encountering groundwater fluoride > 1.5 mg/L, classified as 'Moderate-low Geogenic Fluoride' are dominated by meta-sedimentary lithologies and unconsolidated sediments. Perthite augen gneiss (*n* = 7) is the only anomaly and represents a perthitised alkaline lithology, similar to Perthite gneiss and perthitic syenite mentioned previously. Sample numbers are low and description of the lithology states that it is graded into the previously reclassified Perthite gneiss and perthitic syenite [47], therefore low fluoride concentrations may again represent meta-sedimentary locations within the graded zone. Field visits at the locations of those water points would be required to confirm. The 'Moderate-low Geogenic Fluoride' classification was applied to all remaining meta-sedimentary lithologies with similar dominant mineralogies, and to all six unconsolidated sediment lithologies.

'Low Geogenic Fluoride' lithologies carry the least risk of groundwater fluoride > 1.5 mg/L (<10%) (Figure 4a). This range includes two meta-sedimentary lithologies: the newly classified perthite gneiss and perthitic syenite, and hornblende-biotite gneiss. The latter is a lithology previously connected to elevated geogenic fluoride risk in Central Malawi [6], however doubts about the validity of this connection were expressed due to a low sample number (*n* = 3). Our study increased the sample size to 166, of which only 8% had fluoride concentrations > 1.5 mg/L, therefore, classified here as 'Low Geogenic Fluoride' (Figure 4a). Other lithologies identified in this category include sandstones, basic igneous rocks, marble, and calc-silicate granulite (Figure 4). The 'Low Geogenic Fluoride' classification was applied to all remaining lithologies with similar mineralogy to those identified.

Areas classified as 'Insufficient Data for Classification' are comprised of mostly complex sedimentary sequences where not enough hydrochemical or geological data are available to determine a generic fluoride risk classification. Lithologies within this group are likely to be low risk: most are sandstones, conglomerates, mudstones and breccias (with highly variable carbonate), but the sequences are too complex to determine generic fluoride risk without hydrochemical data. Some mylonites are present but there are not enough available data to determine composition. There are also no corresponding fluoride data from which to calculate statistical correlations. Logging and geochemical sampling from those lithologies would be required to determine geogenic fluoride risk classification.

13.5% of samples from the groundwater data set display fluoride concentrations between the WHO and Malawi standards (1.5–6 mg/L) for fluoride in drinking water. Concentrations > 1.5 mg/L cause varying degrees of fluorosis (Figure 4), therefore, drinking water standards are not aligned with geogenic fluoride risk in Malawi under current policy.

Hot spring activity is highly localised, and the risk of hydrothermal fluoride appears exclusive to those locations. Five locations with fluoride concentrations in the range 3–6 mg/L occur within the rift basin and may represent hot spring activity, or movement of fluoride-rich groundwater along faults hidden beneath unconsolidated basin sediments. Unconsolidated sediments have a statistically low risk of groundwater fluoride (14%-Figure 4a) so such concentrations within this range in the sediments appear anomalous. Known hot springs within unconsolidated sediments display the highest fluoride concentrations found in Malawi (Figure 5) so it is reasonable to assume that anomalously high groundwater fluoride concentrations found within unconsolidated sediments in the rift valley likely represent locations where rift-related faults hidden beneath sediments are exploited as flow conduits for fluoride-rich groundwater. They may also indicate where shallow groundwater is in contact with fluorite mineralisation from past hydrothermal activity along faults, hidden beneath sediments.

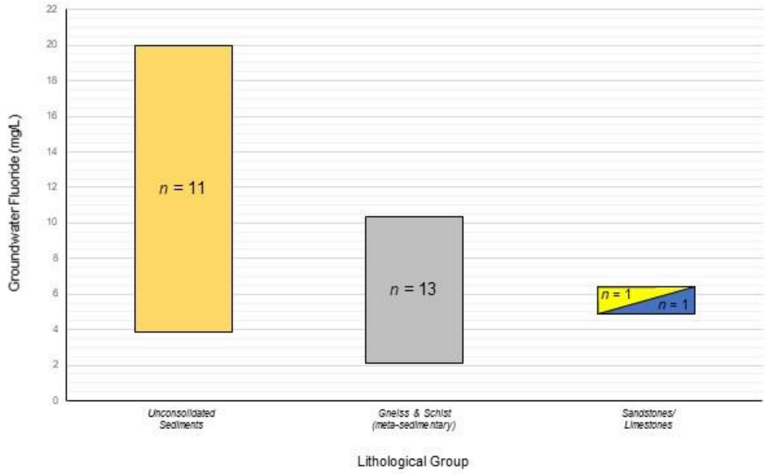


Figure 5. Groundwater fluoride concentration ranges for hot springs, split per lithological group from which they occur.

3.4 National Groundwater Risk Map and Statistics

49,793 groundwater, 'functional' and 'party functional but in need of repair' water points were extracted from mWater and used to calculate statistics for the number of water points and the number of people at risk in each zone. Water points included hot springs, boreholes, shallow wells (protected and unprotected) and natural springs (Figure 6).

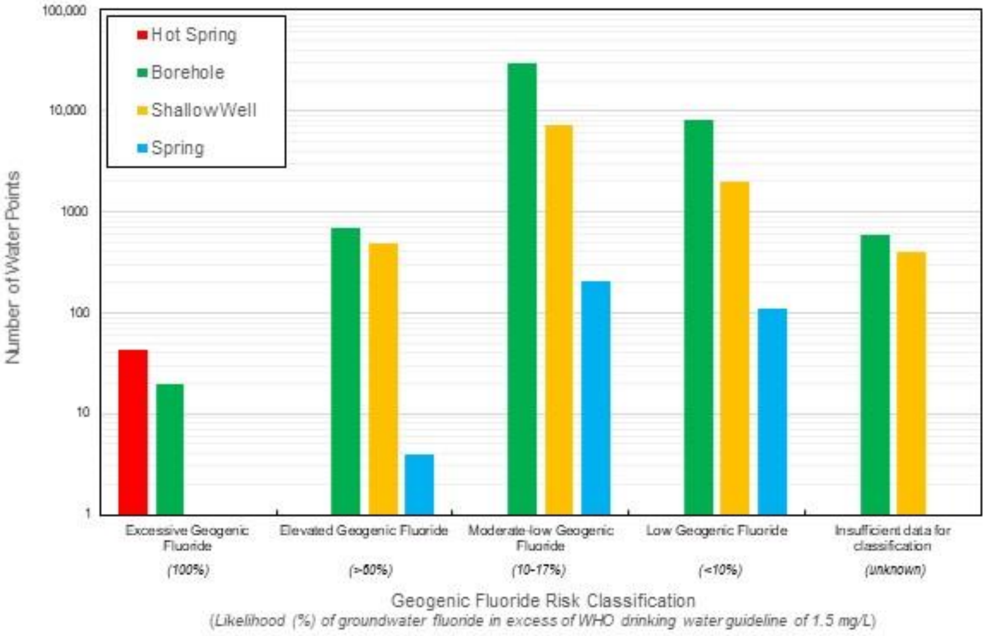
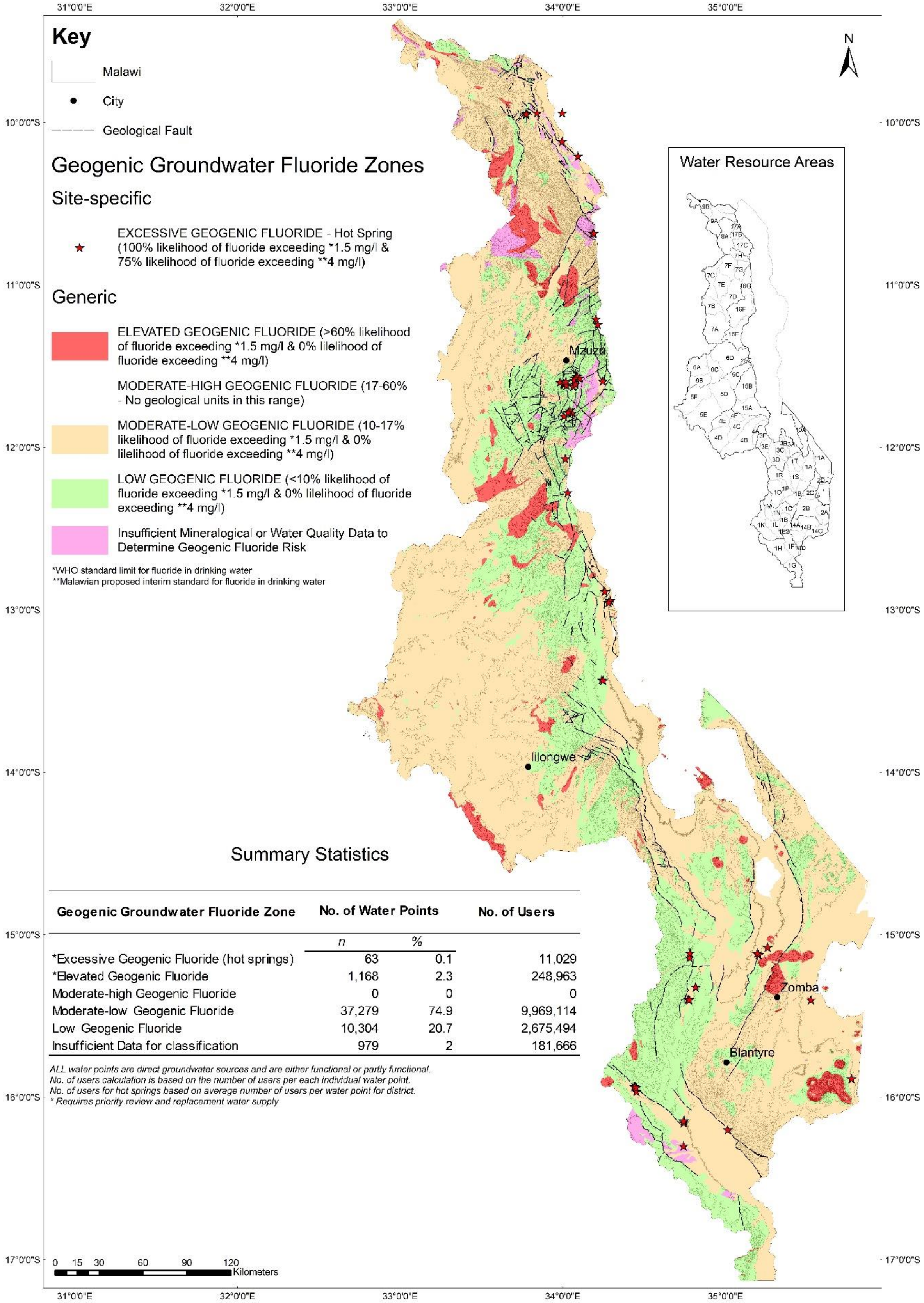


Figure 6. Breakdown summary of all water point data (functional and partly functional, direct groundwater sources–extracted from mWater) used in this study, per geogenic fluoride classification.

A map of groundwater vulnerability from geogenic fluoride was developed for Malawi based on the results from the statistical analysis and subsequent extrapolations (Figure 7a). 63 site-specific 'Excessive Geogenic Fluoride' water points (hot springs) represent highly localised endemic fluorosis areas where local people use them for drinking. These water points pose the highest fluorosis risk in Malawi (Figure 4). The estimated number of people at risk from developing fluorosis from hot springs in Malawi is 11,029 (Figure 7a). This is based on the average number of people per functioning water point, per local district (in the absence of users per water point data for hot springs).

'Elevated Geogenic Fluoride' zones account for 5.18% of Malawi's land surface and are presented as generic zones with >60% risk of encountering groundwater > 1.5 mg/L (Figure 7a). Those represent alkaline igneous lithologies and are localised to plutons and intrusions associated with rifting and deformed meta-equivalents within basement rock. The number of people vulnerable from groundwater fluoride > 1.5 mg/L (thus dental fluorosis) in those zones is an estimated 248,963 (Figure 7a), which constitutes about 1.4% of the population of Malawi. Water points within these zones total 1168 which is about 2.3% of functioning and partly functioning direct groundwater abstraction points. Water points within this category plus all hot springs (*n* = 1233) affect a total of 259,992 rural Malawians across the country (Figure 7a) and represent the worst of the fluorosis risk (Figure 4a).

Water points within 'Moderate-low Geogenic Fluoride' zones constitute 74.9% of water points (*n* = 37,279), affecting a total of 9,969,114 people (Figure 7a). This classification carries a relatively low statistical risk (10–17%) of encountering groundwater fluoride > 1.5 mg/L. While the statistical likelihood is low, this still represents approximately 1–1.6 million people across these zones who may be drinking groundwater with fluoride concentrations elevated enough to cause dental fluorosis. 'Low Geogenic Fluoride' carries a low statistical likelihood (<10%) of encountering elevated groundwater fluoride > 1.5 mg/L but still represents approximately 267,594 people (Figure 7a) who currently may be at risk. Water points within zones with insufficient data for a geogenic fluoride classification constitute 2% of water points (*n* = 979) and currently affect an estimated 181,666 people (Figure 7a).



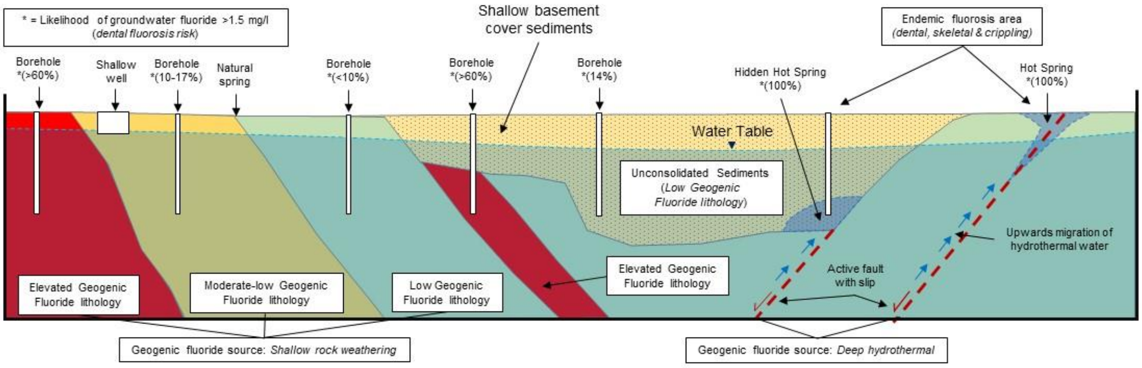
Summary Statistics

Geogenic Groundwater Fluoride Zone	No. of Water Points		No. of Users
	n	%	
*Excessive Geogenic Fluoride (hot springs)	63	0.1	11,029
*Elevated Geogenic Fluoride	1,168	2.3	248,963
Moderate-high Geogenic Fluoride	0	0	0
Moderate-low Geogenic Fluoride	37,279	74.9	9,969,114
Low Geogenic Fluoride	10,304	20.7	2,675,494
Insufficient Data for classification	979	2	181,666

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

(**a**)

Figure 7. *Cont.*



(**b**)

Figure 7. (**a**) Geogenic fluoride groundwater risk map of Malawi. The map is based on the geological map of Malawi (Figure 3), where each lithology is displayed per geogenic fluoride risk classification (Figure 4a) as zones of generic groundwater vulnerability to geogenic fluoride from shallow rock weathering. Hot springs are displayed as site-specific sources of geogenic fluoride from deep hydrothermal sources. The map includes estimated numbers of people vulnerable from geogenic groundwater fluoride in each zone (based on the number of people normally using each water point). (**b**) Conceptual model of known and hypothesised geogenic fluoride sources from a.

Statistics were calculated for 'not functional' water points separately (Table S1–Supplementary Materials). A total of 107 of these are located in 'Elevated Geogenic Fluoride' zones, posing a potential future groundwater fluoride risk to 25,522 people if repaired and not assessed for fluoride. Geogenic fluoride groundwater risk maps were also developed for each major catchment in Malawi with relevant summary statistics displayed as tables (Figures S11–S27-Supplementary Materials). An additional table of water point and users at risk statistics is presented per district (Table 4) for local government use in reviewing the fluoride standard.

4. Discussion

4.1 Discussion of Results

Hot springs are well-documented sources of particularly increased groundwater fluoride concentrations, often displaying the highest concentrations globally (Figure 1), so it was not unexpected that all hot springs in Malawi exceeded the WHO standard [9] for fluoride in drinking water and possessed the highest range of groundwater fluoride concentrations (Figure 4a). Hot springs produce groundwater from deeper reservoirs (i.e., different hydrogeological system) to those associated with shallow rock weathering, so they were classified separately as 'Excessive Geogenic Fluoride'. This classification reflects: (i) deep hydrothermal source reservoir; (ii) significantly higher groundwater fluoride concentrations associated with hot springs; (iii) 100% likelihood of groundwater fluoride concentrations > 1.5 mg/L (Figure 4a); and (iv) the only site-specific groundwater geogenic fluoride risks identified by this study. Fluoride concentrations > 4 mg/L are associated with skeletal and crippling fluorosis (Figure 4) so hot springs represent almost all of the risk of those conditions in Malawi. They constitute the biggest human health risk from fluorosis and are the priority targets for replacement water supplies. The 63 hot springs represent highly localised 'hot-spot' areas of probable endemic fluorosis which currently affect an estimated 11,029 people in Malawi (Figure 7a). It is likely that incidences of both conditions (skeletal, crippling), plus increased incidences of dental fluorosis relative to other locations will be present at and immediately surrounding those sites.

Table 4. Data for the number of water points in each fluoride zone and the corresponding number of people at risk per zone, split per district.

District	No. of Water Points									No. of Users				
	Elevated Geological Fluoride		Moderate-low Geological Fluoride		Low Geological Fluoride		Insufficient Data		Total	Elevated Geological Fluoride	Moderate-Low Geological Fluoride	Low Geological Fluoride	Insufficient Data	Total
Balaka	0	*0.0%*	1108	*73.0%*	410	*27.0%*	0	*0.0%*	1518	0	319,481	146,633	0	466,114
Blantyre	2	*0.1%*	2119	*75.5%*	687	*24.5%*	0	*0.0%*	2808	480	456,009	164,958	0	621,447
Chikwawa	22	*0.9%*	1867	*74.4%*	562	*22.4%*	59	*2.4%*	2510	5875	542,936	192,636	20,106	761,553
Chiradzulu	0	*0.0%*	1125	*67.0%*	554	*33.0%*	0	*0.0%*	1679	0	306,588	156,072	0	462,660
Chitipa	167	*12.3%*	989	*72.9%*	143	*10.5%*	58	*4.3%*	1357	35,470	156,417	35,376	4153	231,416
Dedza	12	*0.7%*	1074	*66.4%*	532	*32.9%*	0	*0.0%*	1618	4987	392,938	178,075	0	576,000
Dowa	70	*3.8%*	1564	*85.2%*	202	*11.0%*	0	*0.0%*	1836	24,452	524,419	78,486	0	627,357
Karonga	10	*0.5%*	1591	*83.8%*	43	*2.3%*	255	*13.4%*	1899	1040	256,355	11,181	45,318	313,894
Kasungu	40	*2.2%*	1387	*74.6%*	432	*23.2%*	0	*0.0%*	1859	9265	374,052	90,238	0	473,555
Lilongwe	101	*2.3%*	3793	*87.0%*	466	*10.7%*	0	*0.0%*	4360	42,377	1,136,296	173,853	0	1,352,526
Machinga	4	*0.3%*	1187	*92.0%*	99	*7.7%*	0	*0.0%*	1290	1600	445,461	29,400	0	476,461
Mangochi	36	*0.9%*	3293	*86.5%*	476	*12.5%*	0	*0.0%*	3805	10,723	883,423	155,745	0	1,049,891
Mchinji	10	*0.5%*	1813	*97.7%*	32	*1.7%*	0	*0.0%*	1855	2900	466,838	6381	0	476,119
Mulanje	0	*0.0%*	1525	*83.4%*	300	*16.4%*	3	*0.2%*	1828	0	357,125	58,563	110	415,798
Mwanza	27	*4.6%*	0	*0.0%*	562	*95.4%*	0	*0.0%*	589	7508	0	129,432	0	136,940
Mzimba	416	*9.6%*	2691	*62.2%*	1207	*27.9%*	11	*0.3%*	4325	56,988	614,476	217,360	1542	890,366
Neno	0	*0.0%*	74	*15.5%*	403	*84.5%*	0	*0.0%*	477	0	22,869	130,738	0	153,607
Nkhata Bay	1	*0.1%*	314	*23.1%*	534	*39.3%*	509	*37.5%*	1358	270	41,962	73,611	99,355	215,198
Nkhotakota	76	*4.9%*	990	*64.0%*	481	*31.1%*	0	*0.0%*	1547	10,908	220,673	90,739	0	322,320
Nsanje	11	*0.8%*	1101	*77.9%*	289	*20.4%*	13	*0.9%*	1414	2580	213,463	45,919	2170	264,132
Ntcheu	9	*0.7%*	536	*41.1%*	760	*58.2%*	0	*0.0%*	1305	5000	219,963	264,214	0	489,177
Ntchisi	3	*0.3%*	873	*77.0%*	258	*22.8%*	0	*0.0%*	1134	1780	254,517	47,766	0	304,063
Phalombe	15	*1.3%*	1068	*92.1%*	77	*6.6%*	0	*0.0%*	1160	5092	249,935	15,876	0	270,903

Rumphi	114	*11.1%*	703	*68.6%*	144	*14.0%*	64	*6.2%*	1025	12,952	100,193	21,705	6207	141,057
Salima	1	*0.1%*	1056	*80.0%*	263	*19.9%*	0	*0.0%*	1320	206	302,130	68,599	0	370,935
Thyolo	0	*0.0%*	1749	*85.6%*	294	*14.4%*	0	*0.0%*	2043	0	446,923	62,739	0	509,662
Zomba	21	*1.2%*	1667	*93.6%*	93	*5.2%*	0	*0.0%*	1781	6510	657,837	28,999	0	693,346
AUNA*	0	*0.0%*	22	*73.3%*	1	*3.3%*	7	*23.3%*	30	0	5835	200	2705	8740
Total	1168	*2.3%*	37,279	*75.0%*	10,304	*20.7%*	979	*2.0%*	49,730	248,963	9,969,114	2,675,494	181,666	13,075,237
% of Malawi Population										*1.4%*	*56.8%*	*15.2%*	*1.0%*	*74%*

All water points are direct groundwater sources and are either functional or partly functional. ‘No. of users’ calculation is based on the number of users per each water point. *AUNA = Area Under National Administration.

Rocks of alkaline igneous composition consistently produce the highest groundwater fluoride concentrations, relative to other rocks (Figure 1) and our results support this conclusively (Figure 4a). Our results contain groundwater fluoride concentrations from three different granitoids which all displayed > 60% likelihood of groundwater fluoride concentrations > 1.5 mg/L, reasonably justifying the extrapolation of the ‘Elevated Geogenic Fluoride’ classification to other granitoid rocks. Hydrochemical data from syenitic rocks were absent so reasonable justifications for inclusion into this classification along with other alkaline igneous rocks had to be established: lithologies of syenitic composition are well-documented sources of elevated groundwater fluoride, comparable to granitic types [10], some syenites often possess significantly higher fluoride content than granites [53]. The fluoride content of the Chipala-Kasungu nepheline syenites of northern Malawi range from 1550–2400 mg/kg [50]. Quartz syenite of the Zomba and Mulanje plutons in southern Malawi have very similar composition to granite [47]. All syenitic-type rocks in Malawi were thus classified as ‘Elevated Geogenic Fluoride’ and mapped as zones of increased generic risk.

Carbonatites are categorised as alkaline igneous rocks but have different composition to granites and syenites. They contain high relative sodium content which increases groundwater fluoride potential via fluorite (CaF_2) equilibration [5]. Malawi carbonatites additionally have extensive occurrences of fluorite and fluoro-apatite veins [48,49], a result of secondary precipitation from post emplacement hydrothermal processes and an additional source of groundwater fluoride. Carbonatites were therefore classified as ‘Elevated Geogenic Fluoride’ alongside other alkaline igneous rocks and mapped as zones of increased generic risk.

Lithologies within the ‘Moderate-low Geogenic Fluoride’ classification contained exclusively unconsolidated sediments and meta-sedimentary rocks (Figure 4a). Unconsolidated sediments display 14% likelihood of encountering groundwater fluoride > 1.5 mg/L, however, this is a category which carries some uncertainty. Unconsolidated sediments in the Southern Region are dominated by rift basin colluvium, alluvium, lacustrine and fluvial sediments (Figure 3). In the Central and Northern Regions, there is an additional category of colluvium which is characterised as ‘thin basement cover’ of unknown thickness and is extensive (Figure 3). Those areas represent a two-tier aquifer system where weathered basement aquifers occur beneath unconsolidated sediment aquifers of variable and unknown thickness. An individual well may be tapping into either, or both of those aquifer systems, depending on its depth. This poses uncertainty when extrapolating geogenic fluoride risk categorisation for the unconsolidated sediments at those locations, as a well may be drilled into an elevated geogenic fluoride lithology (e.g., granite) which is hidden beneath the sediment cover, but showing as low risk on a map (unconsolidated sediments). High hydraulic conductivity and transmissivity values identified in wells within these areas [54] suggest that from the perspective of drinking water boreholes, these areas abstract from unconsolidated sediment aquifers (for the most part) and are thus classified as 'Moderate-low Geogenic Fluoride'. Further groundwater sampling to identify elevated fluoride, pumping test data to determine hydraulic conductivities (proxy for aquifer type: sedimentary aquifers classified by high hydraulic conductivity and transmissivity values; weathered basement aquifers characterised by low hydraulic conductivity and transmissivity values [6]), and/or borehole drilling logs to identify sediment depth vs. well depth, would increase confidence in this classification. All remaining lithologies in Malawi within the 'Meta-sedimentary Rocks' lithological group (Figure 3a) were reasonably classified as 'Moderate-low Geogenic Fluoride' based on existing statistical correlations for this group (Figure 4a).

'Low Geogenic Fluoride' lithologies were characterised by sandstones, marbles, basic igneous rocks and two meta-sedimentary rocks (Perthite gneiss and Hornblende-biotite gneiss) so all remaining sandstones, limestones, marbles and basic igneous rocks across Malawi were grouped within this classification. The two meta-sedimentary rocks present a potential anomaly within the Moderate-low classification; however, relatively high sample numbers (Figure. 4a) present an increased confidence so they were grouped within this classification. Low sample number (*n* = 3) for basic igneous rocks present low confidence in prediction for those lithologies, however, all samples had groundwater fluoride concentrations < 1.5 mg/L (Figure. 4a), hence the classification as 'Low Geogenic Fluoride'. Groundwater fluoride concentrations within basic igneous rocks elsewhere generally reflect this classification, although can sometimes exceed 1.5 mg/L (Figure 1). Further testing of the map (Figure 7a) with additional fluoride analysis will allow confidence to increase in predicting geogenic fluoride risk to groundwater from basic igneous lithologies. While all samples within sandstone (*n* = 3) displayed groundwater fluoride concentrations well below 1.5 mg/L (Figure 4a), a low sample number also presents decreased confidence in prediction, however, global data on groundwater fluoride concentrations from sandstones (Figure 1) conclusively support the classification of these lithologies within 'Low Geogenic Fluoride'. Results for limestones and marbles in Malawi fall within this classification (Figure 4). Limestones elsewhere are associated with low concentrations of groundwater fluoride but can also be associated with more elevated concentrations [10], sometimes up to 5 mg/L (Figure

1). Malawi limestones (incl. meta-equivalents) were classified as ‘Low Geogenic Fluoride’ based on our data (*n* = 8) where all samples were < 1.5 mg/L, however, this prediction may change with increased sampling and testing of the map.

Anomalous elevated groundwater fluoride concentrations located within the rift basin may reveal the locations of fluoride-rich groundwater movement along faults hidden beneath unconsolidated basin sediments, and indeed was previously hypothesised in the Lower Shire Basin to explain the linear appearance of > 6 mg/L fluoride concentrations found at that location [5]. A separate geological study to investigate fault strikes currently hidden beneath basin sediments may assist in the delineation of anomalous fluoride concentrations from that lithology but the data do not yet exist. Investigating those fluoride anomalies may reveal concealed fault strikes in the rift valley where high-fluoride groundwater is mobilised along faults and in contact with shallow groundwater. Mapping of faults beneath basin sediments (inferring based on existing geological, topographical and hydrochemical data) would therefore be a useful a tool for identifying target locations for fluoride assessment and priority replacement water supply. Such an approach may result in an additional zone of increased risk (hidden faults), increasing prediction accuracy for our screening method. Removal of anomalous groundwater fluoride concentrations related to fault strikes (inferred or observed) to be classified and targeted separately, may additionally result in a new, much lower (and more accurate) generic fluoride risk classification for unconsolidated sediments. Dental fluorosis data collected and confirmed by dentists would be additionally useful in identifying areas where there may be fluoride-rich groundwater beneath basin sediments as they would appear as locations with a high number of fluorosis incidences, this would be particularly useful in areas with an absence of groundwater data.

In total, water points (mostly rural) covered by this study serve an estimated 13,075,237 people (Table 4), accounting for 74% of Malawi’s total population [55] and our analysis suggests up to 1.9 million people may be at some risk from geogenic fluoride. An estimated 248,963 people currently use water points within ‘Elevated Geogenic Fluoride’ zones (the highest statistical risk of encountering groundwater fluoride >1.5 mg/L from shallow rock weathering: >60%) and may be at risk from dental fluorosis. Water points within the ‘Moderate-low Geogenic Fluoride’ zones carry significantly less statistical risk of encountering concentrations of groundwater fluoride high enough to cause dental fluorosis (10–17%), however they number 74% of water points covered by this study. This equates to 1–1.6 million people using water points within these zones. With such a high number of people potentially at risk, water points within this category cannot be ignored and will require assessment within the SDG framework. Similarly, 'Low Geogenic Fluoride' carries a low statistical risk (<10%) of elevated groundwater fluoride but still represents up to approximately 267,594 people (Figure. 7a) who currently may be at risk. Water points within zones with insufficient data for a fluoride classification currently affect 181,666 people (Figure. 7a). While the expectation is that these lithologies will be relatively low risk, these will still need to be assessed for completeness within the SDG period and likely will contain some level (albeit low) of fluoride risk.

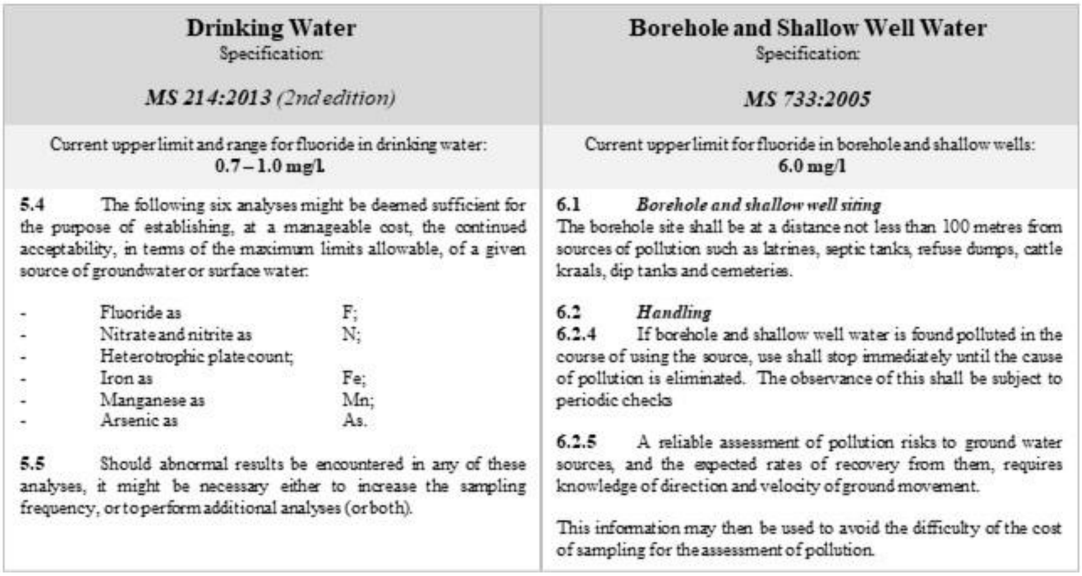
Overall, the results for Malawi (Figure 4a) reflect global trends in groundwater fluoride concentrations and aquifer type (Figure 1), with hot springs and groundwater points within alkaline igneous rocks posing the biggest human health risks. The map produced (Figure 7a) provides a high-resolution preliminary screening tool which can be used to target areas for groundwater fluoride assessment. The screening method was designed to be dynamic, providing increased prediction confidence with the continued addition of new groundwater and geological data. Areas can be prioritised for sampling and potential replacement water supply depending on the statistical likelihood of encountering groundwater with fluoride concentrations > 1.5 mg/L, thus, risk to human health from fluorosis, from highest–lowest geogenic risk.

The national geogenic groundwater fluoride vulnerability map (Figure 7a) is provided and should be used as an investment planning (or review) tool for Donors, NGO's and Water Sector Stakeholders for assessing geogenic fluoride risk. It should be reiterated that this map is presented as a preliminary screening tool to target and prioritise future sampling efforts for existing wells and new ones being drilled, with the addition of groundwater and geological data increasing prediction confidence. To facilitate management of groundwater abstraction, the fluoride risk map for each WRA was individually produced and 15 geogenic fluoride risk maps for each of Malawi's 15 major WRAs can be found in the Supplementary Materials (Figures S11–S27). Water resources (groundwater and surface water) in Malawi are managed by the National Water Resources Authority (NWRA) at (surface water) catchment level under the Water Resources Act (Malawi) 2013 [56]. The national fiscal resources in Malawi are managed through the 28 District Councils, and each District Water Development Officer (DWDO) would have responsibility for planning and monitoring of water resources. Therefore, it is also important to provide detail on fluoride risk for planning at the district scale as provided in Table 4. It is likely that the ministry responsible for water will delegate to local government the responsibility of implementing new groundwater standards in the first instance, and there will be a need to determine the fiscal burden of monitoring and potentially replacing water supplies as the fluoride standard is lowered.

4.2 Policy Review and Implications

A review of groundwater policy, specifically the fluoride standard is needed for Malawi to achieve SDG 6 targets as our results show that the Malawian drinking water standard MS 733:2005 (groundwater and boreholes) for fluoride (6 mg/L) (Figure 8) is not aligned with geogenic and acceptable health risks. The WHO guideline drinking water standard for fluoride is 1.5 mg/L [9] and is aligned with geogenic risk (the link with the WHO guideline standard being that concentrations below 1.5 mg/L are not associated with causing dental fluorosis). Concentrations exceeding 1.5 mg/L cause varying degrees of fluorosis (Figure 4), so retention of this standard runs the risk of (undocumented) dental and skeletal (and possibly crippling) fluorosis in populations who drink from wells with fluoride concentrations above risk standards. The Ministry responsible for water in Malawi and CJF Programme are together developing a plan to incrementally reduce the MS 733:2005 fluoride standard over time, aligning their drinking water fluoride standard with the WHO. Phase 1 of the plan is to reduce the standard from 6 mg/L to 4 mg/L. If implemented, this will manage the risk of skeletal and crippling fluorosis. Phase 2 will see a reduction to 2 mg/L and phase 3 will see a final reduction to 1.5 mg/L (Figure 4a), which will manage the risk of all fluorosis and bring groundwater fluoride policy in line with the WHO. The geogenic fluoride groundwater risk map of Malawi produced in this study (Figure 7a) is proposed primarily as the preliminary screening tool to be used in national efforts to manage groundwater assets for fluoride, but additionally as the basis for policy review. The map is based on the WHO standard of 1.5 mg/L which reflects geogenic risk, if it was based on the Malawian standard of 6 mg/L, only hot springs would show as risk areas as >6 mg/L groundwater fluoride concentrations are exclusive to them in Malawi (except one shallow well in the Southern Region). The gap between the WHO and Malawi standards for fluoride in drinking water reflect the “troublesome” fluoride concentrations (1.5–6 mg/L) identified previously as a key management issue due to diffuse occurrence and out of date fluoride standards [5].

The Malawian standard MS214 for fluoride in general drinking water (piped networks) is in line with WHO guidelines and does not require assessment, with an upper limit and range of 0.7–1.0 mg/L [57]. The standard MS 733:2005 for “raw water” that covers groundwater abstracted from boreholes and wells requires assessment (Figure 8) and was the target of this study. These groundwater sources are the primary water points for rural areas (85% of Malawians). There is a lack of emphasis on fluoride in the Malawi standard documents which were written before the JMP classification as a priority chemical contaminant (WHO and UNICEF, 2017). Fluoride (along with arsenic) will require more focus in the redefinition of standards if SDG 6.1 targets are to be set and achieved in Malawi, specifically 6.1.1 which states the global indicator as: "safely managed drinking water" and describes it as: "Improved source located on premises"…"free from priority chemical contamination" [58]. Lowering the fluoride standard will render many water points unsuitable under this heading and alternative supplies will be required, a significant challenge for the Malawi Government.



Drinking Water Specification: ***MS 214:2013*** *(2nd edition)*	**Borehole and Shallow Well Water** Specification: ***MS 733:2005***
Current upper limit and range for fluoride in drinking water: **0.7 – 1.0 mg/l**	Current upper limit for fluoride in borehole and shallow wells: **6.0 mg/l**
5.4 The following six analyses might be deemed sufficient for the purpose of establishing, at a manageable cost, the continued acceptability, in terms of the maximum limits allowable, of a given source of groundwater or surface water: - Fluoride as F; - Nitrate and nitrite as N; - Heterotrophic plate count; - Iron as Fe; - Manganese as Mn; - Arsenic as As. **5.5** Should abnormal results be encountered in any of these analyses, it might be necessary either to increase the sampling frequency, or to perform additional analyses (or both).	**6.1** ***Borehole and shallow well siting*** The borehole site shall be at a distance not less than 100 metres from sources of pollution such as latrines, septic tanks, refuse dumps, cattle kraals, dip tanks and cemeteries. **6.2** ***Handling*** **6.2.4** If borehole and shallow well water is found polluted in the course of using the source, use shall stop immediately until the cause of pollution is eliminated. The observance of this shall be subject to periodic checks **6.2.5** A reliable assessment of pollution risks to ground water sources, and the expected rates of recovery from them, requires knowledge of direction and velocity of ground movement. This information may then be used to avoid the difficulty of the cost of sampling for the assessment of pollution.

Figure 8. Summary of fluoride-relevant information from Malawi standard documents for drinking water and borehole and shallow well water [13,57].

MS 733 (Figure 8) refers to siting boreholes at least '100 m away from sources of pollution', Fluoride is a geogenic contaminant in groundwater; alkaline igneous rocks have been identified as high-risk sources of fluoride in groundwater and therefore, could be classed as a pollution source (particularly given the JMP classification), although large-scale geogenic sources (e.g., geology) could not be legislated in the same way as an anthropogenic point source (e.g., pit latrine). Hot springs on the other hand can and should be legislated separately in the standards as point sources of various pollutants, including fluoride. More detail on pollution sources (geogenic, anthropogenic) will be required when revising these documents. In the document, under "6.2 Handling", the MS 733:2005 document states that use of a borehole or well should cease immediately if a pollution source is identified, until the cause is eliminated. This is unrealistic for water points within a generic geogenic fluoride source but there is no indication of protocols for such an occurrence. Elevated geogenic fluoride zones cover large areas and many water points (Figure 7a). Site-specific chemical analysis of abstracted water is therefore necessary as it is unknown how many water points within elevated geogenic fluoride zones may be producing water with low fluoride concentrations (there is currently no systematic measurement of fluoride from groundwater supplies). Under MS 733:2005 only hot springs would require assessment.

Additional to reviewing and updating standards for fluoride in drinking water, the WASH sector has the responsibility to ensure that Malawi Government standards for installation are and were followed (including a requirement for chemical testing before installation of a pump or lifting device and use of the water as a drinking water supply). Our data show that many boreholes have been drilled which contain elevated groundwater fluoride which would have been within standards at the time of drilling but would fail water quality tests under proposed new standards. Updated, more stringent standards for fluoride will further the need for more focus on proper due diligence and accurate reporting. If these issues are not addressed, Malawi will continually gain new borehole infrastructure which later fails water quality tests and become stranded assets [2]. Local-scale studies where elevated groundwater fluoride concentrations exist are recommended to better understand the geogenic processes causing them. Such localised investigations may produce site/area-specific management solutions, such as avoiding faults, hot springs, or high risk lithologies.

As Malawi's population continues to rise, stress on water resources will increase and the need for safely managed rural water supply and stricter policy on groundwater quality will become increasingly difficult to achieve, highlighting the need for proactive management of water resources. This study was designed to inform policy makers with an evidence-based prediction method for both environmental management and policy review. Recommended best practices for advocating science-based policy review includes (but are not limited to): (i) accurately characterising the best available policy-relevant science; (ii) presenting a clear and concise argument; (iii) accurately characterising any uncertainty; (iv) transparent representation of scientific basis for policy recommendation, and; (v) avoidance of hyperbole [59]. Thus, prediction maps have been produced here to form the basis for both assessment of existing groundwater supplies for geogenic fluoride (asset management), and as monitoring and investment planning tools as review of the Malawi fluoride standard is taken forward by the government. For Malawi to achieve SDG 6.1 scientists and policy makers must work closely and collaboratively to develop a consistent and accurate approach to reducing both current and future risks.

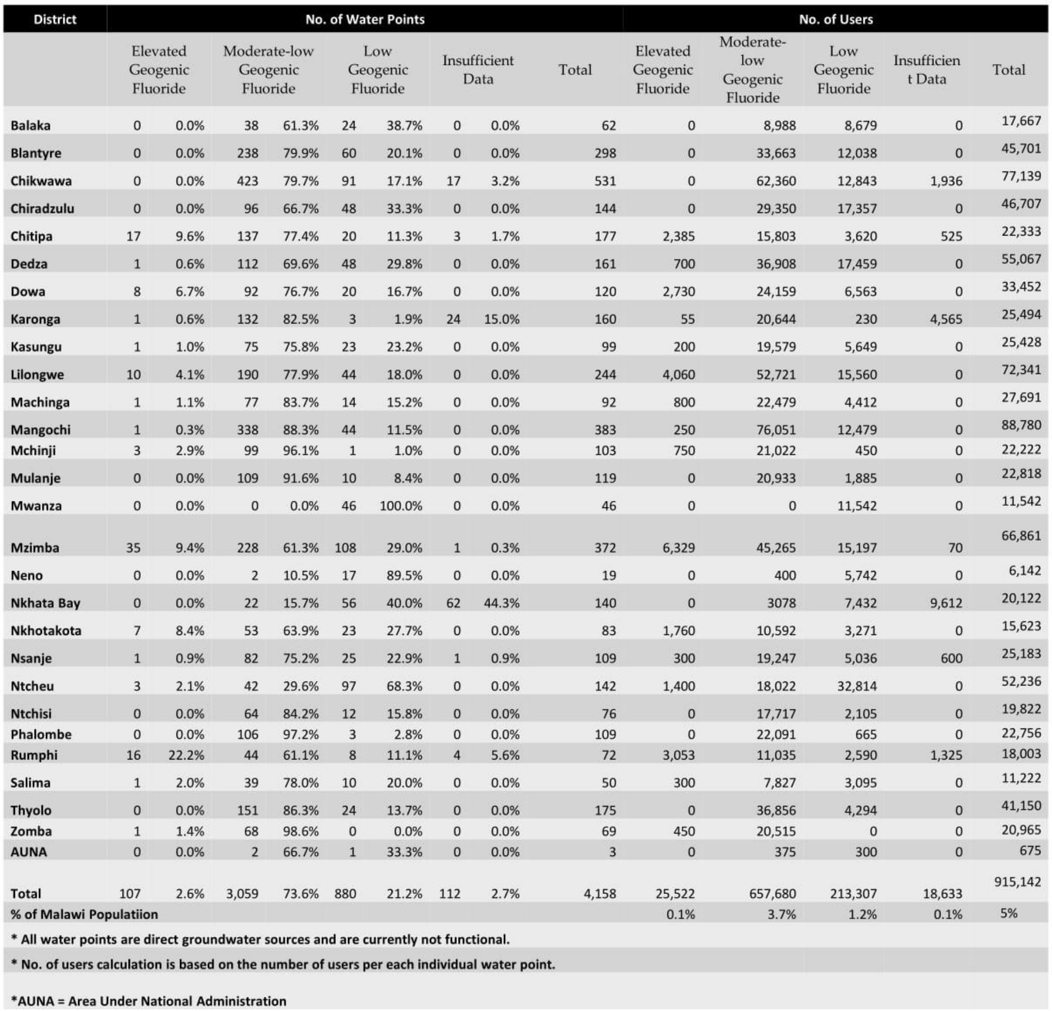
5. Conclusion

In the absence of national data sets for fluoride in Malawi, we show that existing statistical fluoride relationships with geogenic sources can be extrapolated nationally to develop high resolution geogenic fluoride groundwater risk maps. We present a preliminary screening tool for targeted testing of existing groundwater supplies for geogenic fluoride groundwater risk as well as a clear, evidence-based argument for redefinition of groundwater policy (for fluoride) in Malawi. The screening method is dynamic in design, with prediction confidence increasing with informed acquisition of new data as national sampling progresses. At present, our approach is the best available science relevant to fluoride in groundwater in Malawi and will inform a review of Malawi groundwater policy (including fluoride) in support of Sustainable Development Goal (SDG) targets. Our approach will assist national efforts (ongoing) by the Malawian Government to form a pathway for stepped progression of the fluoride standard to adoption of the globally accepted World Health Organisation (WHO) standard for fluoride in drinking water. The method should be integrated into future groundwater resource development strategies employed by the government, donors, and NGOs, to reduce the risk of geogenic fluoride in water supplies.

6.3 Supplementary Materials

The following are available online at https://www.mdpi.com/2073-4441/12/11/3123/s1 Table S1. Table showing data on the number of ‘not functional’ water points in each fluoride zone and the corresponding number of people at risk per zone, split by district. Figure S1. Geological map of Karonga (Malawi’s location on the African continent inset). Figure S2. Geological map of Nyika. Figure S3. Geological map of Nkhata Bay. Figure S4. Geological map of Nkhotakota. Figure S5. Geological map of Lilongwe. Figure S6. Geological map of Salima. Figure S7. Geological map of Dedza. Figure S8. Geological map of Mangochi. Figure S9. Geological map of Zomba. Figure S10. Geological map of Nsanje. Figure S11. Geogenic fluoride groundwater risk map of WRA 1-1 (Upper Shire). Figure S12. Geogenic fluoride groundwater risk map of WRA 1-2 (Middle Shire). Figure S13. Geogenic fluoride groundwater risk map of WRA 1-3 (Lower Shire). Figure S14. Geogenic fluoride groundwater risk map of WRA 2 (Lake Chilwa). Figure S15. Geogenic fluoride groundwater risk map of WRA 3 (SW Lakeshore). Figure S16. Geogenic fluoride groundwater risk map of WRA 4 (Lilongwe-Linthipe). Figure S17. Geogenic fluoride groundwater risk map of WRA 5 (Bua). Figure S18. Geogenic fluoride groundwater risk map of WRA 6 (Dwanga). Figure S19. Geogenic fluoride groundwater risk map of WRA 7 (South Rukuru-North Rumphi). Figure S20. Geogenic fluoride groundwater risk map of WRA 8 (North Rukuru). Figure S21. Geogenic fluoride groundwater risk map of WRA 9 (Songwe-Lufira). Figure S22. Geogenic fluoride groundwater risk map of WRA 10 (SE Lakeshore). Figure S23. Geogenic fluoride groundwater risk map of WRA 11 (Lake Chiuta). Figure S24. Geogenic fluoride groundwater risk map of WRA 14 (Ruo). Figure S25. Geogenic fluoride groundwater risk map of WRA 15 (Nkhotakota). Figure S26. Geogenic fluoride groundwater risk map of WRA 16 (Nkhata). Figure S27. Geogenic fluoride groundwater risk map of WRA 17 (Karonga).

Table S1. Table showing data on the number of ‘not functional’ water points in each fluoride zone and the corresponding number of people at risk per zone, split by district.



District	No. of Water Points									No. of Users				
	Elevated Geogenic Fluoride		Moderate-low Geogenic Fluoride		Low Geogenic Fluoride		Insufficient Data		Total	Elevated Geogenic Fluoride	Moderate-low Geogenic Fluoride	Low Geogenic Fluoride	Insufficient Data	Total
Balaka	0	0.0%	38	61.3%	24	38.7%	0	0.0%	62	0	8,988	8,679	0	17,667
Blantyre	0	0.0%	238	79.9%	60	20.1%	0	0.0%	298	0	33,663	12,038	0	45,701
Chikwawa	0	0.0%	423	79.7%	91	17.1%	17	3.2%	531	0	62,360	12,843	1,936	77,139
Chiradzulu	0	0.0%	96	66.7%	48	33.3%	0	0.0%	144	0	29,350	17,357	0	46,707
Chitipa	17	9.6%	137	77.4%	20	11.3%	3	1.7%	177	2,385	15,803	3,620	525	22,333
Dedza	1	0.6%	112	69.6%	48	29.8%	0	0.0%	161	700	36,908	17,459	0	55,067
Dowa	8	6.7%	92	76.7%	20	16.7%	0	0.0%	120	2,730	24,159	6,563	0	33,452
Karonga	1	0.6%	132	82.5%	3	1.9%	24	15.0%	160	55	20,644	230	4,565	25,494
Kasungu	1	1.0%	75	75.8%	23	23.2%	0	0.0%	99	200	19,579	5,649	0	25,428
Lilongwe	10	4.1%	190	77.9%	44	18.0%	0	0.0%	244	4,060	52,721	15,560	0	72,341
Machinga	1	1.1%	77	83.7%	14	15.2%	0	0.0%	92	800	22,479	4,412	0	27,691
Mangochi	1	0.3%	338	88.3%	44	11.5%	0	0.0%	383	250	76,051	12,479	0	88,780
Mchinji	3	2.9%	99	96.1%	1	1.0%	0	0.0%	103	750	21,022	450	0	22,222
Mulanje	0	0.0%	109	91.6%	10	8.4%	0	0.0%	119	0	20,933	1,885	0	22,818
Mwanza	0	0.0%	0	0.0%	46	100.0%	0	0.0%	46	0	0	11,542	0	11,542
Mzimba	35	9.4%	228	61.3%	108	29.0%	1	0.3%	372	6,329	45,265	15,197	70	66,861
Neno	0	0.0%	2	10.5%	17	89.5%	0	0.0%	19	0	400	5,742	0	6,142
Nkhata Bay	0	0.0%	22	15.7%	56	40.0%	62	44.3%	140	0	3078	7,432	9,612	20,122
Nkhotakota	7	8.4%	53	63.9%	23	27.7%	0	0.0%	83	1,760	10,592	3,271	0	15,623
Nsanje	1	0.9%	82	75.2%	25	22.9%	1	0.9%	109	300	19,247	5,036	600	25,183
Ntcheu	3	2.1%	42	29.6%	97	68.3%	0	0.0%	142	1,400	18,022	32,814	0	52,236
Ntchisi	0	0.0%	64	84.2%	12	15.8%	0	0.0%	76	0	17,717	2,105	0	19,822
Phalombe	0	0.0%	106	97.2%	3	2.8%	0	0.0%	109	0	22,091	665	0	22,756
Rumphi	16	22.2%	44	61.1%	8	11.1%	4	5.6%	72	3,053	11,035	2,590	1,325	18,003
Salima	1	2.0%	39	78.0%	10	20.0%	0	0.0%	50	300	7,827	3,095	0	11,222
Thyolo	0	0.0%	151	86.3%	24	13.7%	0	0.0%	175	0	36,856	4,294	0	41,150
Zomba	1	1.4%	68	98.6%	0	0.0%	0	0.0%	69	450	20,515	0	0	20,965
AUNA	0	0.0%	2	66.7%	1	33.3%	0	0.0%	3	0	375	300	0	675
Total	107	2.6%	3,059	73.6%	880	21.2%	112	2.7%	4,158	25,522	657,680	213,307	18,633	915,142
% of Malawi Populatiion										0.1%	3.7%	1.2%	0.1%	5%

*** All water points are direct groundwater sources and are currently not functional.**

*** No. of users calculation is based on the number of users per each individual water point.**

***AUNA = Area Under National Administration**

Table A1. Table showing data on number of ‘not functional’ water points in each fluoride zone and the corresponding number of people at risk per zone, split by district.

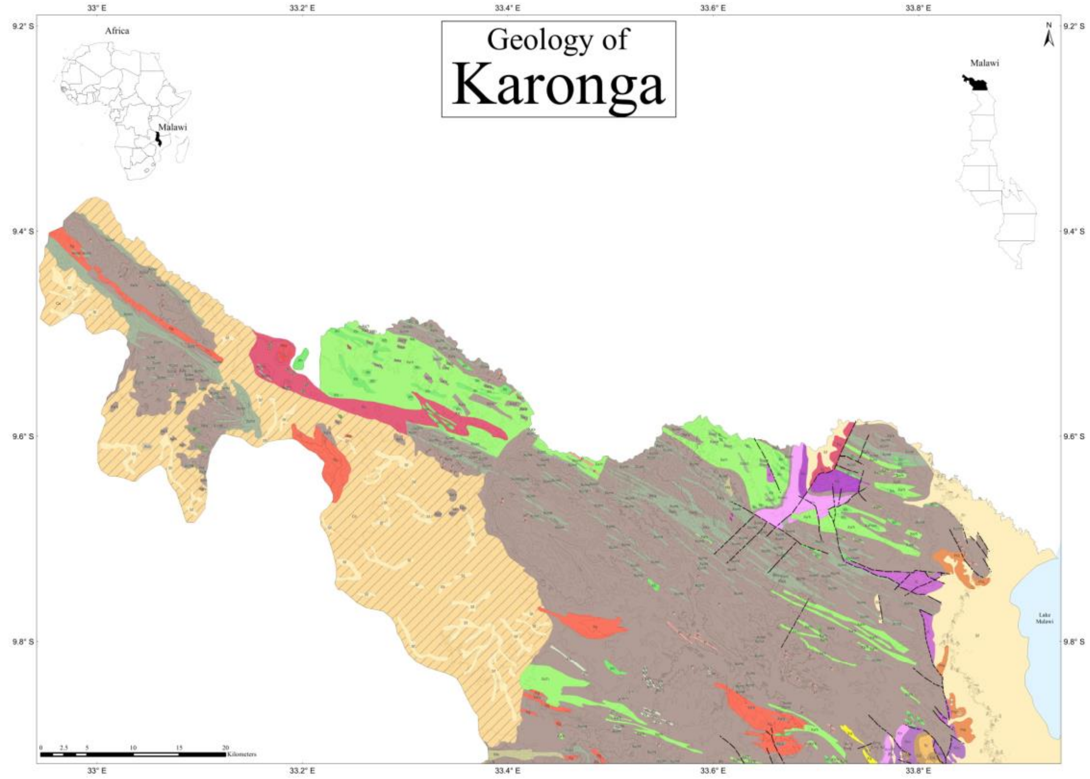


Figure S1. Geological map of Karonga (Malawi’s location on the African continent inset).

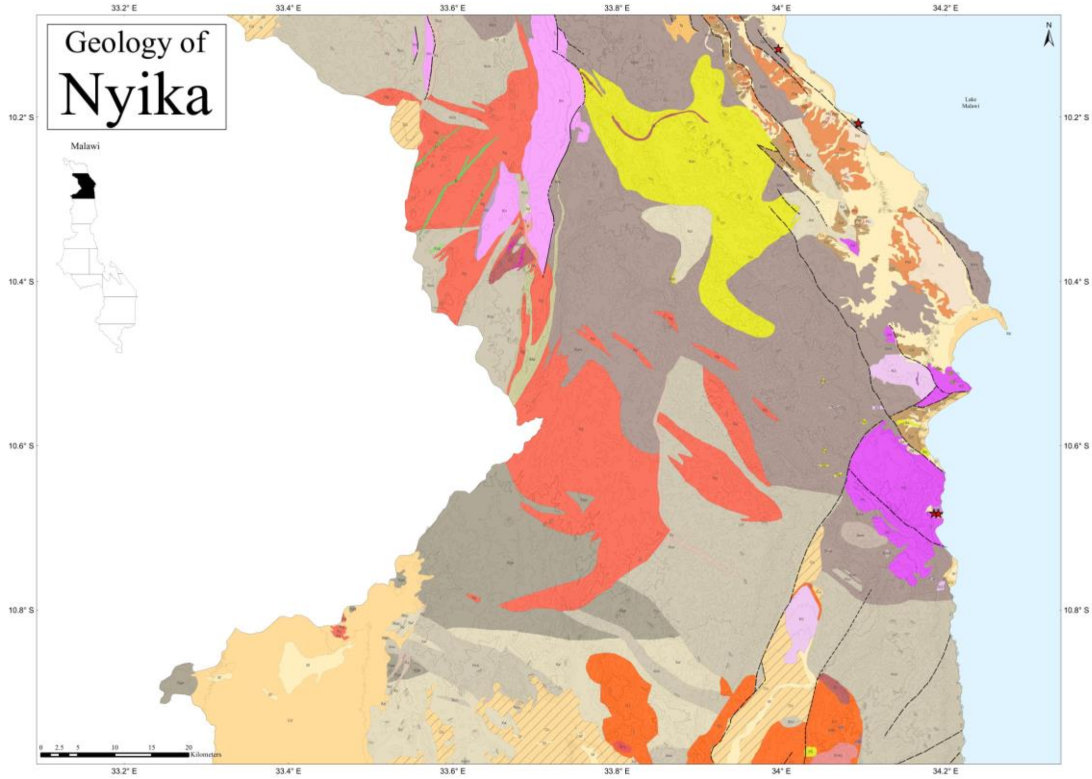


Figure S2. Geological map of Nyika.

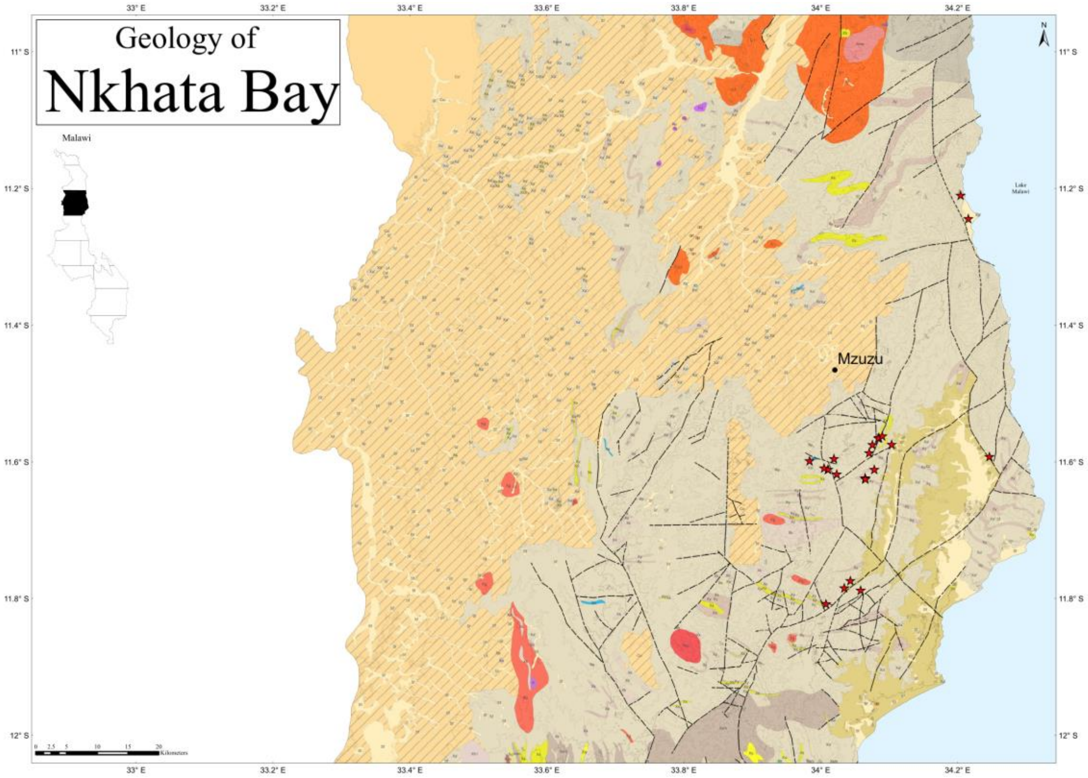


Figure S3. Geological map of Nkhata Bay.

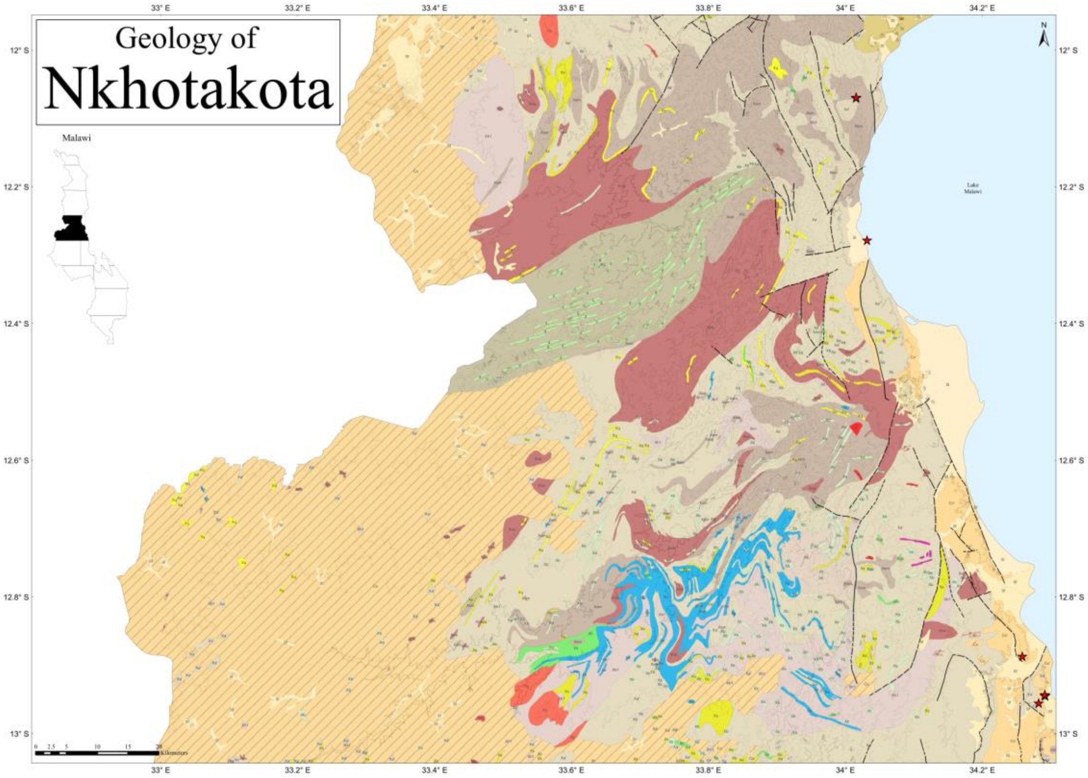


Figure S4. Geological map of Nkhotakota.

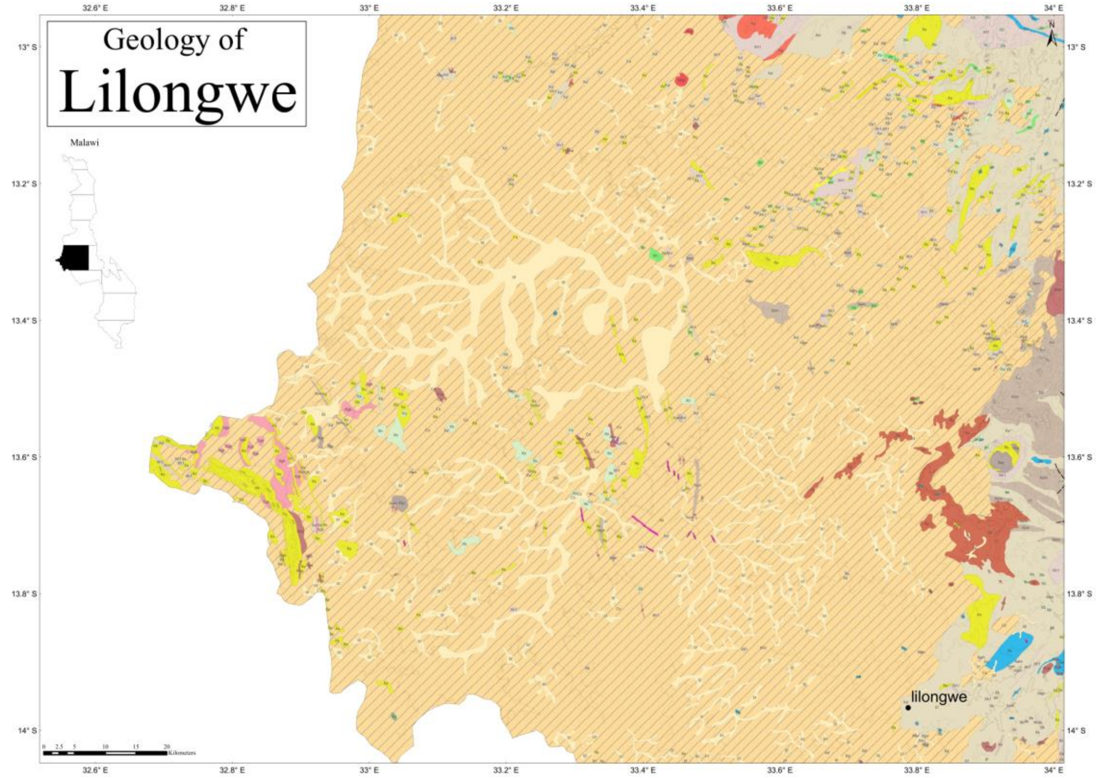


Figure S5. Geological map of Lilongwe.

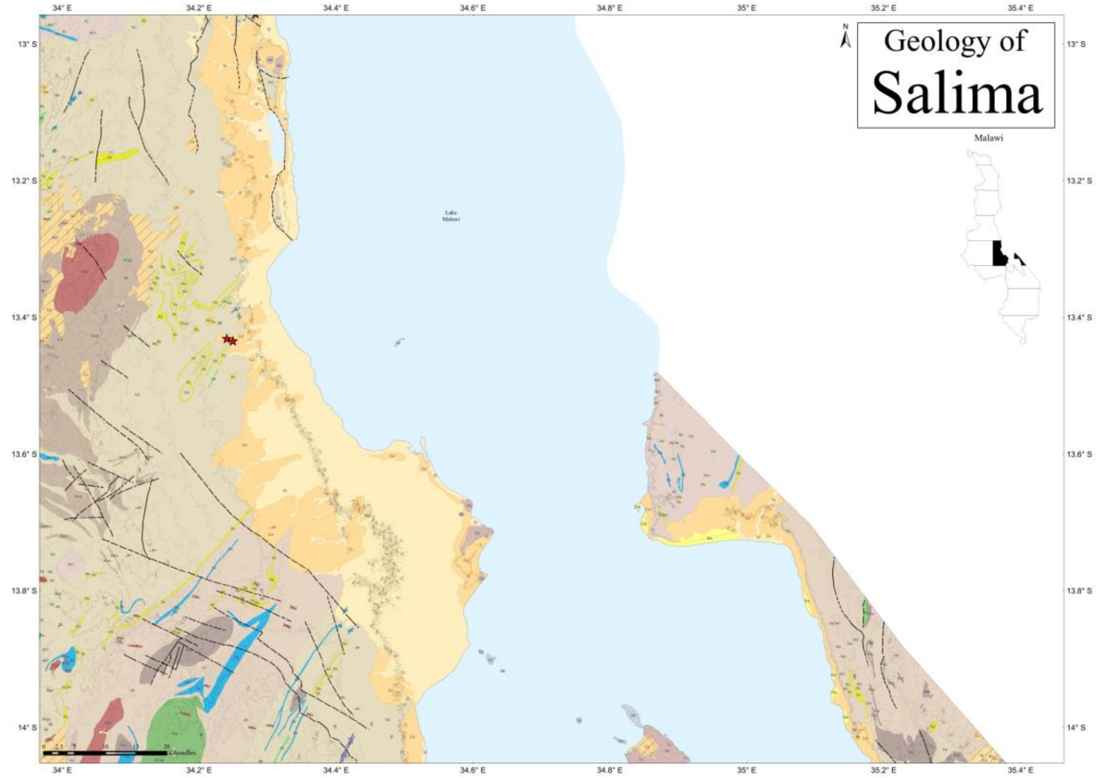


Figure S6. Geological map of Salima.

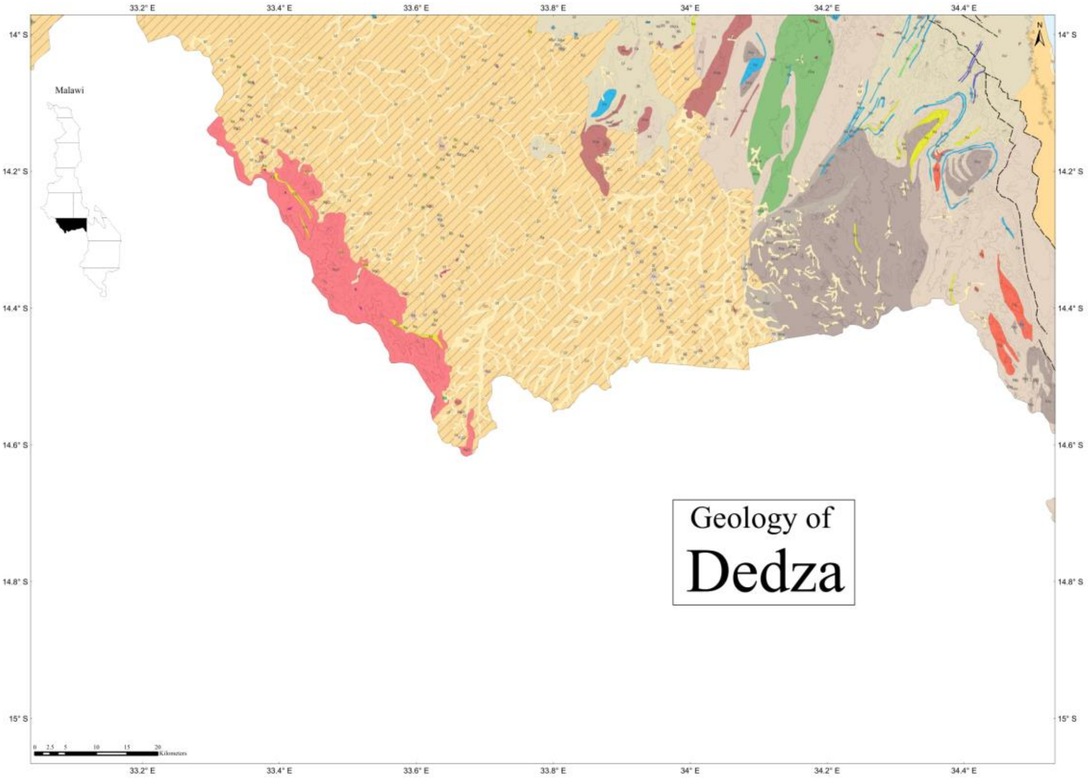


Figure S7. Geological map of Dedza.

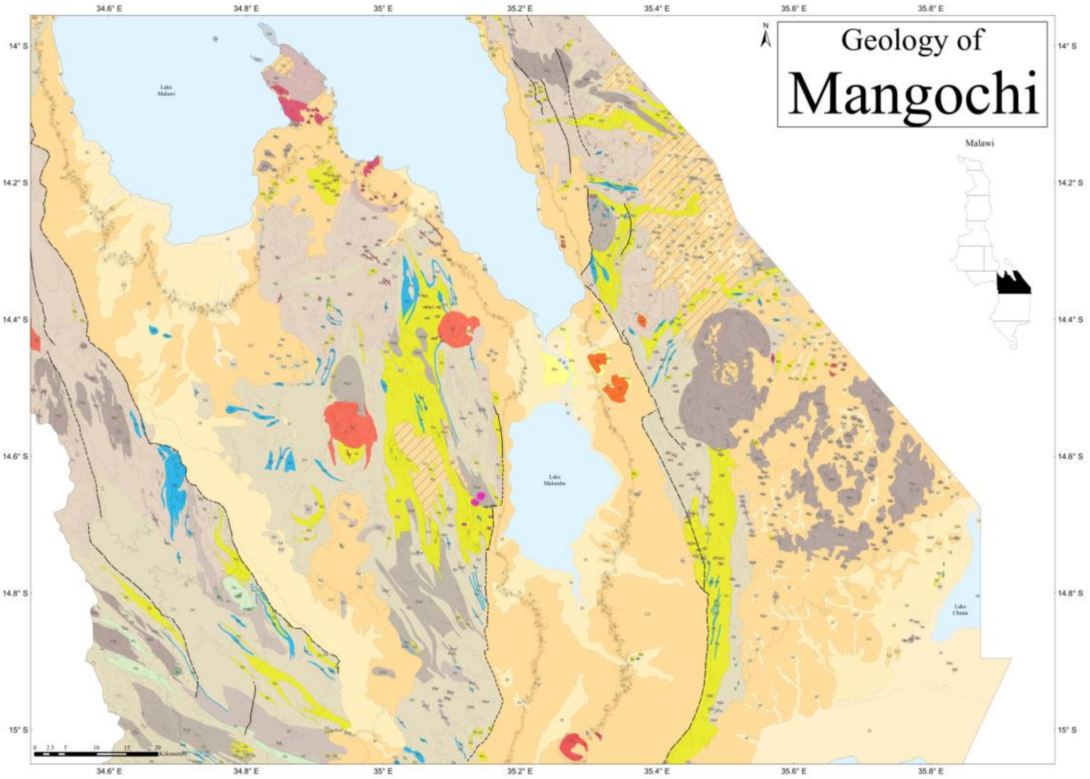


Figure S8. Geological map of Mangochi.

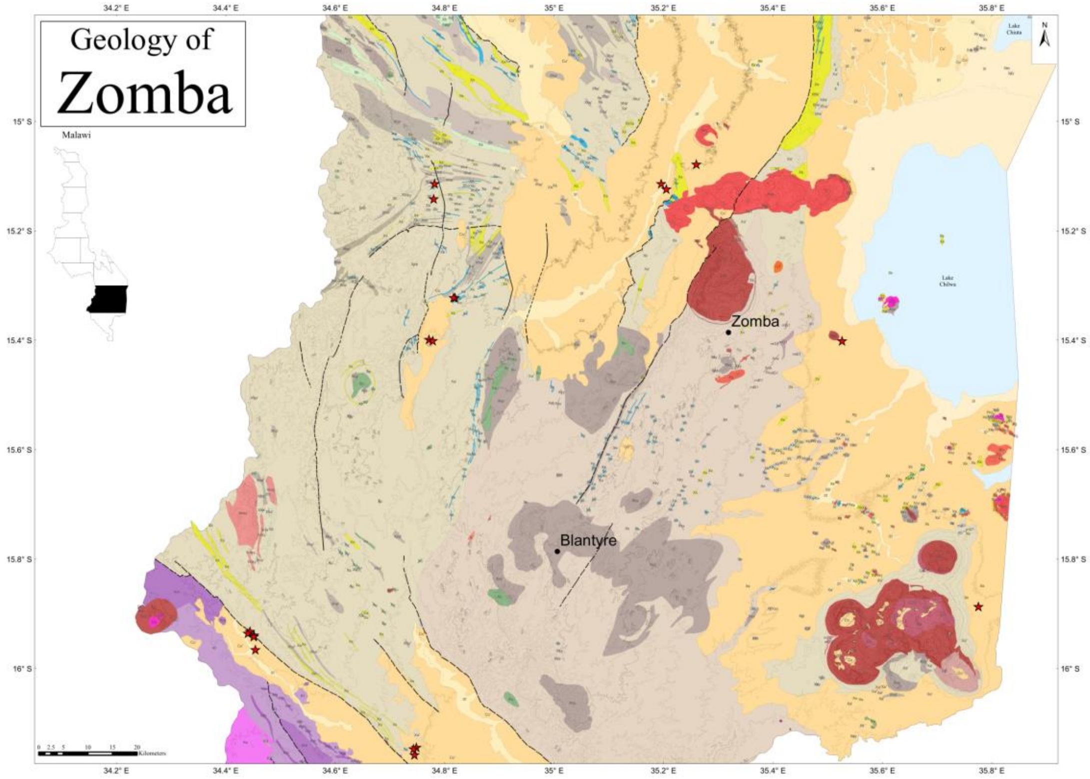


Figure S9. Geological map of Zomba.

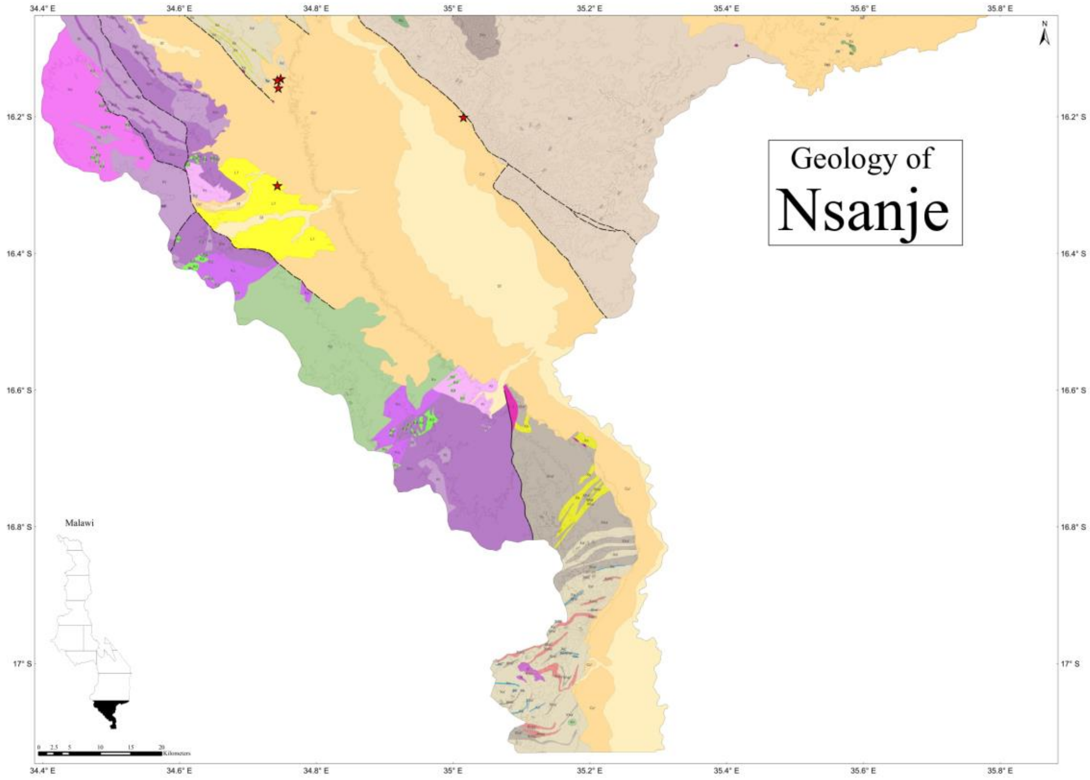
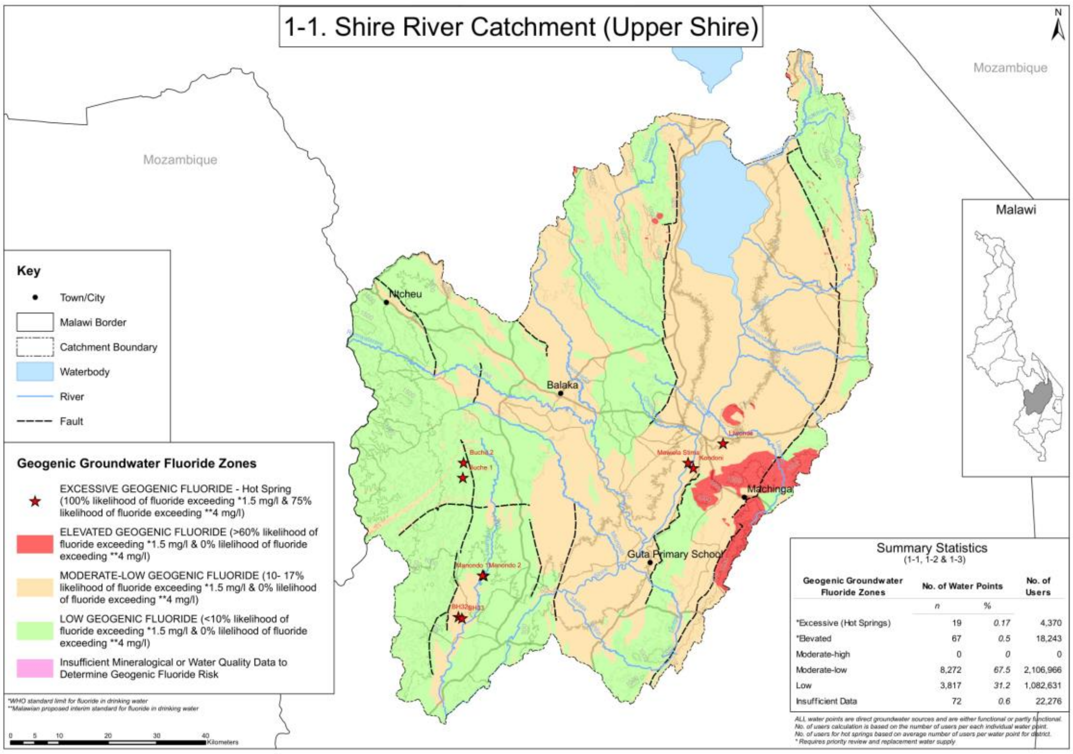


Figure S10. Geological map of Nsanje.



Summary Statistics
(1-1, 1-2 & 1-3)

Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	*%*	
*Excessive (Hot Springs)	19	*0.17*	4,370
*Elevated	67	*0.5*	18,243
Moderate-high	0	*0*	0
Moderate-low	8,272	*67.5*	2,106,966
Low	3,817	*31.2*	1,082,631
Insufficient Data	72	*0.6*	22,276

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S11. Geogenic fluoride groundwater risk map of WRA 1-1 (Upper Shire).

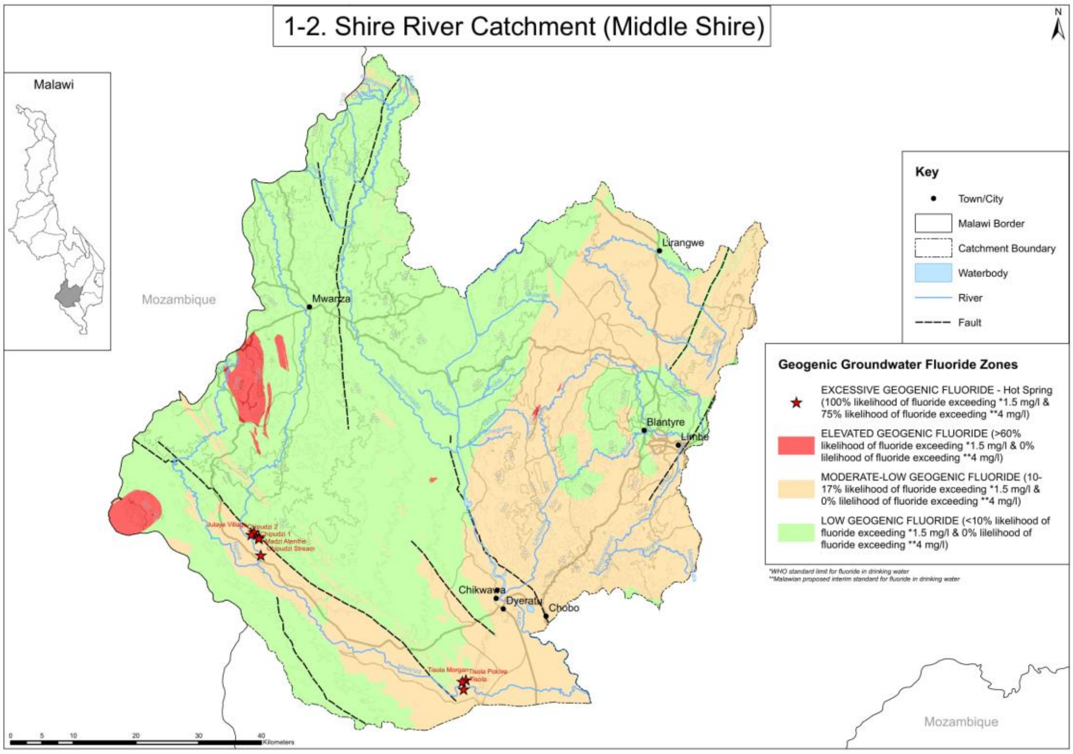


Figure S12. Geogenic fluoride groundwater risk map of WRA 1-2 (Middle Shire).

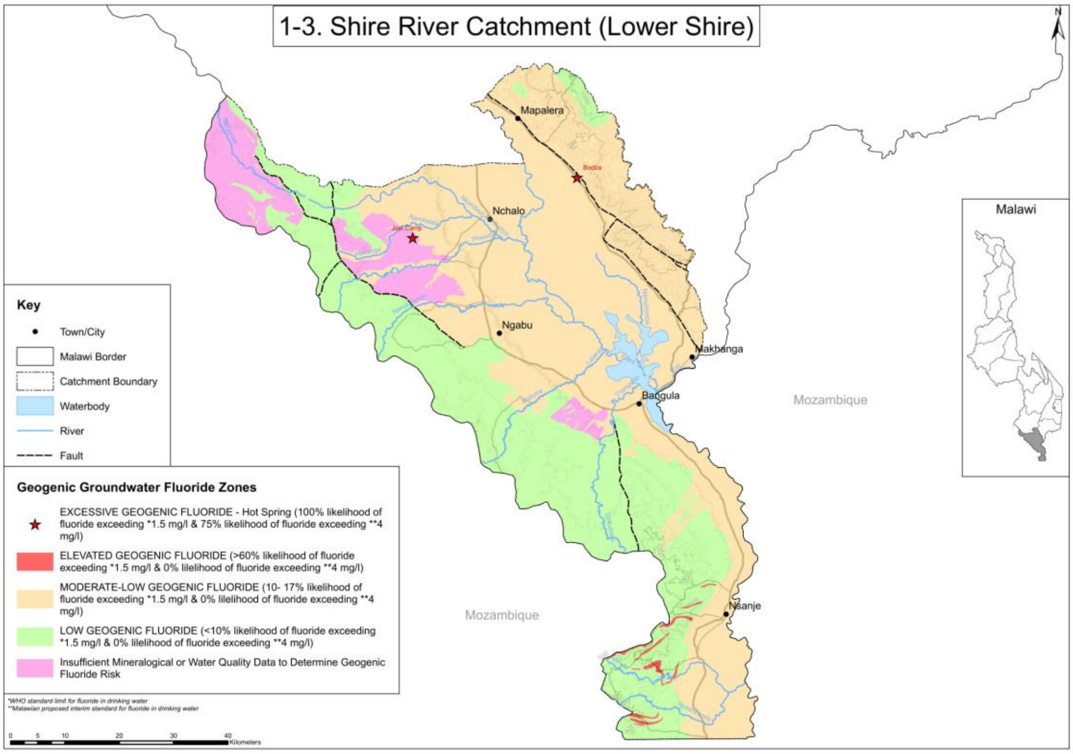
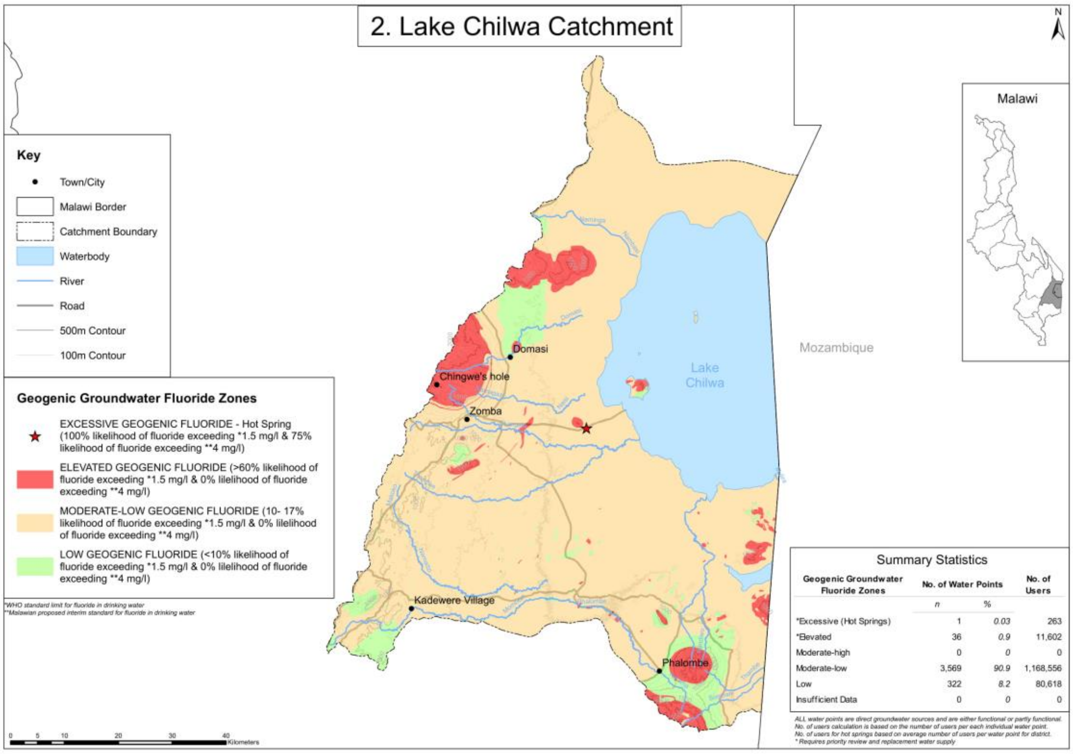


Figure S13. Geogenic fluoride groundwater risk map of WRA 1-3 (Lower Shire).

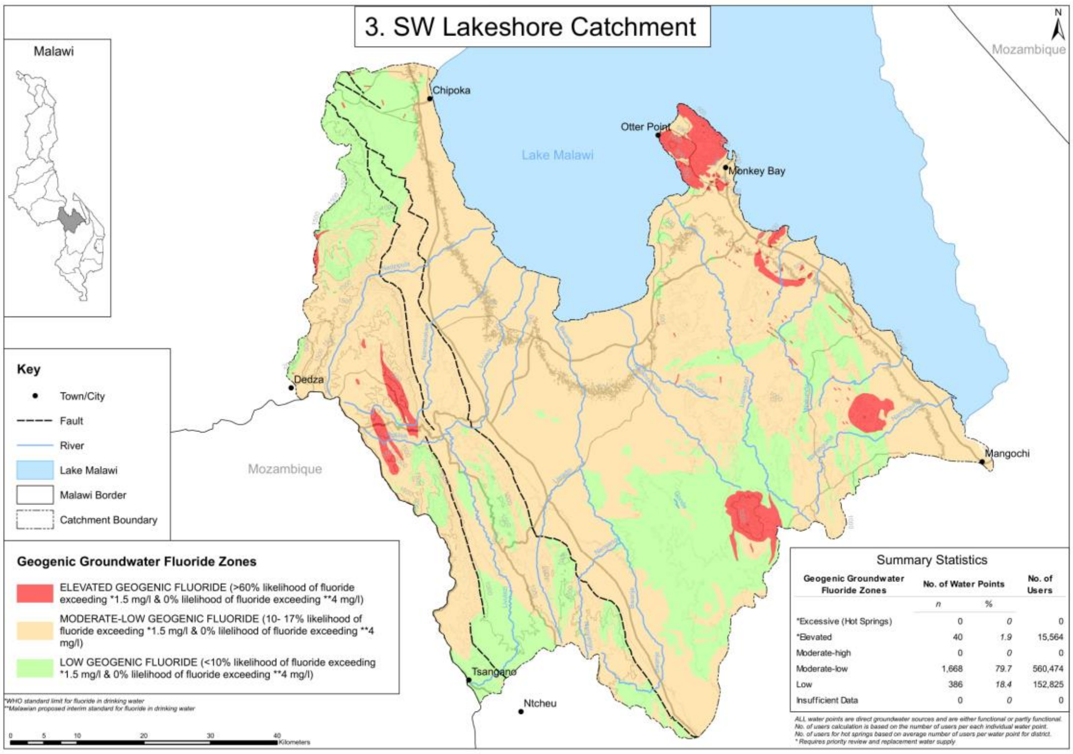


Summary Statistics

Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	%	
*Excessive (Hot Springs)	1	*0.03*	263
*Elevated	36	*0.9*	11,602
Moderate-high	0	*0*	0
Moderate-low	3,569	*90.9*	1,168,556
Low	322	*8.2*	80,618
Insufficient Data	0	*0*	0

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S14. Geogenic fluoride groundwater risk map of WRA 2 (Lake Chilwa).

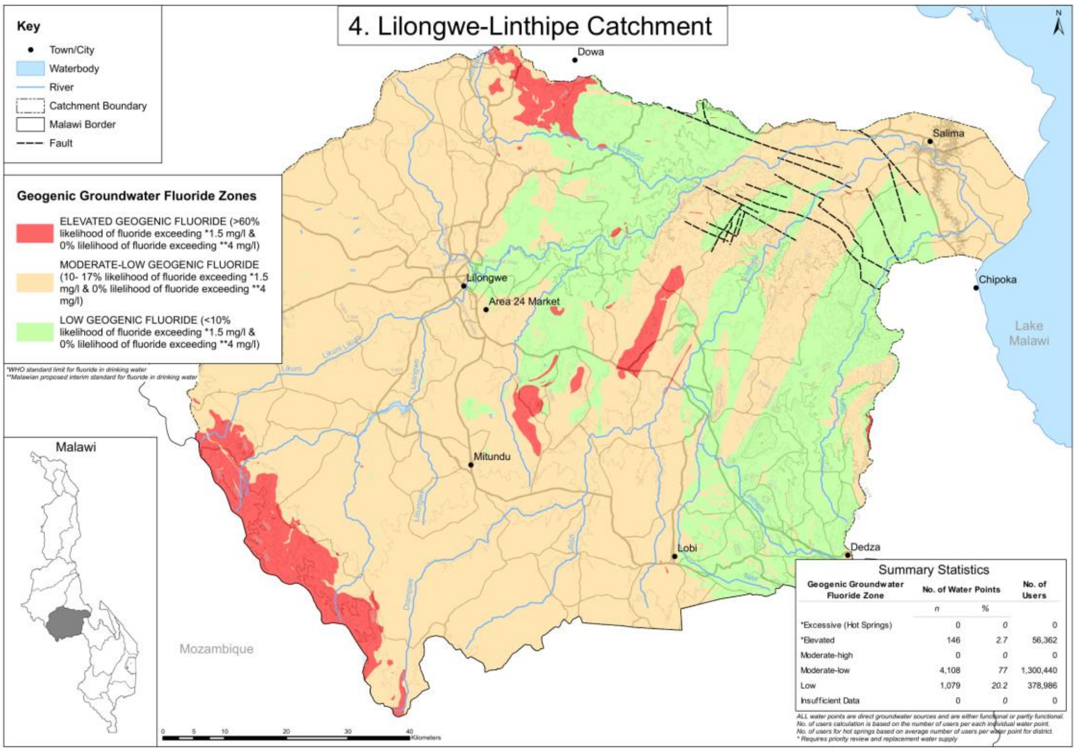


Summary Statistics

Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	%	
*Excessive (Hot Springs)	0	*0*	0
*Elevated	40	*1.9*	15,564
Moderate-high	0	*0*	0
Moderate-low	1,668	*79.7*	560,474
Low	386	*18.4*	152,825
Insufficient Data	0	*0*	0

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S15. Geogenic fluoride groundwater risk map of WRA 3 (SW Lakeshore).

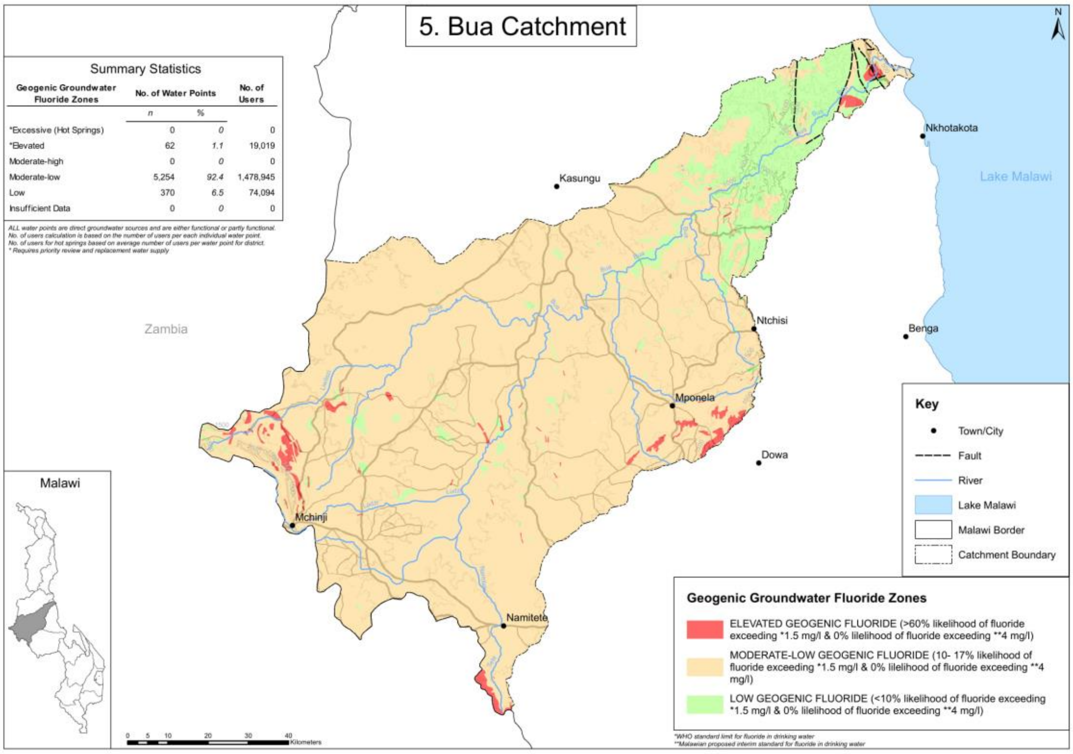


Summary Statistics

Geogenic Groundwater Fluoride Zone	No. of Water Points		No. of Users
	n	%	
*Excessive (Hot Springs)	0	*0*	0
*Elevated	146	2.7	56,362
Moderate-high	0	*0*	0
Moderate-low	4,108	77	1,300,440
Low	1,079	20.2	378,986
Insufficient Data	0	*0*	0

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S16. Geogenic fluoride groundwater risk map of WRA 4 (Lilongwe-Linthipe).

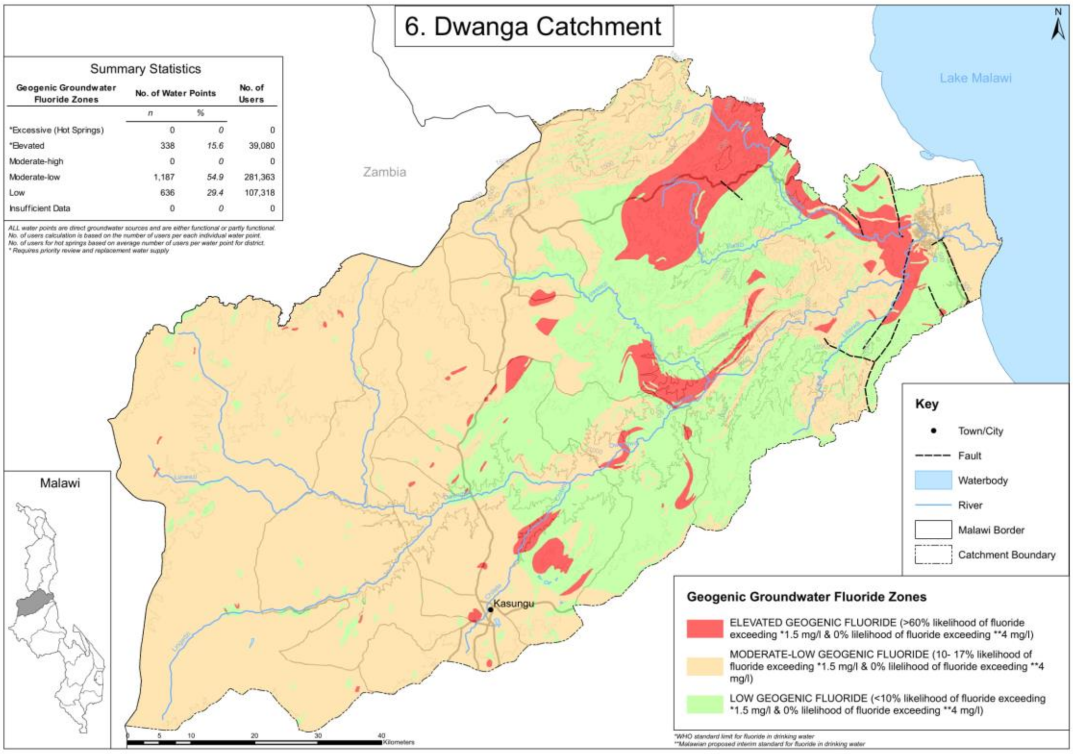


Summary Statistics

Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	%	
*Excessive (Hot Springs)	0	*0*	0
*Elevated	62	*1.1*	19,019
Moderate-high	0	*0*	0
Moderate-low	5,254	*92.4*	1,478,945
Low	370	*6.5*	74,094
Insufficient Data	0	*0*	0

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S17. Geogenic fluoride groundwater risk map of WRA 5 (Bua).

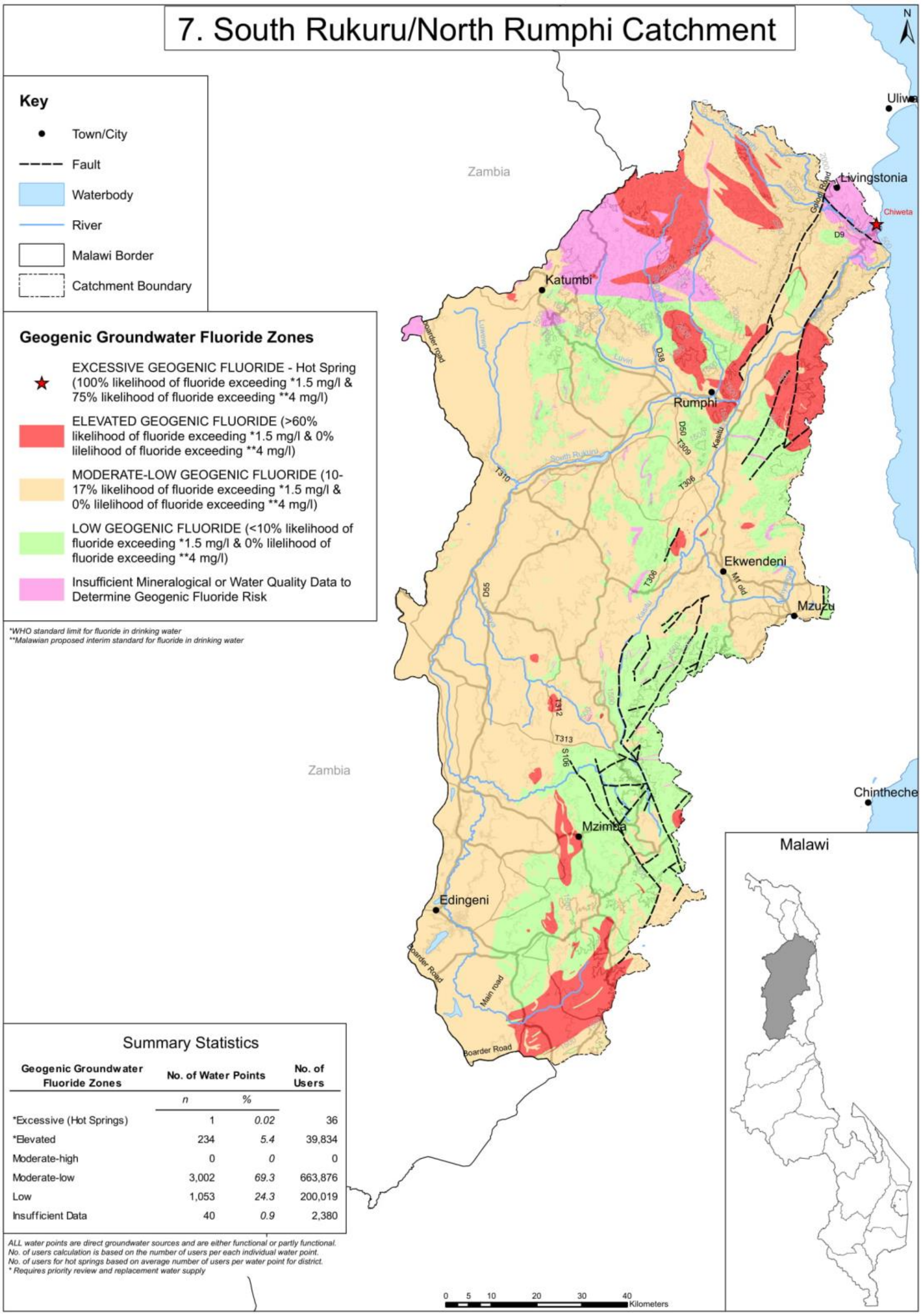


Summary Statistics

Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	%	
*Excessive (Hot Springs)	0	*0*	0
*Elevated	338	*15.6*	39,080
Moderate-high	0	*0*	0
Moderate-low	1,187	*54.9*	281,363
Low	636	*29.4*	107,318
Insufficient Data	0	*0*	0

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S18. Geogenic fluoride groundwater risk map of WRA 6 (Dwanga).

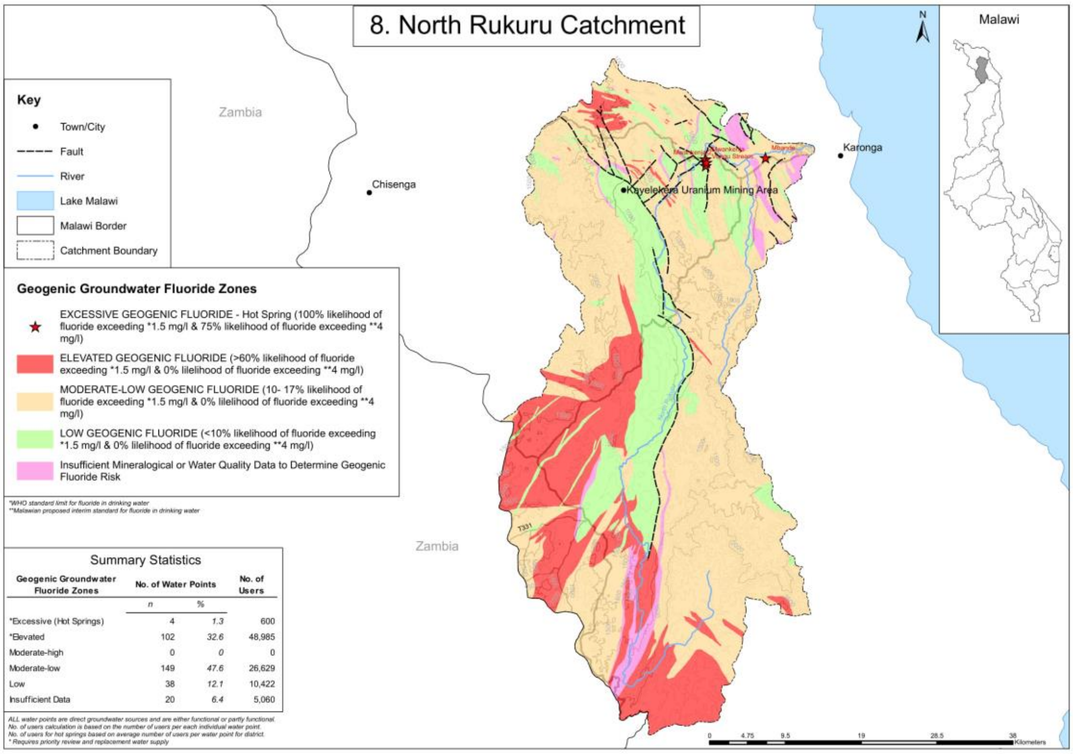


Summary Statistics

Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	%	
*Excessive (Hot Springs)	1	*0.02*	36
*Elevated	234	*5.4*	39,834
Moderate-high	0	*0*	0
Moderate-low	3,002	*69.3*	663,876
Low	1,053	*24.3*	200,019
Insufficient Data	40	*0.9*	2,380

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S19. Geogenic fluoride groundwater risk map of WRA 7 (South Rukuru-North Rumphi).

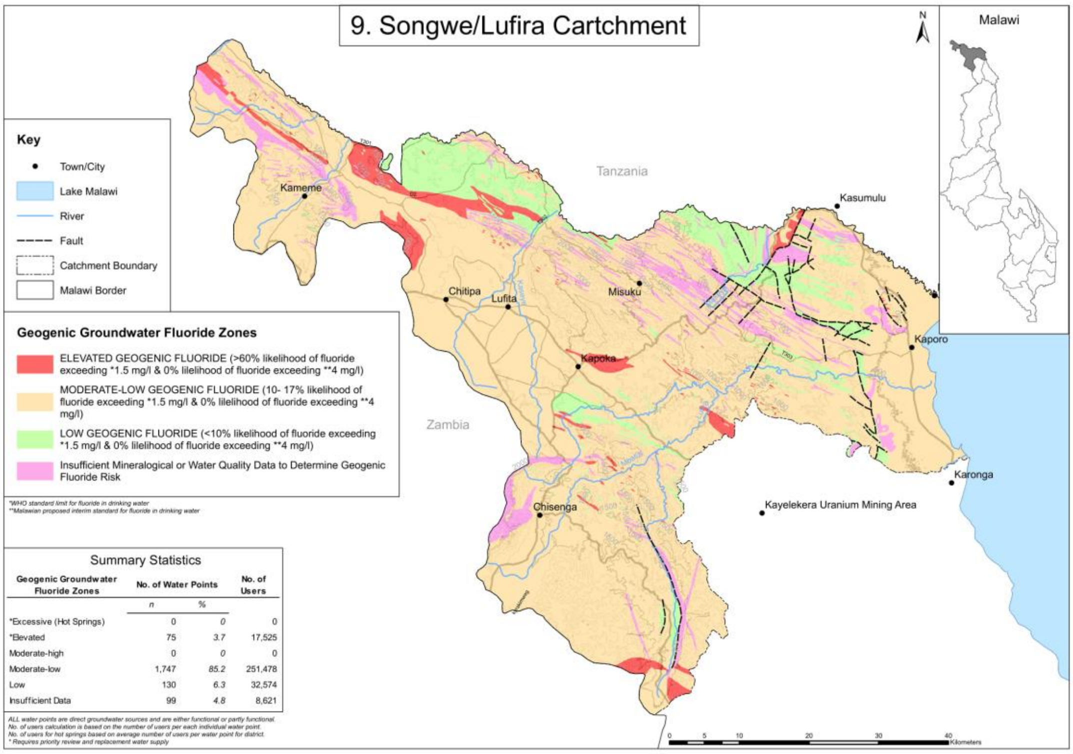


Summary Statistics

Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	*%*	
*Excessive (Hot Springs)	4	*1.3*	600
*Elevated	102	*32.6*	48,985
Moderate-high	0	*0*	0
Moderate-low	149	*47.6*	26,629
Low	38	*12.1*	10,422
Insufficient Data	20	*6.4*	5,060

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S20. Geogenic fluoride groundwater risk map of WRA 8 (North Rukuru).

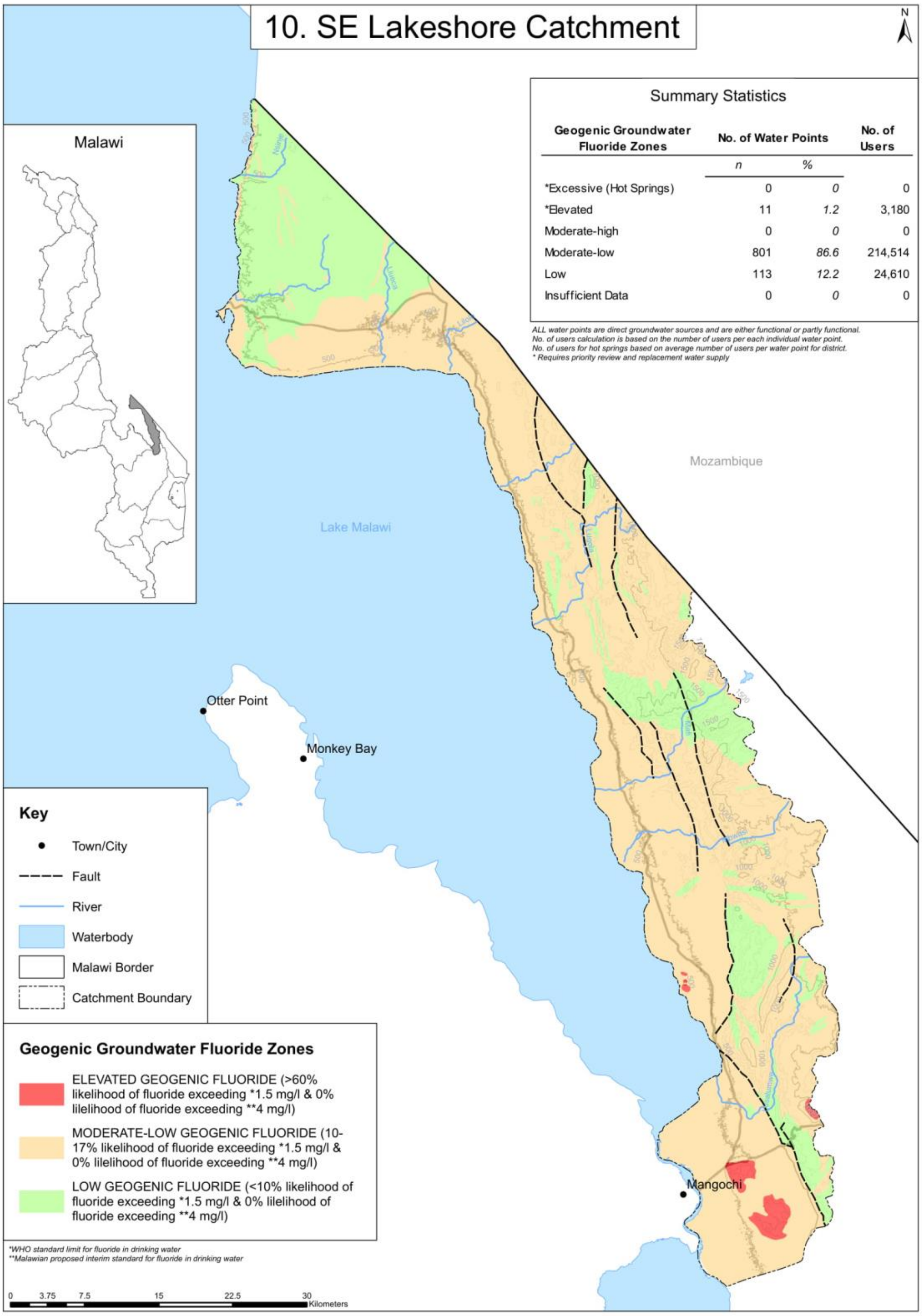


Summary Statistics

Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	*%*	
*Excessive (Hot Springs)	0	*0*	0
*Elevated	75	*3.7*	17,525
Moderate-high	0	*0*	0
Moderate-low	1,747	*85.2*	251,478
Low	130	*6.3*	32,574
Insufficient Data	99	*4.8*	8,621

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S21. Geogenic fluoride groundwater risk map of WRA 9 (Songwe-Lufira).

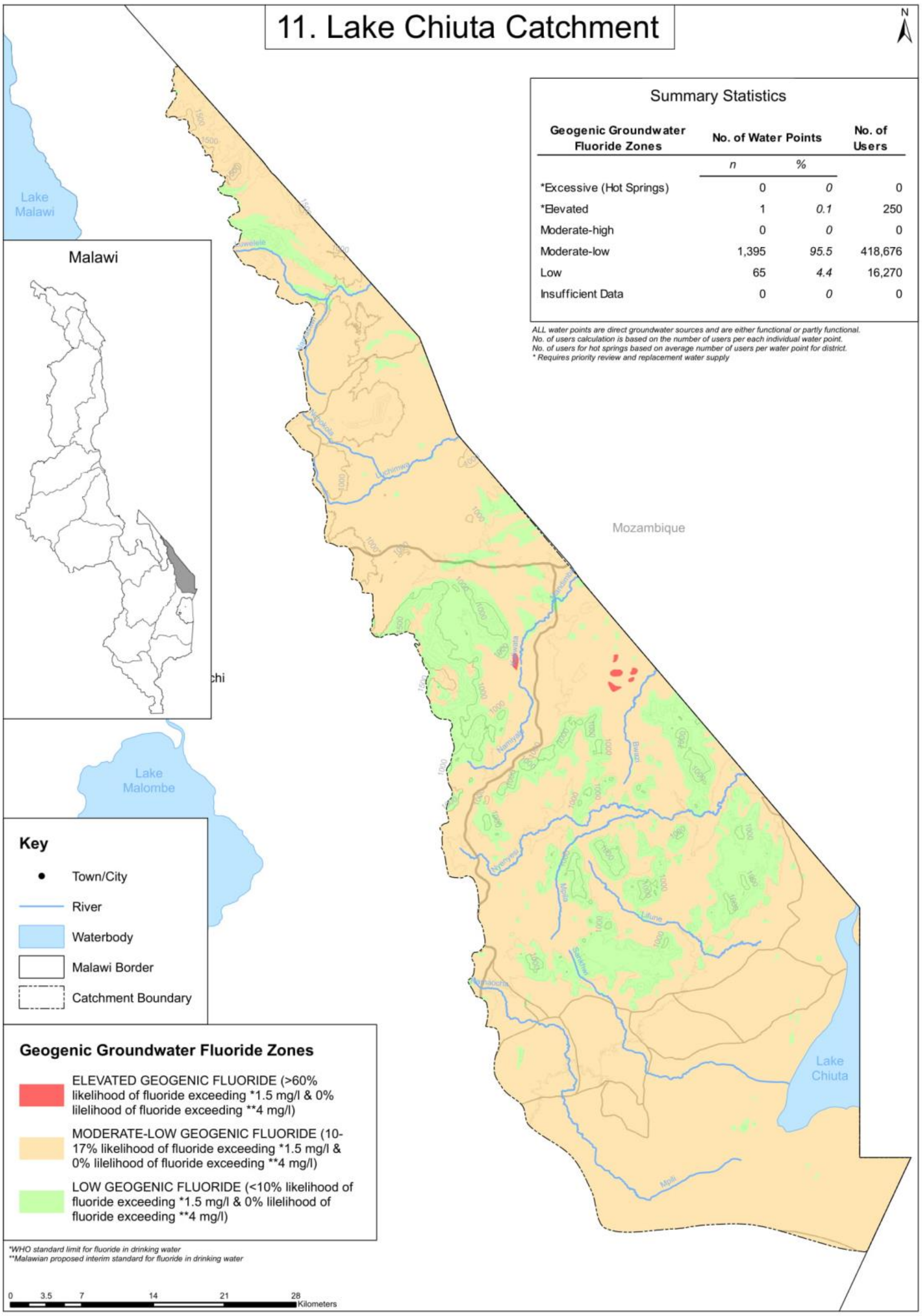


Summary Statistics

Geogenic Groundwater Fluoride Zones	No. of Water Points n	No. of Water Points %	No. of Users
*Excessive (Hot Springs)	0	0	0
*Elevated	11	1.2	3,180
Moderate-high	0	0	0
Moderate-low	801	86.6	214,514
Low	113	12.2	24,610
Insufficient Data	0	0	0

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
* Requires priority review and replacement water supply

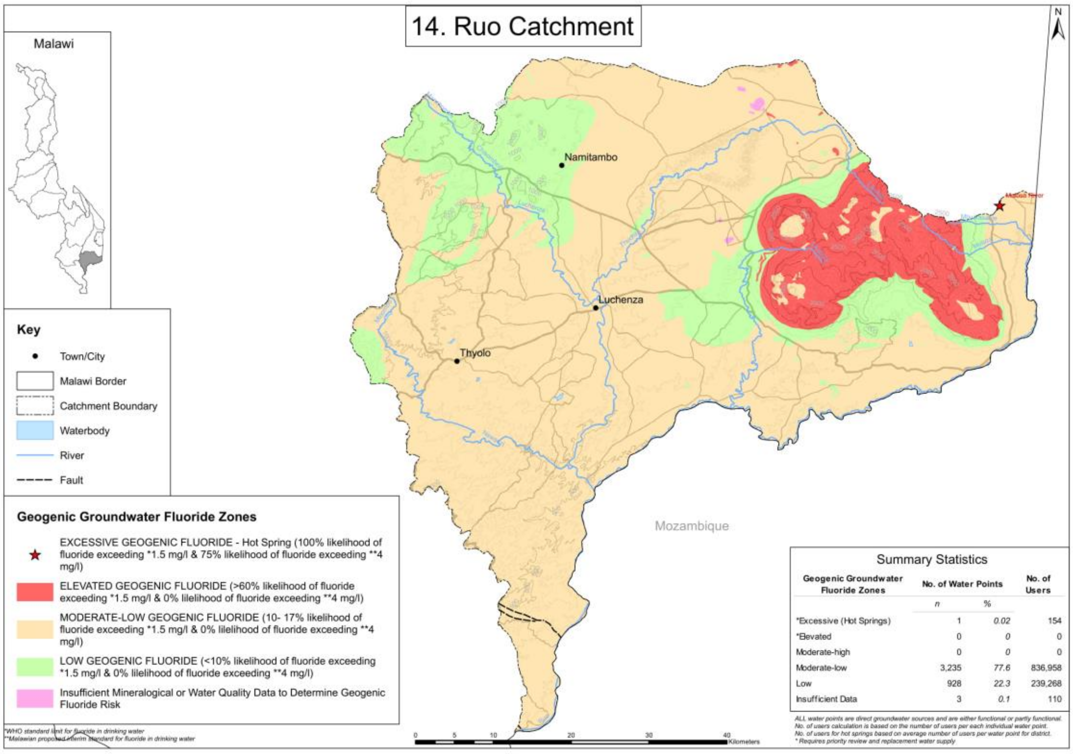
Figure S22. Geogenic fluoride groundwater risk map of WRA 10 (SE Lakeshore).



Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	*%*	
*Excessive (Hot Springs)	0	*0*	0
*Elevated	1	*0.1*	250
Moderate-high	0	*0*	0
Moderate-low	1,395	*95.5*	418,676
Low	65	*4.4*	16,270
Insufficient Data	0	*0*	0

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S23. Geogenic fluoride groundwater risk map of WRA 11 (Lake Chiuta).

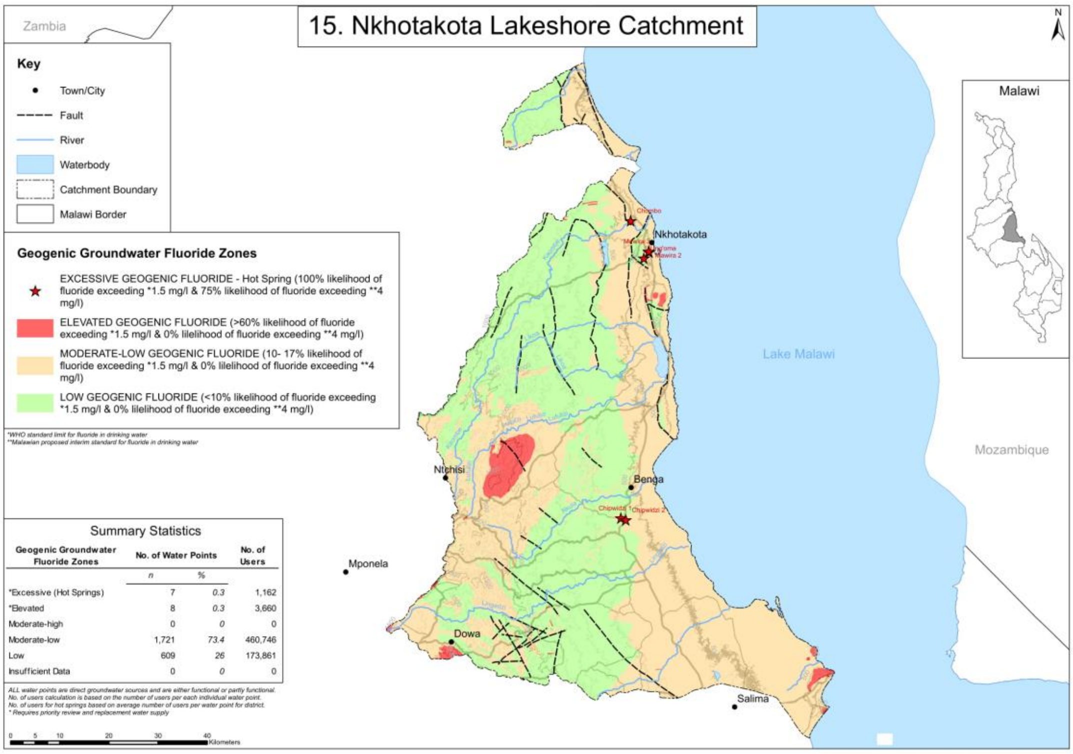


Summary Statistics

Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	*%*	
*Excessive (Hot Springs)	1	*0.02*	154
*Elevated	0	*0*	0
Moderate-high	0	*0*	0
Moderate-low	3,235	*77.6*	836,958
Low	928	*22.3*	239,268
Insufficient Data	3	*0.1*	110

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S24. Geogenic fluoride groundwater risk map of WRA 14 (Ruo).

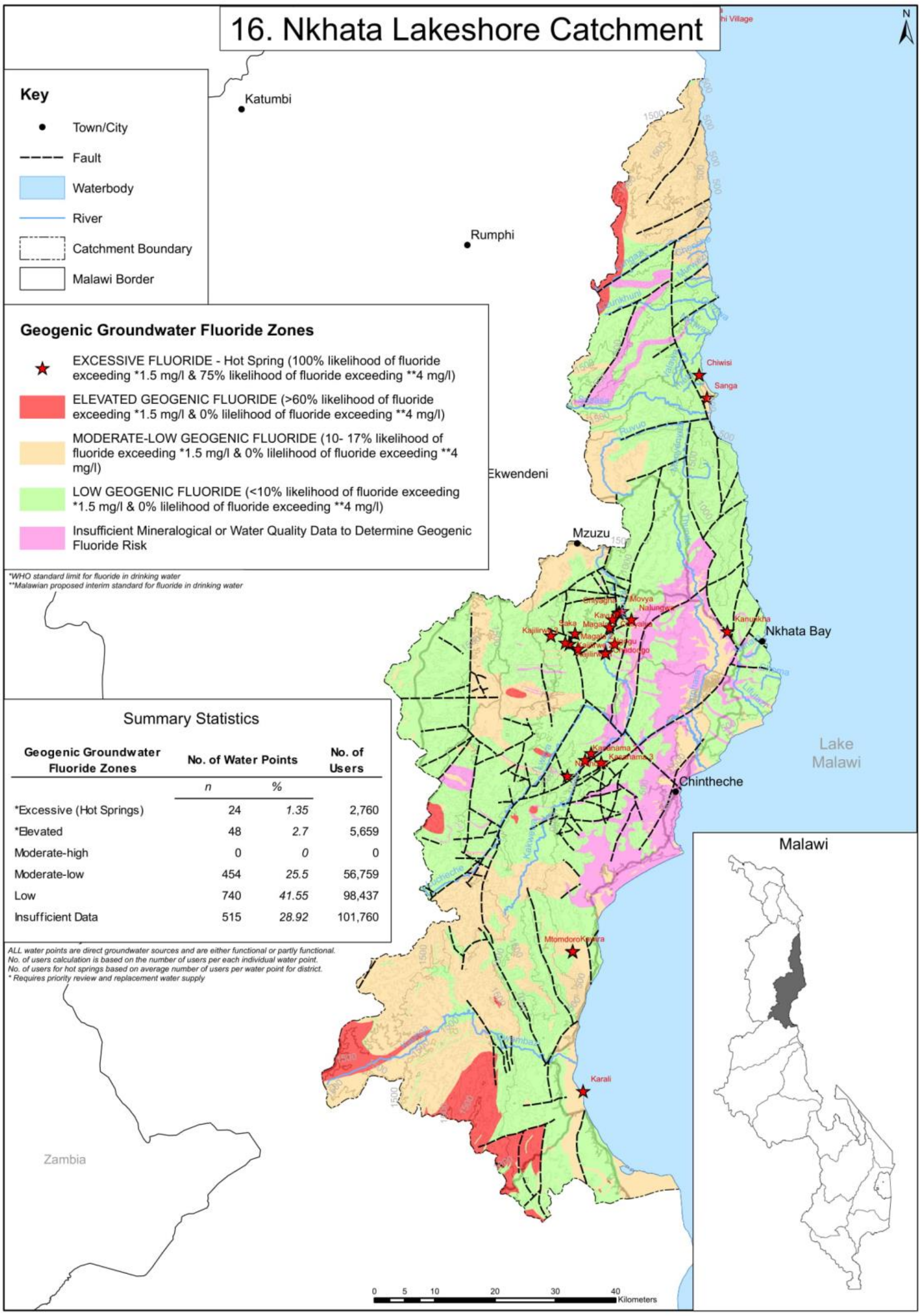


Summary Statistics

Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	*%*	
*Excessive (Hot Springs)	7	*0.3*	1,162
*Elevated	8	*0.3*	3,660
Moderate-high	0	*0*	0
Moderate-low	1,721	*73.4*	460,746
Low	609	*26*	173,861
Insufficient Data	0	*0*	0

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S25. Geogenic fluoride groundwater risk map of WRA 15 (Nkhotakota).

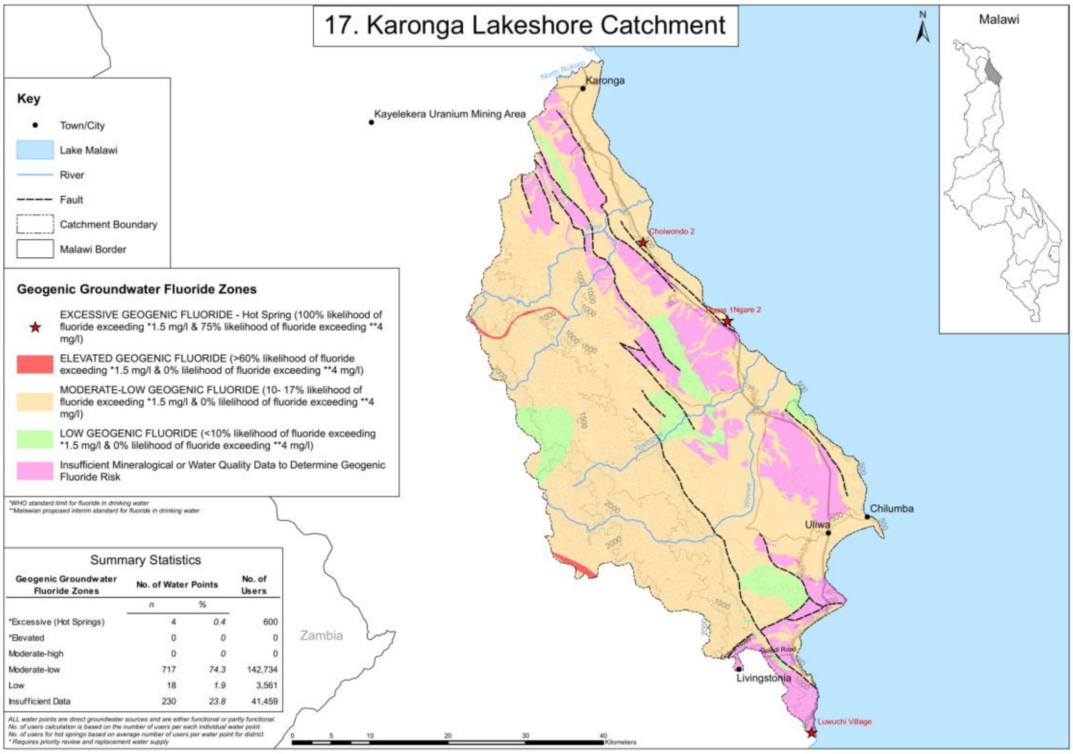


Summary Statistics

Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	*%*	
*Excessive (Hot Springs)	24	*1.35*	2,760
*Elevated	48	*2.7*	5,659
Moderate-high	0	*0*	0
Moderate-low	454	*25.5*	56,759
Low	740	*41.55*	98,437
Insufficient Data	515	*28.92*	101,760

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S26. Geogenic fluoride groundwater risk map of WRA 16 (Nkhata).



Summary Statistics

Geogenic Groundwater Fluoride Zones	No. of Water Points		No. of Users
	n	*%*	
*Excessive (Hot Springs)	4	*0.4*	600
*Elevated	0	*0*	0
Moderate-high	0	*0*	0
Moderate-low	717	*74.3*	142,734
Low	18	*1.9*	3,561
Insufficient Data	230	*23.8*	41,459

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure S27. Geogenic fluoride groundwater risk map of WRA 17 (Karonga).

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6.4 Summary and Context

This chapter addressed and fulfilled RQ. 4: ‘Can the groundwater fluoride prediction method developed be scaled nationally to cover all lithologies using existing data?‘. The screening method for predicting groundwater fluoride developed in the previous chapter was adapted and scaled to cover all lithologies and hot springs in Malawi. The synthesis of site-specific groundwater fluoride (hydrothermal) prediction, generic groundwater fluoride (lithological) prediction and the development of a hierarchy of risk factors for each type of geogenic fluoride source has resulted in a versatile high resolution prediction map for groundwater fluoride that is effective nationally. The method is dynamic and can be updated with new data, allowing for improved prediction confidence with each addition.

This chapter additionally revisited RQ. 3: ‘What is the direct link between geogenic groundwater fluoride and human health risk in Malawi and is the current fluoride standard for drinking water aligned with health risks?’. Developing a national prediction method for screening groundwater fluoride risk prompted a more detailed review of fluoride-relevant policy. The Malawian standard documents for drinking water were interrogated and specific recommendations made on how they may be improved within the context off SDG 6, and how a stepped progression of the fluoride standard to bring it in line with observed health risks may be implemented.

The ‘unconsolidated sediments’ lithology within the Malawi rift basin presented an accuracy issue where anomalous elevated groundwater fluoride concentrations potentially associated with hidden hot springs interfered with risk statistics for unconsolidated sediments (a lithology associated with moderate-low groundwater fluoride risk). It was recognised in the paper that the issue would be an obvious hinderance to groundwater fluoride prediction accuracy in the rift basin sediments of southern Malawi. It will be necessary to delineate those anomalous elevated groundwater fluoride concentrations associated with hidden hydrothermal activity so prediction confidence could be refined via more accurate risk factor statistics for unconsolidated sediments. That issue will be addressed in the next chapter.

Chapter 7 REFINING GROUNDWATER FLUORIDE PREDICTION

7.1 Introduction

The previous chapter addressed and fulfilled RQ. 4: ‘Can the groundwater fluoride prediction method developed be scaled nationally to cover all lithologies using existing data?’. The adapted method resulted in a national prediction map for groundwater fluoride from major geogenic sources. Groundwater fluoride risk factors were developed based on statistical risk of geogenic sources producing groundwater fluoride exceeding the WHO global drinking water standard of 1.5 mg/L. Groundwater fluoride risk factors were translated to geological ‘zones’ of risk on the maps and national statistics were calculated for numbers of water points and water point users at risk from each risk zone.

This chapter will address RQ. 5: ‘Can the groundwater fluoride prediction method developed be refined to delineate hidden hot spring influence from unconsolidated sediments?’. The previous chapter identified an issue where anomalous elevated groundwater fluoride concentrations associated with (hypothesised) hidden hot springs were interfering with prediction accuracy for unconsolidated sediments in the rift basin. This chapter addresses the research question via two primary research objectives. RO. 5.1: ‘. Investigate and identify hidden hot spring locations within unconsolidated sediments using proxy indicators, including a collaboration with dentists to use dental data as additional proxy indicator locations where severe dental fluorosis occurs’, was written as a published, peer-reviewed paper in the international journal ‘Water’ The paper is included in the next section (7.2).

RO. 5.2: ‘Separate hidden hot spring-influenced water points from unconsolidated sediments in the risk model and recalculate accurate statistics for both hot springs and unconsolidated sediments’ was addressed in its own section (7.3) to update prediction confidence. RO 5.2 was successful and resulted in refinement of the prediction method.

7.2 Paper

'Hidden hot springs' as a source of groundwater fluoride and severe dental fluorosis in Malawi

Marc J. Addison [1,*], Michael O. Rivett [1], Owen L. Phiri [2], Nigel Milne [3], Vicky Milne [3], Alex D McMahon [4], Lorna MD Macpherson [4], Jeremy Bagg [4], David I Conway [4], Peaches Phiri [5], Emma Mbalame [5], Innocent Manda [5] and Robert M. Kalin [1]

[1] Department of Civil & Environmental Engineering, University of Strathclyde, Glasgow G1 1XJ, Scotland, UK; marc.addison@strath.ac.uk (M.J.A.); michael.rivett@strath.ac.uk (M.O.R.); robert.kalin@strath.ac.uk (R.M.K.)

[2] Central Water Laboratory, P.O. Box 458, Lilongwe, Malawi; 2002linowen@gmail.com (O.L.P.)

[3] Smileawi. The Hollies Dental Practice, 143 Alexandra Parade, Dunoon, Argyll PA23 8AW, Scotland, UK;
smileawi@gmail.com (N.M.); vicky.milne@hotmail.com (V.M.)

[4] Dental School, University of Glasgow, 378 Sauchiehall Street, Glasgow G2 3JZ, Scotland, UK; alex.mcmahon@glasgow.ac.uk (A.D.M.); Lorna.Macpherson@glasgow.ac.uk (L.M.D.M.); Jeremy.Bagg@glasgow.ac.uk (J.B.); David.Conway@glasgow.ac.uk (D.I.C.)

[5] Water Resources and Supply Department, The Ministry of Forestry and Natural Resources, Government of Malawi, Private Bag 390, Lilongwe 3, Malawi; peachesphiri@gmail.com (P.P.); emmambalame@gmail.com (E.M.); ikmanda@yahoo.co.uk (I.M.)

* Correspondence: marc.addison@strath.ac.uk or marcjaddison@gmail.com

Abstract

Hidden hot springs likely impact rural water supplies in Malawi's Rift Valley with excess dissolved fluoride leading to localised endemic severe dental fluorosis. Predicting their occurrence is a challenge; Malawi's groundwater data archive is sporadic and incomplete which prevents the application of standard modelling techniques. A creative alternative method to predict hidden hot spring locations was developed using a synthesis of proxy indicators (geological, geochemical, dental) and is shown to be at least 75% effective. An exciting collaboration between geoscientists and dentists allowed corroboration of severe dental fluorosis with hydrogeological vulnerability. Thirteen hidden hot springs were identified based on synthesised proxy indicators. A vulnerability prediction map for the region was developed and is the first of its kind in Malawi. It allows improved groundwater fluoride prediction in Malawi's rift basin which hosts the majority of hot springs. Moreover, it allows dentists to recognise geological control over community oral health. Collaborative efforts have proven mutually beneficial, allowing both disciplines to conduct targeted research to improve community wellbeing and health and inform policy development in their respective areas. This work contributes globally in developing nations where incomplete groundwater data and vulnerability to groundwater contamination from hydrothermal fluoride exist in tandem.

KEYWORDS: fluoride; groundwater supply; hot springs; oral health; dental fluorosis; human health risk; rural community water supply; Malawi Rift Valley

1. Introduction

Hot springs are known globally for particularly high groundwater fluoride concentrations [1–4]. The highest concentrations are usually associated with rift valley floors [5]. Hot springs arise from discharge of hydrothermal groundwater at the Earth's surface and are often associated with pools of steaming hot water, discharging gas bubbles, sulphurous smells, mineral encrustations, and extremophile bacteria. Heating of groundwater occurs where there is a relatively shallow subterranean heat source (magmatic or non-magmatic) which circulates, heats, and transports hydrothermal groundwater to the surface from depth by exploiting planes of weakness in the Earth's crust (faults and lithological boundaries) as fluid flow conduits. Hot springs are usually located in increased numbers where the Earth's crust is thinnest, particularly rift valleys where tectonic plates are moving apart (rifting). The East African Rift System (EARS) is an active continental rift valley and a well-documented source of hydrothermal activity [1,6–8]. The primary concern herein is the vulnerability of drinking water and potential health impacts of 'Hidden hot springs'—a term coined to describe the circumstance whereby hydrothermal groundwater from depth fails to discharge directly at ground surface as a spring *per se*, but rather discharges into groundwater at the sediment base of the rift basin and therefore is buried beneath sediments and hidden from view. As such, hidden hot springs may result in hydrothermal fluoride-rich groundwater mixing with shallow groundwater and contamination of rural community water supply.

While optimal intake of fluoride (0.5 – 1.5 mg/L) can prevent dental decay, ingestion of excess fluoride concentrations in groundwater can cause severe dental fluorosis, which results from hypo-mineralisation of the enamel caused by exposure to excessive fluoride during tooth development [9]. Dental fluorosis incidence has been shown to correlate strongly with drinking water sources, with hot springs linked to severe dental fluorosis [9,10]. Consistent ingestion of fluoride concentration range 1.5 – 4 mg/L promotes development of severe dental fluorosis. Concentrations >4 mg/L are linked to skeletal fluorosis [11]. Accordingly, the World Health Organisation (WHO) has set a recommended global standard for fluoride in drinking water of 1.5 mg/L [12]. Malawi's standard for untreated water delivered from boreholes and shallow wells (in common with some other developing countries struggling to implement this standard) is higher at 6 mg/L [13]. Prolonged and excessive exposure to groundwater fluoride occurs where a regular drinking supply (borehole, well, or spring) is hydraulically connected to a geogenic fluoride contamination source. Hot springs are high-risk supplies and often result in localised endemic severe dental fluorosis [1,9]. Rural Malawians (82% of the population) are particularly at risk due to their reliance on untreated groundwater for domestic supply. Defluorination techniques are expensive and yield poor results [14] meaning they are often not viable options, particularly for rural communities in lesser developed countries.

Dental fluorosis incidence provides a proxy indicator of locally elevated groundwater fluoride. Previous work [15] identified increased incidence of the visible signs of dental fluorosis (non-severe) near water points drilled into lithologies classified as generic geogenic fluoride sources. As expected, even higher health risks were apparent for hot spring supplies. Hot springs in Malawi mostly exceed the 1.5 mg/L WHO guideline with as many as 75% over 4 mg/L [15]. One local study tentatively linked hot springs to severe dental fluorosis cases, however that conclusion was not confirmed by dentists [10]. Unfortunately, Malawi has very few dentists (~36 in 2019 [16]) and published data on dental fluorosis confirmed by dentists is extremely rare. This study sought to overcome that dearth and provide corroborating oral health data substantiating links between groundwater fluoride occurrence in supply and (severe) dental fluorosis incidence. That was achieved through opportunistic collaboration of University of Strathclyde geosystem expertise with Smileawi (a Scottish dental charity operating in Malawi) and the University of Glasgow Dental School, who were running a joint project evaluating oral health of school children across Malawi in June 2019.

The uncertainty of dilution of hidden hot spring concentrations of fluoride prior to reaching water supplies by shallow groundwater mixing, and attendant uncertainty in health risks posed, provides significant rationale. The aim was hence to synthesise multiple proxy indicators to predict hidden hot spring occurrence in the unconsolidated sediments of Malawi's rift valley, underpinning the development of a hidden hot spring vulnerability prediction map for the region. The primary objective was to identify basic geochemical proxy indicators which could locate hidden hot springs from incomplete archive groundwater quality data. Typical developing world problems of sporadic and incomplete groundwater data exist in Malawi which prevents the application of standard geochemical modelling techniques. An alternative set of basic geochemical proxy indicators of hidden hot spring activity was required so that groundwater data could be screened for hidden hot springs, making the best use of existing data. It should be noted that basic proxy indicators are not intended to replace sampling or modelling, rather they are intended to screen for potential hidden hot spring activity where complete groundwater data are not available. The secondary objective was to work collaboratively (geoscientists and dentists) to identify and to corroborate hidden hot spring locations with medically confirmed incidence of severe dental fluorosis. The collaborative work and sharing of data proved to be substantially effective for both disciplines. Future research implications were significant, providing proxy indicator locations for targeted groundwater sampling by geoscientists, and a national prioritised set of locations for targeted oral health (fluorosis) sampling by dentists.

2. Materials and Methods

2.1 Identification of geochemical proxy indicators for hot springs

Malawi forms the southernmost extent of the EARS (Figure 1) and is characterised as a magma-poor rift segment [17] experiencing no current active volcanism associated with rifting (although it has in the past) and less intense hydrothermal activity than EARS countries further north [6–8]. The EARS segment occurs north-south in Malawi, with around 65% of the main rift submerged beneath Lake Malawi in the northern and central parts of the country. The remaining segment occurs onshore in the southern part of the country due to southward shallowing of the Malawi Rift [18]. Hot springs are documented along the western shores of Lake Malawi and in the rift basin sediments on land further south [19–24]. Known hot springs there occur near geological faults associated with rifting (Figure 2). Hydro-geochemical compositions suggest most are influenced by mixing of deep hydrothermal groundwater with shallow, cool groundwater [19]. Most hot springs in Malawi are buried beneath unconsolidated basin sediments with tell-tale geochemical signatures reflecting deeper, hidden geological sources [20].

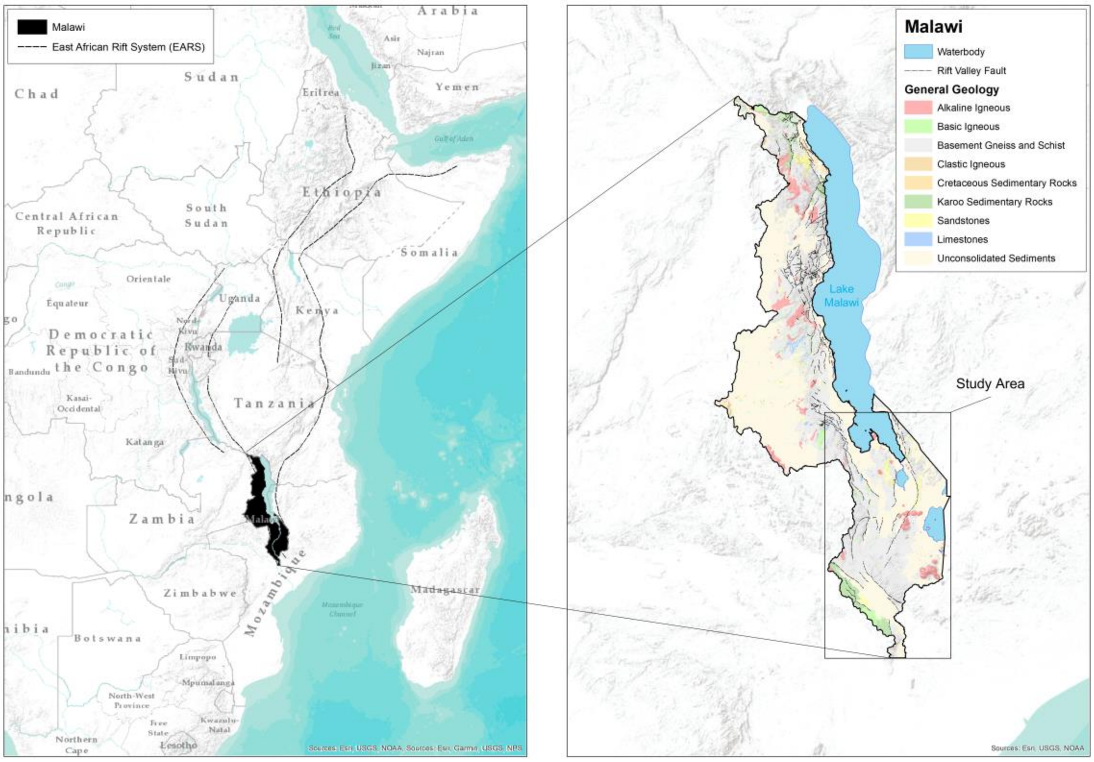


Figure 1. *Left* Malawi's location on the African continent at the southern periphery of the East African Rift System (EARS). *Right* Topographical map of Malawi with generalised geology and rift-related faulting within the Malawi Rift Valley.

While there is no volcanism in Malawi, active rifting (evidenced by regular earthquakes) still occurs [21] and it is those active rift-related normal faults which control the upwards migration of hydrothermal groundwater from depth to hot springs [24]. Extensional strain is accommodated across both rift margin and intrabasin faults which is regarded significant in that hydrothermal activity is as probable within the rift valley as it is at the margins where the largest faults occur [25]. That was apparent in our previous work [15]—two rift basin hot springs appearing anomalous due to an absence of nearby faults were attributed to a recently discovered intrabasin fault [25], coincident with their location causing local hydrothermal activity. The wider inference being that intrabasin faults hidden beneath sediments may be responsible for hidden hot springs at the sediment base elsewhere, which due to their (hypothesised) hidden locations beneath sediments would require proxy indicators to locate and identify. Malawi additionally hosts two hot springs which are located outside of the rift and not associated with faults. The hot springs (discussed later) appear to be related to adjacent Chilwa Alkaline Province (CAP) intrusions; igneous intrusions associated with the most recent phase of rifting where the intrusion-country rock lithological boundary acts as the vertical transport conduit for hydrothermal groundwater (Figure 2). The CAP intrusions outcrop extensively across southern Malawi and may provide additional (residual) heat to hydrothermal systems in the region [17].

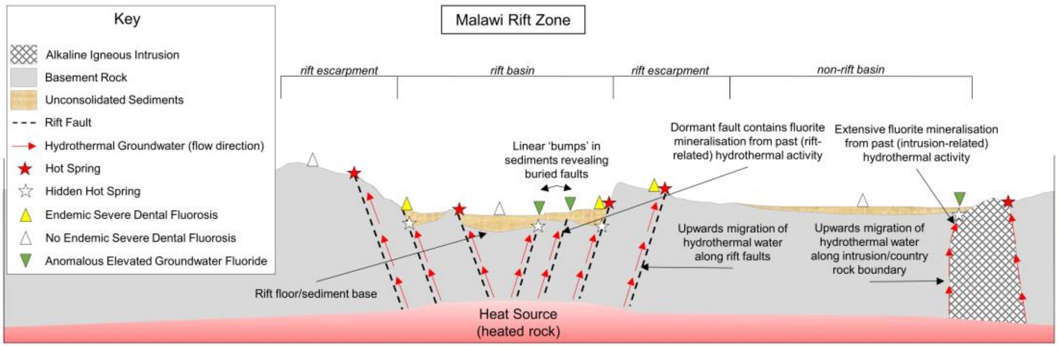


Figure 2. Schematic cross-sectional conceptual model of the study area showing mechanisms responsible for hot spring and hidden hot spring occurrences of different types. Image is intended as an idealised example and is not to scale.

Fluoride occurrence in groundwater arises from dissolution of fluoride-bearing minerals in rocks. Some lithologies contain higher ratios of fluoride-bearing minerals and thus produce groundwater with higher dissolved fluoride concentrations. For example: boreholes drilled into alkaline igneous rocks (granite, syenite) have been shown to pose >60% risk of elevated groundwater fluoride (>1.5 mg/L) in Malawi compared to basement rocks and sediments which pose <20% risk [15,26]. Geogenic fluoride is the dominant fluoride contamination source in Malawi as other sources (anthropogenic, surface water) were previously shown to be negligible [15]. Elevated temperature provides a catalyst for dissolution of fluoride-bearing minerals in the subsurface. Heating of groundwater at depth within rift valleys (Figure 2) therefore provides opportunity for particularly elevated fluoride concentrations recorded in hot springs [1,15,18]. Previous work documented 63 known hot springs nationally for Malawi and mapped them as site-specific locations of relatively obvious high ("excessive") risk from elevated groundwater fluoride, arising from their vulnerability to geogenic fluoride sources [15]. That contrasts with some anomalously high groundwater fluoride concentrations in supply boreholes found [15] within unconsolidated rift basin sediments, a lithology linked to low groundwater fluoride, which could reasonably be accounted for by hidden hot springs at some localities. It is reasonably questioned too whether some somewhat elevated borehole supply concentrations in the "troublesome 1.5 – 6 mg/L" window, breaching current WHO guidelines [18] may likewise be due to hidden hot spring component contributions variously diluted in basin sediments by shallow groundwater mixing. This work herein seeks to overcome the recognised deficiency of our previous groundwater vulnerability mapping of fluoride risk [15] and examine the potential for hydraulic connection of supply area to hidden hot spring contributions and population risk from endemic fluorosis.

2.2 Identification of Geochemical Proxy Indicators for Hot Springs Using Model Data

A temperature proxy indicator for hot springs was identified by previous work where all groundwater samples from a study in southern Malawi >32 °C corresponded exclusively to known hot springs [18]. This proxy alone was useful for identifying hot springs which occur above ground, but a hot spring buried beneath sediments may display temperatures below 32 °C due to mixing of hydrothermal water with cooler, shallow groundwater (non-hydrothermal). It is possible that hydrothermal groundwater mixed with shallow groundwater would display higher temperatures than those not connected to a hydrothermal system; however, that would be dependent on the degree of mixing and the initial temperature of the groundwaters involved and may be highly variable. A temperature proxy alone therefore is not sufficient to identify and confirm hidden hot springs beneath Malawi's Rift Valley sediments, so additional proxy indicators were required to enhance prediction confidence.

Model geochemical data were obtained from existing data collected directly from known hot springs, and non-hydrothermal shallow groundwater in the Malawi Rift Valley. Model data were intended to provide endmembers for both hot springs, and non-hydrothermal shallow groundwater in Malawi. The endmembers were used to identify basic key geochemical proxy indicators exclusive to Malawi hot springs. The bulk of geochemical data was collected by us during the period 2016–2018 (dry season) in Malawi's rift basin sediments (hot springs: n = 10; non-hydrothermal shallow groundwater: n = 12). Data was augmented by additional (Malawi) hot spring data from literature (n = 16) which had corresponding hydrochemical profiles [23,24]. The combined model data comprised two 'endmember' components: a 'Hot Spring' data set (n = 26), and a 'Shallow Groundwater' data set (n = 12) (Figure 3).

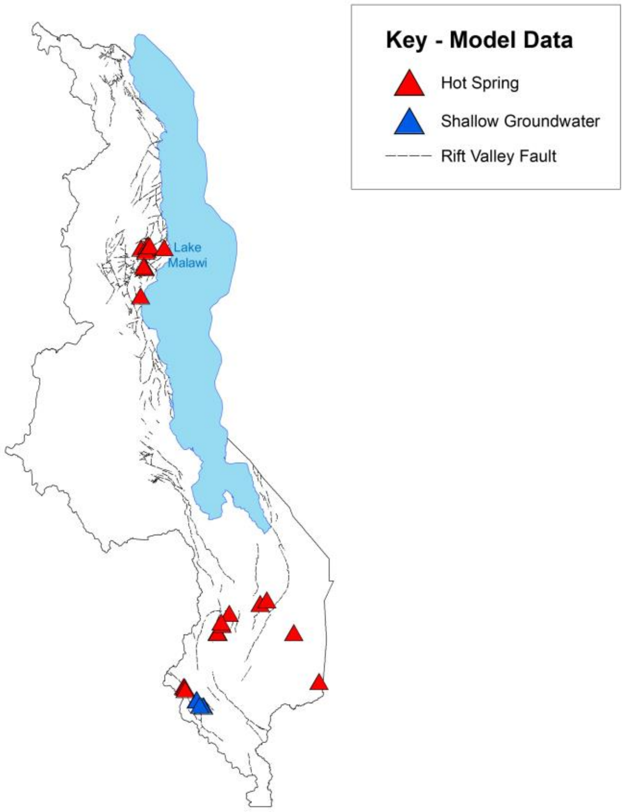


Figure 3. Map of Malawi showing locations of model hot spring and shallow groundwater data.

2.3 Identification of Hidden Hot Spring Locations from Archive Groundwater Data

The purpose of identifying proxy indicators for hot springs was to predict locations of possible hidden hot springs beneath rift valley sediments. To achieve this, geochemical data from boreholes and wells were required where hydrochemical profiles were complete enough to sufficiently match any proxy indicators identified from the model data. Previous work in southern Malawi collated an archive data set of groundwater quality data for the region [18]. This data set was used to develop a prediction method for groundwater vulnerability to geogenic fluoride for Malawi [15]. The data set was used within this study (referred to herein as the 'Archive' data set), as it contained all geochemical parameters identified from model data to be proxy indicators: fluoride (F^-), sodium (Na^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}), and was extensive, covering a wide variety of locations across the southern region (n = 1026). Piper plots of all data were not possible due to incomplete geochemical data (hence the need for basic geochemical proxy indicators). The geochemical proxy indicators identified from the model data were applied to the archive data to screen for potential hidden hot spring locations. It was expected that variable mixing ratios would be evident in samples suspected to be hidden hot springs due to mixing with shallow groundwater. Geochemically, hidden hot springs were expected to plot between known hot springs and non-hydrothermal shallow groundwater on proxy indicator plots. Proxy indicator matches for some ions were expected, with the exception of fluoride which was expected to be elevated relative to samples not suspected as hidden hot springs. Those data (water points) which matched all four geochemical proxy indicators represented locations for hidden hot springs (identified by geochemical proxy indicators), buried beneath sediments in the Malawi Rift Valley and were subsequently plotted onto a map of geology. Temperature data were not available for the archive data set but for reasons stated previously, it is likely that hidden hot springs may not conform to the temperature proxy identified by our previous work [18].

2.4 Inferring Rift Valley Faults

Additional to the identification of hidden hot spring locations from archive hydrochemical data, faults hidden beneath rift valley sediments were inferred onto a geological map. It was previously hypothesised that mapping of hidden faults may reveal locations that are vulnerable to hot spring activity, and thus would assist in locating undiscovered hydrothermal sources of elevated groundwater fluoride [15]. That was achieved by combining the use of digital elevation data (DEM) in ArcGIS (10.6) (Redlands, California, US) with digitised structural geological data (digitised after others: [25,27]). Vertical exaggeration was applied to the DEM to look for linear changes in elevation (proxy for faults) in rift basin sediments in the southern part of Malawi. Once identified, a comparison was made to existing geological data (known faults) to assess whether it was likely to be a buried fault or continuation of a known rift valley fault. Those which satisfied both criteria were mapped as 'Inferred Faults'. The term "inferred" was used to describe faults or continuations of known faults which are buried beneath sediments, hidden from view. Additionally, hidden hot spring locations identified from the archive data were cross-checked with locations of inferred faults to provide supporting evidence for hidden hot springs where they coincided (faults being conduits for hydrothermal water). That process was additionally useful by providing supporting evidence for locations of inferred faults where they coincided with known hot springs which occur at the surface.

2.5 Severe Dental Fluorosis Incidence as a Proxy Indicator

A cursory review of dental fluorosis literature was published in our previous work [18] in which only brief mentions of the condition were found in published works, with only one study presenting data for four schools in Machinga District: Mtubwi F.P School, Liwonde L.E.A School, Mmanga F.P. School and Mombe School [10]. A more thorough review of Malawi literature was conducted to update our original review and investigate current understanding and extent of severe dental fluorosis in Malawi. More specifically, an attempted collation of locations with confirmed severe dental fluorosis incidence was necessary to investigate the hypothesis that locations with increased incidence of the condition may present proxy indicator locations for hidden hot springs in the basin sediments of the rift valley [15].

To augment existing severe dental fluorosis data collated from literature in Malawi, our dental team (Smileawi and the University of Glasgow Dental School) collected medical data on severe dental fluorosis incidence during an independent study on oral health in school children in 2019. The study was a cross-sectional pilot survey of child oral health in Malawi. A purposive convenience sample of five schools (four in Mzimba District, one in Dedza District) was selected based on contacts of the charity Smileawi. The Mzimba schools were: Ekwaiweni Primary School, Dunduzu Primary School, Malivenji Primary School, Ekwendeni School for the Blind and the Dedza school was Mua Primary School. The head teachers at the schools agreed to participate. All children who were physically well, between the ages of 4 – 12 years and attending the schools, were eligible for inclusion.

The team of examiners included three highly experienced UK dentists and six supervised senior dental students from the Universities of Glasgow and Dundee. All examiners had temporary registration with the Medical Council of Malawi and had received training in the method for undertaking the oral examinations, which was based upon the basic dental inspection standardisation procedures of the National Dental Inspection Programme of Scotland [28] and included additional fluorosis detection and assessment of aesthetic concern. Within each school, on the day of survey examination, each child was allocated a survey ID number by the translator, who completed the 'Child Questionnaire' with each participant. The questionnaire included items on the socio-demographics of the child and their family, home district area/village, household water supply and oral health related behaviours. Ethical approval for the survey was received from the University of Malawi College of Medicine Research and Ethics Committee (COMREC). Consent for each child to participate was through a 'negative consent' process. Parents received a letter and were asked to return the letter to the school if they did not want their child to participate.

Examination followed standardised examination procedures and included charting of dental caries (decayed, missing and filled teeth), recording the presence or absence of dental fluorosis on the upper anterior teeth (central and lateral incisors and canines) and a clinical assessment of whether any fluorosis present was at a severe level relative to a referent colour photographic image of a dentition previously scored as the threshold level of fluorosis of aesthetic concern [29,30]. Photographic images of teeth were recorded to document varying severity of dental fluorosis at the schools visited (shown later). The examination findings were recorded alongside the completed child questionnaire, and data were entered onto a database on the day of the examination visit. All entries were subsequently checked for quality and completeness by a study administrator.

2.6 Groundwater Sampling at Locations Identified by Dental Data

A separate hydro-geochemical sampling campaign was conducted after the dental team survey to collect groundwater samples from supply boreholes at the same schools surveyed by the dental team and those previously identified as endemic fluorosis schools from Malawi literature. Fluoride concentration data were available for the school boreholes in Machinga District, however complete geochemical profiles were not published [10]. Those same locations were sampled for groundwater to acquire geochemical profiles that could be matched with geochemical proxy indicators identified for hot springs. Groundwater from 10 public supply boreholes within 1.25 km from Mua Primary School in Dedza District (including the school borehole) were sampled in response to a high number of severe dental fluorosis cases recorded at the school by the dental survey team. Every water point within 1.25 km of the school (the halfway distance to the next nearest school) was sampled to ensure the groundwater fluoride source causing the observed severe dental fluorosis was sampled. Groundwater samples were collected at school boreholes sampled by the dental team in Mzimba District as a control group. The four Mzimba District schools displayed zero incidence of severe dental fluorosis and were located outside of the rift valley and at least 30 km from the nearest fault so it was expected that the boreholes would not match all four geochemical proxy indicators for hot spring activity and yield low fluoride concentrations.

Samples were analysed for major anion-cation geochemistry and then cross-checked with our geochemical proxy indicators for hot spring correlations. All boreholes were purged for five minutes prior to sampling, duplicate sampled, with one sample from each site preserved for metals. Samples were then analysed in Malawi’s Central Water Laboratory (Water Resources Department within the Ministry of

Forestry and Natural Resources) for anions and cations. All samples passed QA/QC protocols with ion charge balance uncertainties < 2%.

A modified Piper plot was developed (using the few data with corresponding complete geochemical profiles) to support the use of basic geochemical proxy indicators. Fluoride is the significant anion in this study, so it replaced chloride on the Piper plot. Fluoride concentrations in mg/L are 1–2 orders of magnitude lower than other ions so they were multiplied by 10 to increase trend visibility on the plot. Five known hot spring samples from the model data had complete geochemical profiles and were included in the Piper plot to represent endmember hydrothermal water. None of the shallow groundwater samples from the model data had complete geochemical profiles, so two highland natural spring samples were included in the piper plot to represent endmember shallow groundwater (recent recharge) in Malawi. Groundwater samples collected for this study were analysed for full ion geochemistry and were included in the Piper plot to investigate mixing trends relative to the endmembers. Hidden hot springs (initially identified using basic geochemical proxy indicators) were expected to plot between both endmembers, reflecting mixing of hydrothermal waters with shallow groundwater at the sediment base. Non-hydrothermal shallow groundwater (not matching all four basic geochemical proxy indicators) were expected to plot toward the natural spring samples. The Piper plot was thus designed to support the effectiveness of basic geochemical proxy indicators using the few data that had corresponding complete geochemical profiles.

2.7 Data Synthesis and Hidden Hot Spring Prediction

A hidden hot spring vulnerability prediction map for the southern part of Malawi was developed in ArcGIS (10.6). The map developed (presented later) displays the result of a synthesis of identified primary and secondary proxy indicators for hot spring activity (Table 1) after application to our archive geochemical and severe dental fluorosis incidence data.

Table 1. Proxy indicators for hot spring activity considered within this study to locate and identify hidden hot springs in the southern part of Malawi's unconsolidated rift basin sediments .

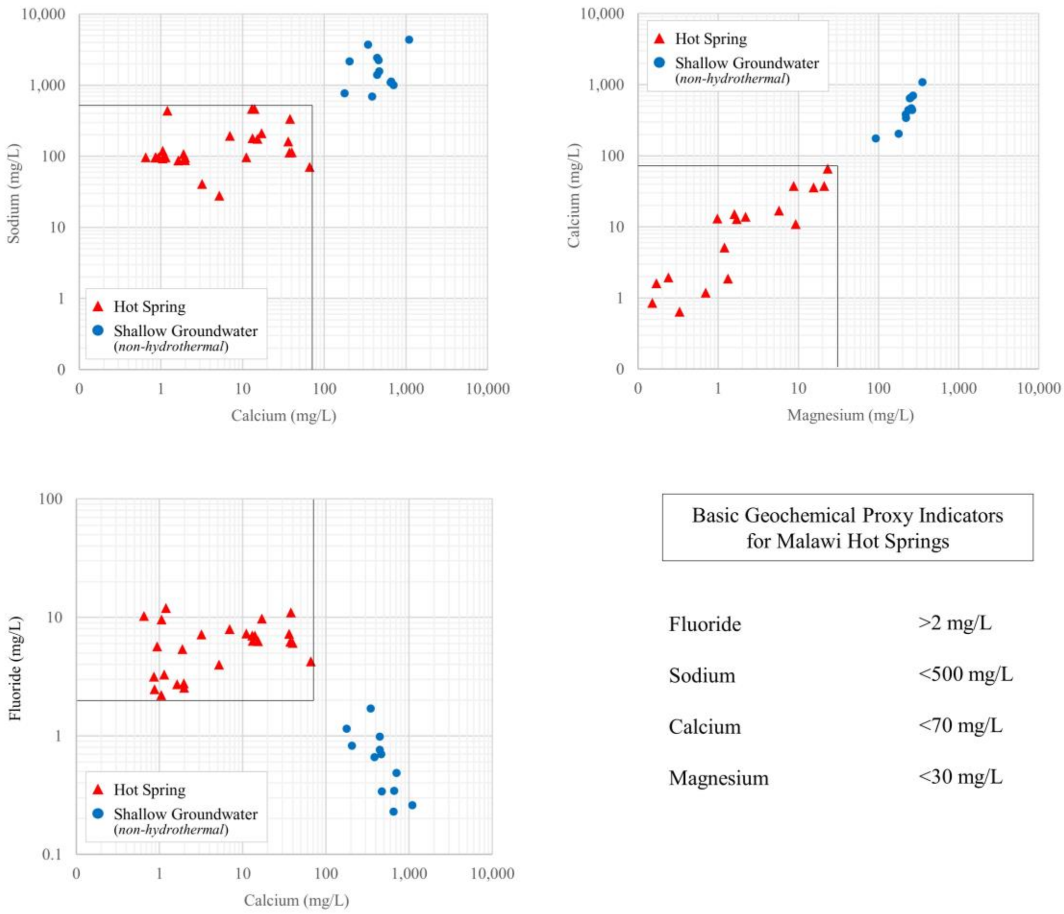
Proxy Indicator	Question	Explanation	Potential Issues
Geological	Is the location within the rift valley?	Hot springs in Malawi are caused by heat associated with continental rifting so locations within the rift valley are much more vulnerable to hydrothermal activity.	
Dental Health	Are there increased localised incidences of severe dental fluorosis?	Dental fluorosis is caused by excess fluoride ingestion, particularly from drinking water. Increased localised incidences of severe dental fluorosis suggest that there is a water source nearby which consistently produces water with particularly elevated fluoride concentrations, i.e. a hot spring.	
Geochemical	Does drinking water chemistry from boreholes and wells match geochemical proxy indicators identified to be indicative of Malawi hot springs?	Hot spring groundwater has distinctly different geochemical signatures to shallow, non-hydrothermal groundwater. Some specific dissolved elemental concentrations are shown to be exclusive to Malawi hot springs and can be used as proxy indicators (discussed later).	
**Groundwater Temperature*	*Is the local groundwater temperature anomalously elevated?*	*Hot springs are thermal groundwaters and usually reflect significantly higher temperatures (>32 °C) than those of shallow groundwaters in Malawi (22 - 26 °C).*	*Mixing with shallow groundwater within aquifers may lower hydrothermal groundwater temperatures.*
**Known Hydrothermal Activity*	*Is there known hydrothermal activity nearby?*	*The occurrence of known hydrothermal activity in an area is a good indication that there may be undiscovered hot springs in the same area.*	*Not effective in areas where all hydrothermal activity is hidden beneath rift valley sediments.*

**secondary proxy indicators - subject to issues which may render them ineffective*

3. Results and Discussion

3.1 Identification of Geochemical Proxy Indicators for Hot Springs

Four basic geochemical proxy indicators for hot spring activity were identified from the model data (F^-, Na^+, Ca^{2+}, Mg^{2+}); each displayed a geochemical signature notably different for hot springs than for shallow (non-hydrothermal) groundwater samples from the same rift basin environment (Figure 4). Na^+/Ca^{2+} and Ca^{2+}/Mg^{2+} ratios displayed strong increasing linear trends from hot springs towards shallow groundwater samples with distinct groupings of each sample type: all samples displaying <500 mg/L Na^+, <70 mg/L Ca^{2+} and <30 mg/L Mg^{2+} were hot springs [15,23,24]. Distinct groupings were also visible with the F^-/Ca^{2+} ratio where all samples with >2 mg/L F^- and <70 mg/L Ca^{2+} were hot springs. There was a significant gap (spanning an order of magnitude) of 108 mg/L between the maximum Ca^{2+} concentration of hot springs (66 mg/L) and the minimum Ca^{2+} concentration of non-hydrothermal samples (178 mg/L). The same gap in F^- concentrations was less significant at only 0.51 mg/L. The F^-/Ca^{2+} plot shows a decreasing linear trend in shallow groundwater samples which is expected due to fluorite (CaF_2) equilibration occurring in shallow groundwater in Malawi's rift basin alluvial aquifers, however, the trend is less obvious in hot spring samples, possibly due to oversaturation of fluorite (CaF_2) (SI = 0 – 1) occurring in some hydrothermal waters [18].



Basic Geochemical Proxy Indicators for Malawi Hot Springs

Fluoride	>2 mg/L
Sodium	<500 mg/L
Calcium	<70 mg/L
Magnesium	<30 mg/L

Figure 4. Basic geochemical proxy indicators for hot spring activity, identified from the model data, collected directly from hot springs and supply boreholes

within the Malawi Rift Valley. All shallow groundwater samples were non-hydrothermal and occurred within rift basin sediments.

Elevated fluoride is the significant proxy indicator; however, elevated fluoride by itself does not suggest hot spring activity. There are many reasons for groundwater samples to match the other three proxy indicators (<500 mg/L Na^+, <70 mg/L Ca^{2+} and <30 mg/L Mg^{2+}); however, when combined with elevated fluoride (>2 mg/L) they are shown represent hidden hot springs (Figure 4). The other three proxy indicators are thus intended to be used in conjunction with elevated fluoride which is why a sample must match all four to be classified as a hidden hot spring. Fluoride concentrations from the model data are significantly higher in hot springs when compared to shallow (non-hydrothermal) groundwater. Only 5% of shallow groundwater samples had fluoride concentrations which exceeded the WHO water quality limit of 1.5 mg/L with a maximum concentration of only 1.7 mg/L. In contrast, 100% of hot spring samples exceeded 1.5 mg/L, with 58% exceeding the current (very high) Malawian standard for untreated drinking water of 6 mg/L and a maximum concentration of 12 mg/L. The median groundwater fluoride concentration in hot springs (5.88 mg/L) is an order of magnitude higher than that of non-hydrothermal samples (Table 2).

3.2 Hidden Hot Spring Locations Identified from Archive Geochemical Data

A total of nine samples from the archive groundwater data set (n = 1026) matched all four geochemical proxy indicators for hot spring activity and were classified as hidden hot springs. Those locations represent drinking water points where groundwater samples from boreholes and wells reflect geochemical signatures identified to be indicative of Malawi hot springs, in contrast to the majority which reflect geochemical signatures identified to be indicative of non-hydrothermal shallow groundwater. Fluoride concentrations from hidden hot springs in the range 2 – 4.4 mg/L mostly reflect those of endmember hot springs from the model data, the obvious difference being a lack of concentrations exceeding 6 mg/L. That may be attributed to expected mixing trends with shallow groundwater in the unconsolidated rift basin aquifers which may dilute fluoride concentrations, or it may simply be that the hidden hot springs do not produce groundwater fluoride in the higher concentration range (>6 mg/L), as is the case with 40% of known hot springs from the model data (Table 2).

Table 2. Summary statistics of groundwater fluoride concentrations from the model data (hot springs and shallow groundwater shown separately), and hidden hot springs identified from the archive groundwater data set.

Data Set	*n*	Fluoride Concentration (mg/L)								
		<1.5	>1.5	1.5 - 6	>6	Min.	Max.	Mean	Median	Std. Dev.
Model Data (*shallow groundwater*)	*19*	94.74%	5.26%	5.26%	0%	0.23	1.70	0.70	0.66	0.38
Model Data (*hot springs*)	*25*	0%	100%	42%	58%	2.21	12.00	5.77	5.88	2.81
Archive Groundwater (*hidden hot springs*)	*9*	0%	100%	100%	0%	2.00	4.40	2.76	2.55	0.75

Hidden hot spring locations identified from the archive data by geochemical proxy indicators were plotted onto a map of regional geology and known hot spring locations for the southern part of Malawi (Figure 5). Additional to known faults, the map displays inferred faults in the rift valley as described in Section 2.3. Hidden hot spring locations are numbered 1 – 9. All (except one) hidden hot springs occur directly adjacent to a known or inferred fault within the rift valley (Figure 5). Three occur in faulted areas where there is known hot spring activity: one in the Middle Shire River Basin (3), ~40 km northwest of Blantyre, and two in the Lower Shire Basin (1,2), ~35–40 km south-southwest of Blantyre City. Five occur in the Upper Shire River Basin: four in a cluster around the shores of Lake Malombe and the southernmost shore of Lake Malawi (5,6,7,8), and one due west immediately proximal to a large rift margin normal fault (4). The only hidden hot spring to occur outside of the rift valley (~60 km southeast of Zomba City) is located in unconsolidated sediments in an area with no faulting immediately adjacent to an alkaline igneous intrusion composed of granite (9). The latter occurs in a region characterised by the occurrence of the Chilwa Alkaline Province (CAP), alkaline igneous intrusions (mostly plutons) associated with the most recent phase of rifting and contains two known hot springs which are also located immediately adjacent to alkaline intrusions composed of granite and syenite (Figure 5).

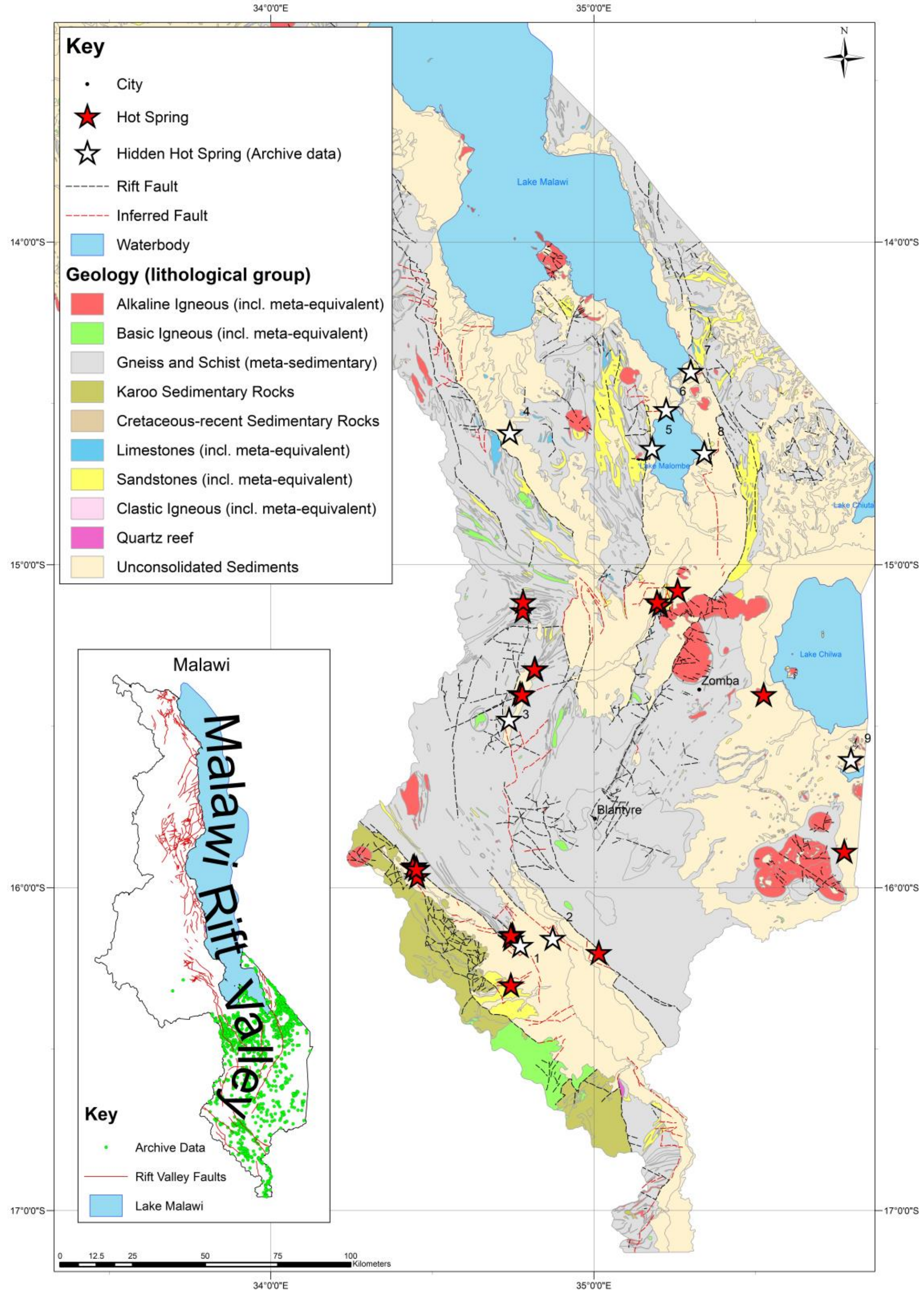


Figure 5. Regional geological map of the southern part of Malawi showing locations of all known hot springs (red stars) and hidden hot springs (white stars) identified from the archive data using geochemical proxy indicators. Hidden hot spring locations are numbered 1 – 9. Map shows known rift faults (black dashed lines) and inferred rift faults (red dashed lines) which have been

projected to display hidden faulting in basement rock buried beneath sediment cover in the rift basin. *Inset*: Simplified map of Malawi showing the Malawi Rift valley, distribution of rift valley faults, and distribution of archive (groundwater) data points prior to application of proxy indicators (n = 1026).

3.3 Severe Dental Fluorosis Incidence as a Proxy Indicator

Malawi literature on dental fluorosis was particularly sparse. The updated review found no new published works presenting dental fluorosis data since the original review [18]. Only one study (the same study identified by our original review) published data on dental fluorosis in school children [10]. The study investigated dental fluorosis at four schools inside the rift valley in Malawi's Machinga District, two of which reported increased incidence of dental and severe dental fluorosis: Liwonde L.E.A School and Mtubwi Primary School (Figure 6). Pupils who were born or had lived in the area for more than two years were identified, then pupils from that group with dental and severe dental fluorosis were counted (standard 3 and 4 age). A significantly higher proportion of pupils presented signs of severe dental fluorosis at Mtubwi Primary School than at Liwonde L.E.A. School, despite being only 2 km apart. That was attributed to the fact that most households around Liwonde L.E.A. School obtain their drinking water from the Southern Region Water Board (treated surface water and in-piped network), rather than local boreholes, whilst most households around Mtubwi Primary School drink from local boreholes. The boreholes at both schools and those at surrounding villages all tested very high for fluoride concentrations (range: 3.2 – 10.3 mg/L), leading them to conclude that drinking water was the cause at both locations and classified the areas which included each school and their surrounding villages as "endemic fluorosis areas" [10]. Their data (two school locations with high incidence of severe dental fluorosis) were subsequently incorporated into this study as proxy indicator locations (from dental data—Table 1) for hidden hot springs (Figure 6). No information was presented on the methods of assessing fluorosis. The study was the best (and only) available dental fluorosis study in Malawi, with data, which could be utilised as proxy indicator locations for hidden hot springs.

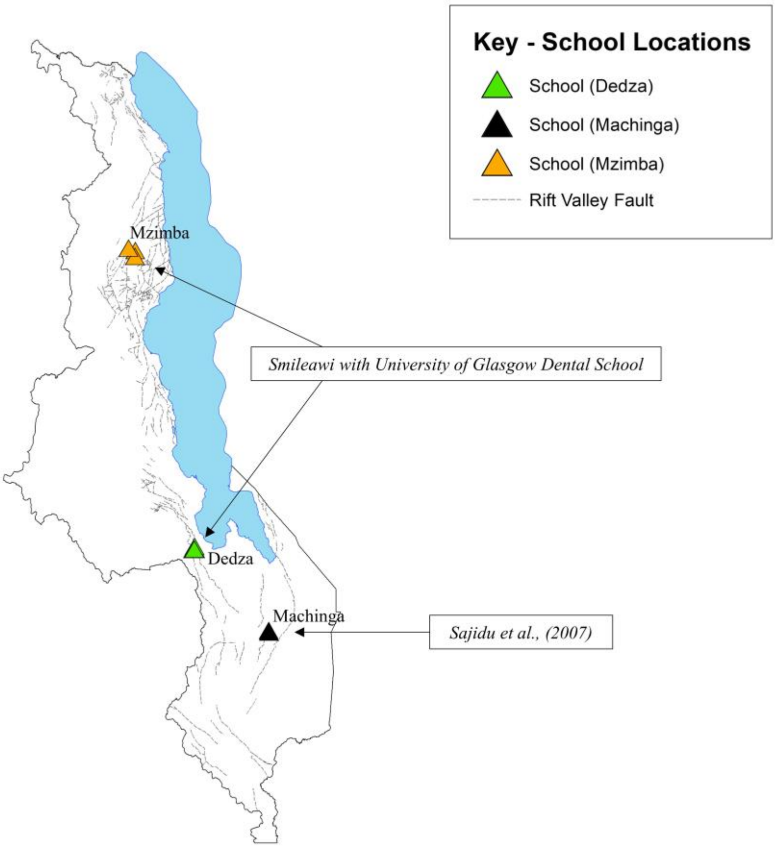


Figure 6. Map of Malawi showing locations of schools sampled during dental surveys for dental fluorosis in children. Four schools in Mzimba District and one school in Dedza District were sampled by our dental team (Smileawi and the University of Glasgow Dental School) in 2019. Two schools in Machinga District were identified from Malawi literature as being endemic severe dental fluorosis areas [10].

Four of the schools visited by the dental team were located outside of the rift valley (Mzimba District) in Malawi's Northern part, one school was located inside the rift valley directly adjacent to a large rift basin margin fault (Dedza District) in the Central part of the country (Figure 6). All school children from schools in Mzimba District exhibited no severe dental fluorosis, with only a small number (1 – 3% of all children examined) showing signs of mild dental fluorosis (Table 3). In contrast, Mua Primary School in Dedza District (the only school visited within the rift valley) had a much higher proportion of children with dental fluorosis (36% of all children examined) and was the only location where there were children with severe dental fluorosis (Figure 7). With severe dental fluorosis present only at that school (n = 50), it is likely that the location is near (or is within walking distance of) at least one water point with consistently elevated fluoride concentrations (i.e., water point hydraulically connected to a hidden hot spring). The small overall proportion of children with severe dental fluorosis (7% of all children examined) suggested that the fluoride source was likely highly localised, with possibly only one or two water points affecting a small geographical area where people use the source for their regular drinking water supply.

Figure 7. Examples of photographic images of school children's anterior teeth from the Smileawi/University of Glasgow dental survey showing increasing severity of dental fluorosis. Severe dental fluorosis was only found at Mua Primary School in Dedza District. Dental fluorosis at mild levels appears as small, white opacities of teeth with minimal concern, however at moderate levels teeth can be mottled and cause aesthetic concern. More severe levels can lead to pitting and staining of enamel with loss of enamel integrity leading to tooth breakdown [31].

Table 3. Number and Percentage of children with dental fluorosis and severe dental fluorosis at each of the schools which were sampled by both dental and groundwater sampling teams. Percentage values for 'all fluorosis' and 'severe fluorosis' reflect the proportion of the total number of pupils examined at each school in each case.

School Name	District	Pupils examined	All Fluorosis		Severe Fluorosis	
			n	%	*n*	%
Ekwaiweni Primary School	Mzimba	701	8	1	0	0
Dunduzu Primary School	Mzimba	614	6	1	0	0
Malivenji Primary School	Mzimba	462	8	2	0	0.
Ekwendeni School for the blind	Mzimba	32	1	3	0	0
Mua Primary School	Dedza	679	243	36	50	7

3.4 Groundwater sampling at locations identified by dental data

School boreholes are used for drinking water supply at each of the schools sampled. Village boreholes are used for domestic drinking water supply. Two school boreholes from Machinga District and one village borehole from Dedza District (all three locations inside the rift valley) (Figure 6), plotted firmly within all four geochemical proxy indicators for hot spring activity and contained the highest fluoride concentrations of all locations (Figure 8). The remaining nine borehole samples from Dedza District (Mua Primary School and surrounding village boreholes) did not plot within all four proxy indicators. Eight samples plotted within proxy indicators for Ca^{2+}, Na^{+}, and Mg^{2+}, but not for F^{-}; one which plotted very close to the F^{-} proxy indicator (1.88 mg/L), therefore, may represent a possible hidden hot spring sample which has been diluted. One sample did not plot within any proxy indicator. All except one sample from Dedza contained fluoride concentrations well below the WHO guideline standard of 1.5 mg/L (Figure 8). Two samples from Mzimba District plotted within all geochemical proxy indicators for hot spring activity except fluoride, with an upper concentration of only 0.92 mg/L F^{-} (Figure 8) which is well within the WHO guideline standard. The remaining sample from Mzimba District plotted out with all proxy indicators. As stated previously, only samples which match all four geochemical proxy indicators were considered as hidden hot spring locations, therefore only the Machinga District locations (Mtubwi and Liwonde L.E.A. school boreholes) and one Dedza District location (village borehole within 1.25 km of Mua Primary School) were considered as such using basic geochemical proxy indicators.

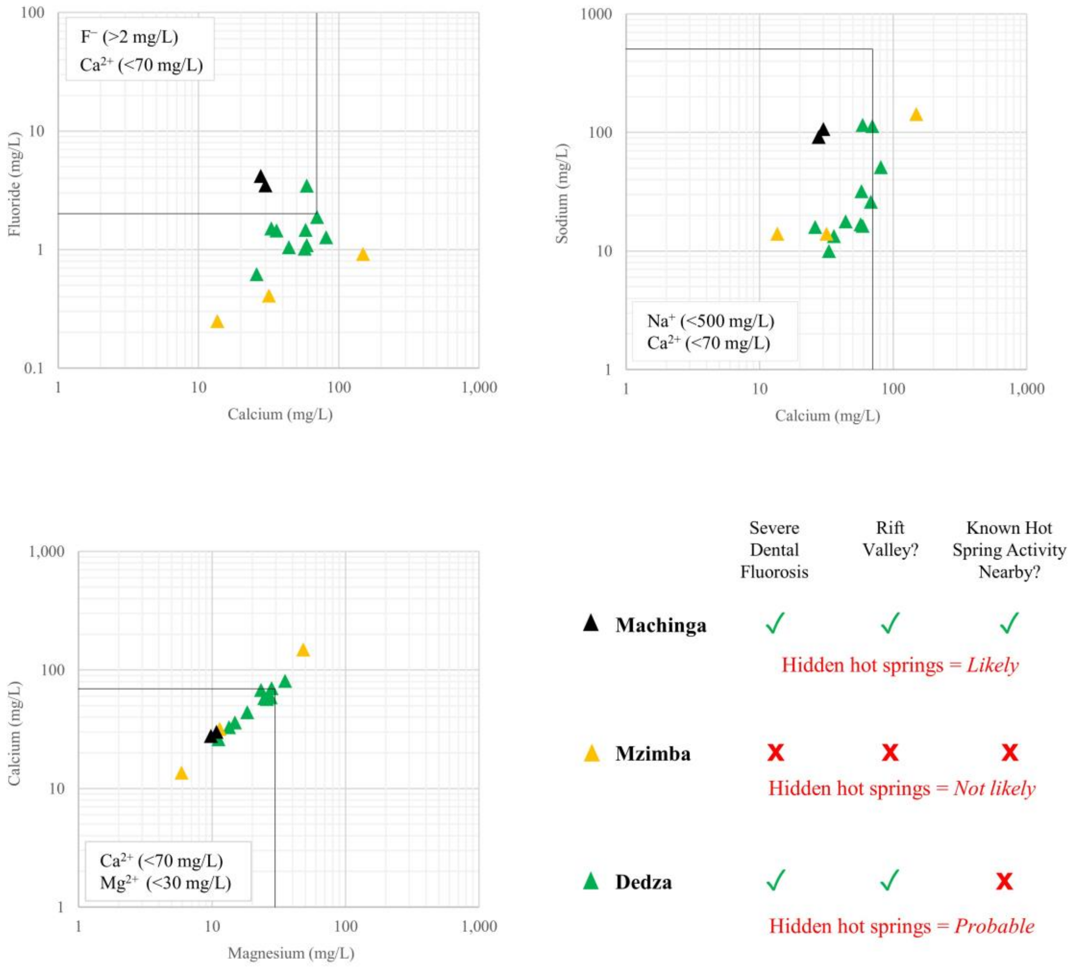


Figure 8. Geochemical data from school and village boreholes at Mzimba and Dedza, and those schools identified in Malawi literature as endemic fluorosis areas in Machinga District [10]. Black lines indicate geochemical proxy indicators for hot spring activity identified from the model data (Figure 4). *lower right*: Additional proxy indicators for hot spring activity (Table 1) for each area, with an overall prediction for hidden hot spring occurrence at each location.

A more detailed geochemical analysis of the school and village samples was performed via a modified Piper plot (Figure 9) where chloride was replaced by fluoride (×10). As expected, hidden hot spring samples identified by dental, geological, and basic geochemical proxy indicators plot as a mixing between (model) hydrothermal and shallow groundwater endmembers. Hidden hot springs represent hydrothermal water diluted by shallow groundwater at the sediment base which is reflected clearly in the Piper plot. Basic geochemical proxy indicators in the previous section identified one possible hidden hot spring sample which matched all proxy indicators except fluoride (although was close at 1.88 mg/L). That sample plotted within the hidden hot springs cluster on the Piper plot (Figure 9), indicating that basic geochemical proxy indicators were 75% effective at identifying hidden hot springs from those data. However, the borehole is located less than 40 m from the Dedza hidden hot spring identified by basic geochemical proxy indicators and is potentially abstracting groundwater from the same hidden hot spring (albeit more diluted). The sample does, however, reflect a hidden hot spring geochemical profile on the Piper plot so was thus included as a fourth hidden hot spring from those data.

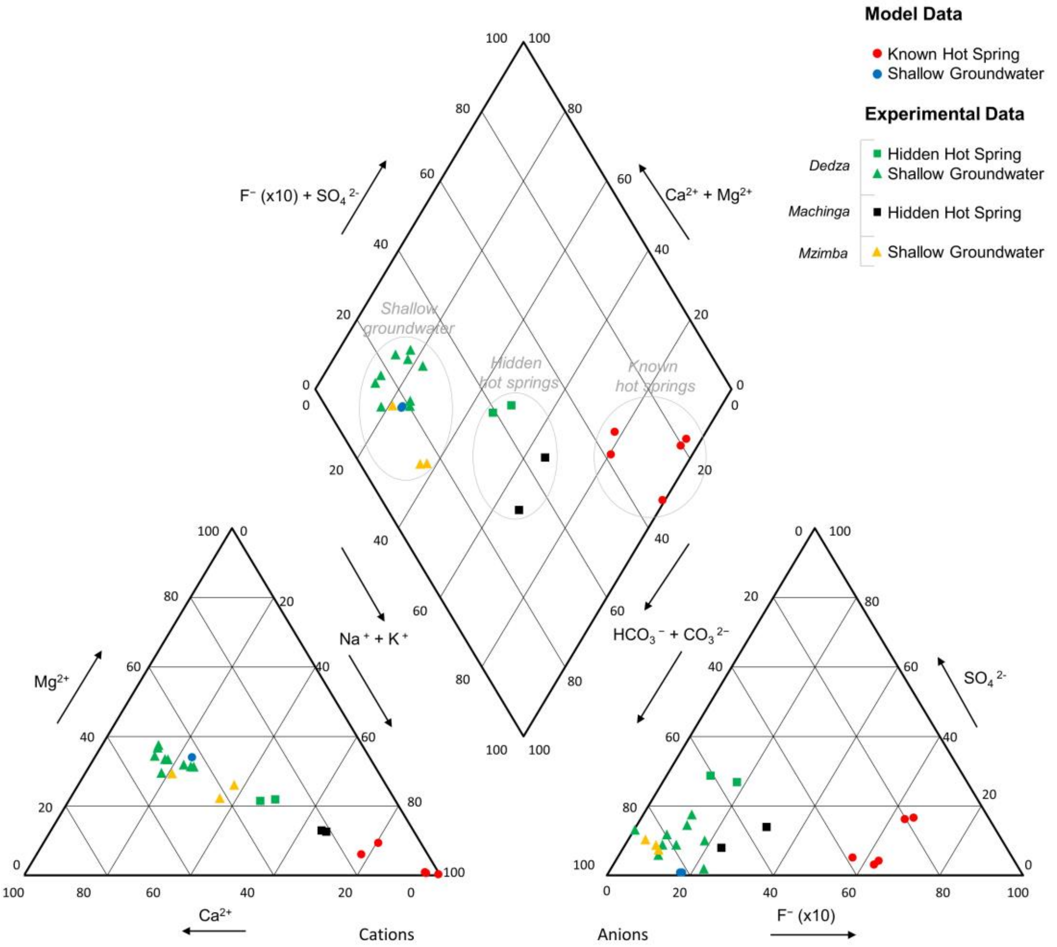


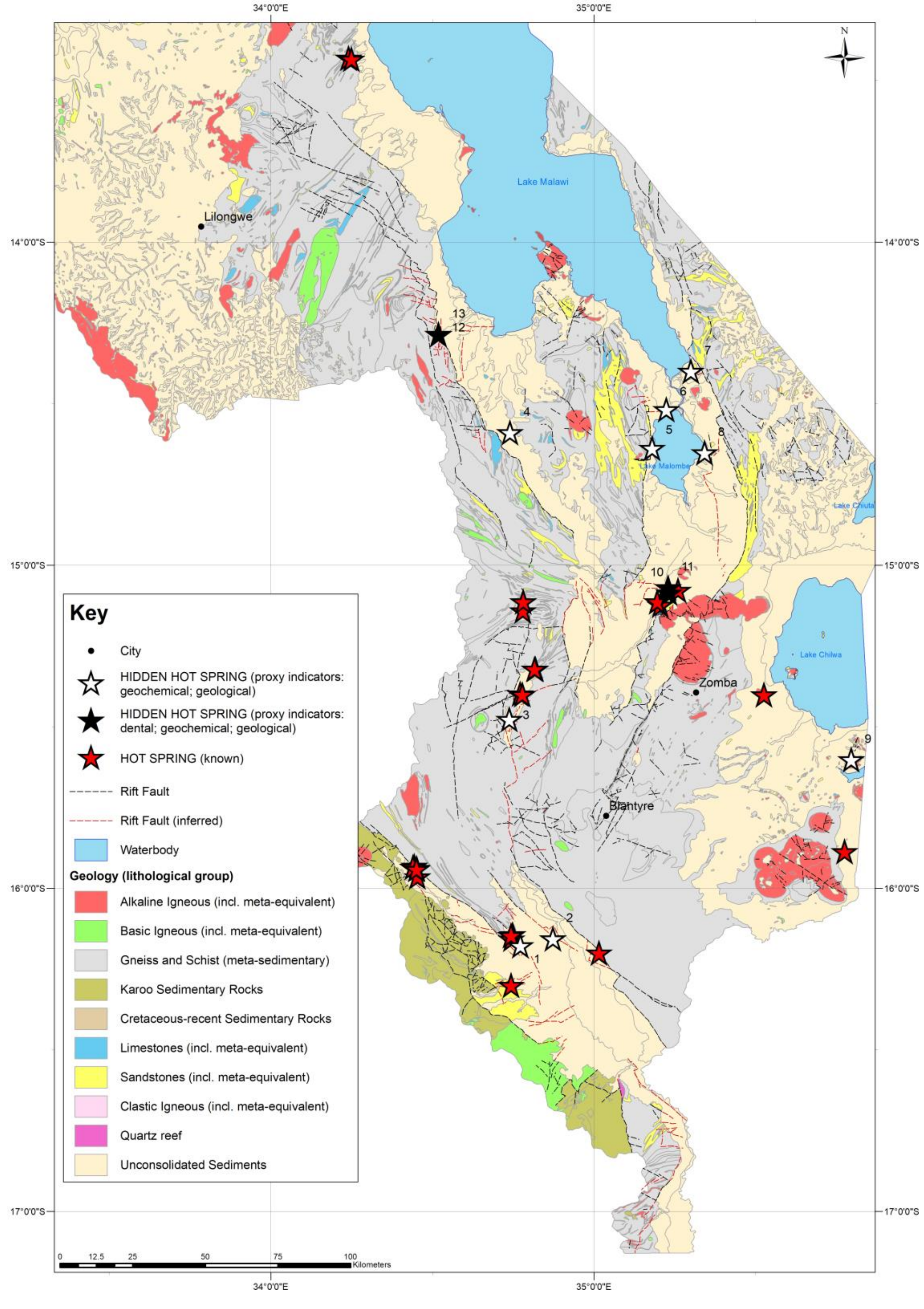
Figure 9. Piper plot displaying model data from endmember hot springs with complete hydrochemical profiles (*n* = 5) [23], non-hydrothermal shallow groundwater with complete hydrochemical profiles (*n* = 2) [26], and experimental data from Machinga, Dedza and Mzimba collected for this study.

Schools within Mzimba District (our control group) do not occur within the rift valley, are at least 30 km from the nearest fault, have no known hot spring activity nearby, and did not show severe dental fluorosis in any of the children at the schools visited, so it was hypothesised that hidden hot springs at those locations were not likely. Groundwater sampling at those school boreholes confirmed the hypothesis; none of the samples matched all four geochemical proxy indicators for hot spring activity (Figure 8). School locations in Machinga District are located within the rift valley, do have known hot spring activity nearby and a high ratio of severe dental fluorosis in school children was reported [10], so hidden hot spring activity was hypothesised to be likely at that location. Sampling of the school boreholes confirmed that hypothesis: both school borehole groundwater samples matched all four geochemical proxy indicators for hot spring activity (Figure 8). The location of Mua Primary School within Dedza District does not have any known hot spring activity nearby, however the location is within the rift valley (directly proximal to a large active rift fault) and displayed increased incidence of medically confirmed severe dental fluorosis in school children (identified by our dental team). It was thus hypothesised that hidden hot spring activity was probable at that location. Groundwater sampling of the school borehole did not confirm that hypothesis; the groundwater sampled matched three geochemical proxy indicators but displayed a fluoride concentration of only 0.4 mg/L, and therefore did not suggest a hidden hot spring.

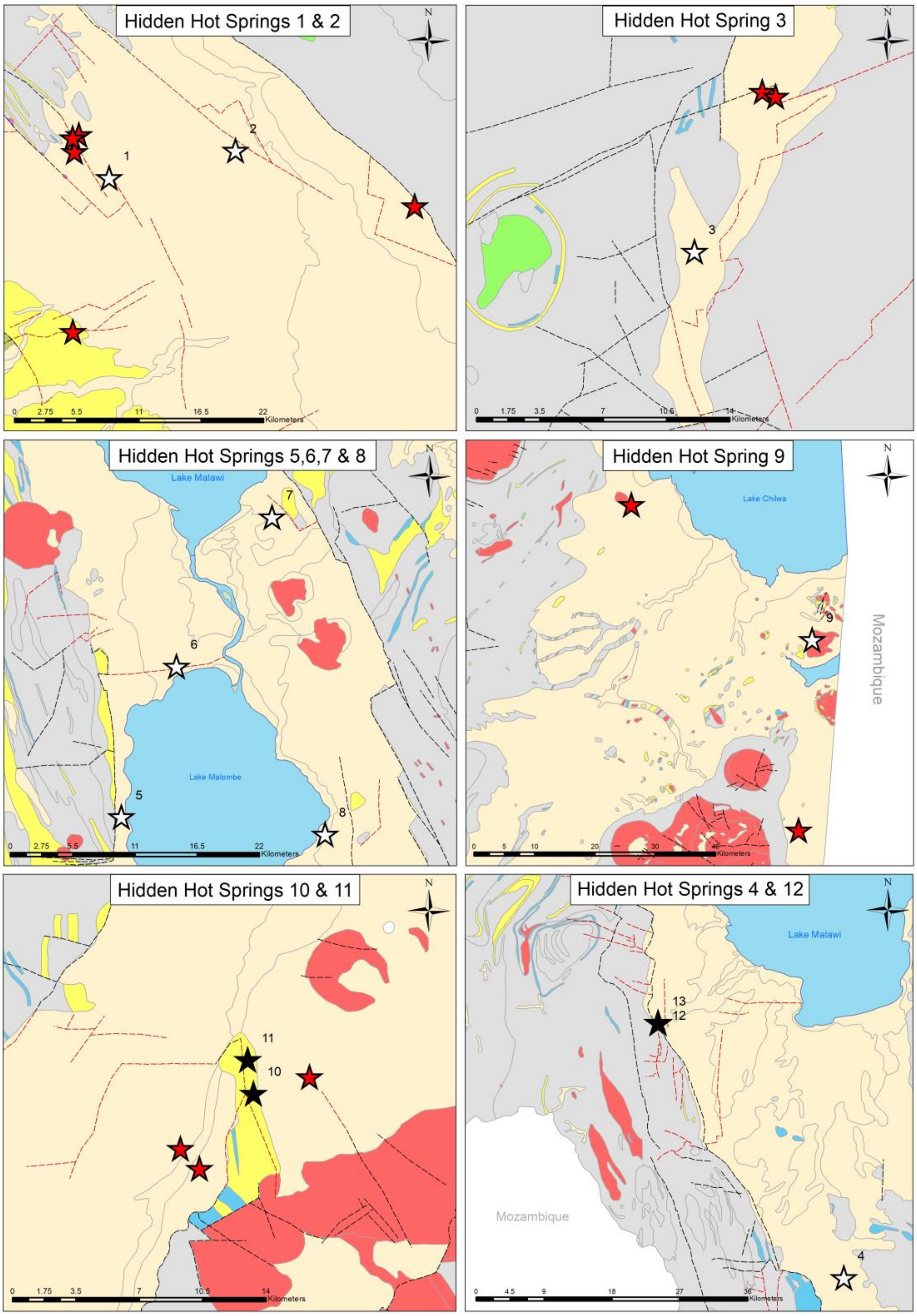
Lack of confirmation from groundwater sampling at Mua Primary School in Dedza District triggered a second round of groundwater sampling to widen the search radius and identify the source of groundwater causing severe dental fluorosis observed at the school. The rift valley location and the high incidence of severe dental fluorosis suggested a nearby borehole with groundwater containing consistent elevated fluoride concentration, likely well above 1.5 mg/L (due to the severity of dental fluorosis observed in the children at the school). The small overall proportion of children with severe dental fluorosis at the school (7%) (Table 3) suggested a highly localised source of groundwater fluoride. It was reasonably hypothesised that sampling of groundwater from those boreholes and wells within 1.25 km of the school (1.25 km radius was estimated based on the halfway distance to the next nearest school, assuming all children walk to school in rural Malawi) would yield at least one location with a groundwater geochemical signature identified to be indicative of hot springs. A hidden hot spring, discharging at the sediment base and mixing with shallow groundwater was therefore probable within that radius. The second groundwater sampling round confirmed the hypothesis: from 10 groundwater samples, one collected from a village borehole matched all four geochemical proxy indicators for hot spring activity and displayed a fluoride concentration of 3.46 mg/L (Figure 8).

3.5 Data synthesis and Hidden Hot Spring Prediction

Results were collated to develop a hidden hot spring vulnerability prediction map of the southern part of Malawi (Figure 10a). Our analysis of severe dental fluorosis data resulted in an additional four hidden hot spring locations being added to the nine already identified from geochemical data. All four hidden hot springs from Machinga and Dedza Districts, originally identified by dental data and subsequently confirmed by geochemical data, were added as point source hidden hot spring locations and were numbered 10, 11, 12 and 13. (Figure 10).


34°0'0"E
35°0'0"E
N
Lake Malawi
Lilongwe
14°0'0"S
13
12
7
6
4
5
8
Lake Malombe
Lake Chiuta
15°0'0"S
10
11
Lake Chilwa
Zomba
3
9
Blantyre
16°0'0"S
2
1
17°0'0"S
Key
City
HIDDEN HOT SPRING (proxy indicators: geochemical; geological)
HIDDEN HOT SPRING (proxy indicators: dental; geochemical; geological)
HOT SPRING (known)
Rift Fault
Rift Fault (inferred)
Waterbody
Geology (lithological group)
Alkaline Igneous (incl. meta-equivalent)
Basic Igneous (incl. meta-equivalent)
Gneiss and Schist (meta-sedimentary)
Karoo Sedimentary Rocks
Cretaceous-recent Sedimentary Rocks
Limestones (incl. meta-equivalent)
Sandstones (incl. meta-equivalent)
Clastic Igneous (incl. meta-equivalent)
Quartz reef
Unconsolidated Sediments
0
12.5
25
50
75
100
Kilometers

(a)



(b)

Figure 10. (**a**) Hidden hot spring vulnerability prediction map of the southern part of Malawi. Data are plotted onto regional geology to provide geological context to hidden hot spring locations. Hidden hot springs identified from geochemical data only, and those identified from dental data which were subsequently confirmed by geochemical proxy indicators, are displayed

separately. (**b**) Local-scale geological maps showing hidden hot spring locations from (**a**), scaled to provide more detail on geology, known hot spring locations and rift valley faults (observed and inferred).

Hidden hot springs 1 and 2 are located within the rift valley in an area with five known hot springs and numerous active rift faults. Hidden hot spring activity is therefore likely at that location. Hidden hot spring 1 occurs within basin sediments along a truncated fault which hosts known hydrothermal activity in the form of three hot springs (Figure 10). That particular location was the most likely candidate for a hidden hot spring due to its close proximity to both the fault and nearby known hot springs. Hidden hot spring 2 was located in the same rift basin sediments as 1 (Lower Shire Basin) immediately adjacent to a large rift fault (Figure 10). Whilst there were no known hot springs along that inferred rift basin normal fault, it was reasonable to assume that there may be hydrothermal discharge hidden beneath basin sediments, evidenced by known hot spring occurrence in the same area. The occurrence of a hidden hot spring (identified from geochemical data) along the same fault provides additional supporting evidence for that hypothesis. Basin sediments are deepest near the northwest-southeast-trending basin margin fault so hydrothermal discharge along faults which are not exposed at the surface would likely discharge in that manner. The known hot spring east of hidden hot spring 2 discharges along the basin margin fault (which is exposed at the surface) explaining why it occurs at the surface at that location, rather than the sediment base.

Hidden hot spring 3 displays a similar situation to 2, where there are known hot springs in the same (much smaller) basin directly related to active faults (Figure 10). Faulting is more complex in that area; the basin which hosts the hot springs and hidden hot spring is a mini fault-controlled rift basin within the larger Malawi Rift basin on its western flank (Figure 10). Proximity to active faults and known hot springs makes hidden hot spring 3 a likely candidate for hydrothermal discharge under those sediments and it is likely that additional water points located within that smaller basin would yield groundwater geochemical profiles indicative of hot springs, including elevated fluoride.

Hidden hot springs 5,6,7 & 8 are located on or immediately adjacent to faults within the rift valley between the eastern basin margin fault and an intra-rift graben to the west (Figure 10). The area around Lake Malombe and the southern extent of Lake Malawi is characterised by an absence of known hot spring activity. It may be that any hot springs in the area are hidden beneath basin sediments mixing with shallow groundwater which would explain the hidden hot spring geochemical profiles for those four water points. Their occurrence along active rift faults (inferred) provides supporting evidence for hidden hot springs at those locations. The fact that faults at those locations had to be inferred due to being buried beneath rift basin sediments supports the hypothesis that the hot springs may also be hidden, discharging at the sediment base.

Hidden hot spring 9 is located adjacent to a CAP intrusion (Figure 10). Two other hot springs in that area occur adjacent to CAP intrusions in the same manner, allowing us to reasonably assume that the same process for hydrothermal discharge for those known hot springs is also responsible for the hidden hot spring in the same basin. Due to an absence of faults at this off-rift location the likely vertical transport mechanism for hydrothermal water is a country rock-intrusion lithological boundary in each case (Figure 2). Historical post-emplacement hydrothermal activity is evidenced by fluorite-apatite mineral veins associated with carbonatite cores in the region [32] indicating that there are additional fluid flow conduits (fractures) internally within the CAP intrusions which extend deep enough for hydrothermal fluid to exploit. Residual (decaying) Cretaceous-age heat from emplacement of the CAP intrusions [33] has been suggested as an additional source of hydrothermal heat in the region [17] indicating that hydrothermal activity is as likely within that ‘off-rift’ basin where the CAP intrusions occur, as it is within the rift valley.

Hidden hot springs 10 and 11 represent locations identified initially as possible hidden hot spring locations from severe dental fluorosis incidence data as a proxy indicator, which were later corroborated by geochemical proxy indicators from groundwater quality data collected to support dental data and thus classified as hidden hot springs. They were previously identified as endemic severe dental fluorosis areas using severe dental fluorosis incidence (non-medical observations) with observed elevated groundwater fluoride concentrations from borehole samples. Further study was recommended to determine the geological cause of elevated fluoride [10] which we have since achieved within our study. Sampling groundwater from the school boreholes for complete geochemical profiles (absent from literature) and subsequent cross-checking with our geochemical proxy indicators allowed us to reasonably hypothesise that hidden hot springs, discharging at the sediment base and mixing with shallow groundwater, were the most likely cause of observed elevated groundwater fluoride at those locations, thus explaining the geological cause of locally endemic severe dental fluorosis. Proximity to buried rift valley faults and three known hot springs further supported that hypothesis. The hydrothermal conduit which feeds the hidden hot springs is most likely a fault located ≈400 m west of hidden hot springs 10 and 11 (Figure 10b). It has been shown previously that hot springs discharging beneath sediments (similar to our hidden hot springs) contaminate shallow groundwater with elevated fluoride to a radial extent of 1 km [2]. Fluoride concentration data for the area around hidden hot springs 10 and 11 collected by [10] show elevated fluoride concentrations occurring over an area of ≈16 km^2. Either there are multiple hidden hot springs beneath those sediments which are yet to be discovered, or radial hot spring contamination is more extensive in the aquifer, contaminating shallow groundwater over a wider area. Additional groundwater sampling for complete geochemical profiles from boreholes is recommended in the areas surrounding the schools to determine the extent of fluoride contamination from hidden hot springs locally. Hydrogeological investigations to determine hydraulic conductivity, transmissivity and flow direction within the unconsolidated aquifer would further support the development of an integrated conceptual model which may better describe hidden hot spring behaviour. Replacement water supplies are recommended in the interim for hidden hot springs 10 and 11 (school boreholes) as they are used daily by school children for drinking purposes and present an immediate oral health risk.

Hidden hot springs 4, 12 and 13 are located within unconsolidated sediments proximal to an active rift margin fault (hypothesised conduit for hydrothermal groundwater) on the rift valley side (Figure 10). That location makes them prime candidates for hot spring activity, particularly hidden hot springs 12 and 13 which are located directly proximal to the fault (even though there is no known hot spring activity nearby). Sediments are deepest at the basin margin, so it is likely that any hot spring activity along that fault may be buried. Furthermore, hydrothermal heat source along that segment of the Malawi Rift Valley may be depleted relative to locations further south due to an absence of nearby CAP intrusions which provide additional heat source for hydrothermal activity where they occur [17]. A depleted heat source may explain the observed absence of known hot spring activity along that section of the rift. There may be additional faulting beneath sediments at those locations which are not visible at the surface and therefore could not be inferred. Groundwater from hidden hot springs 12 and 13 are delivered via 60 m boreholes fitted with Afridev handpumps. The boreholes are public supply water points and serve around 1000 people for their daily domestic supply. The water points pose an immediate severe dental fluorosis risk and therefore replacement water supply should be acquired for those who rely upon them.

Overall, this study shows at least thirteen hidden hot springs in the southern part of Malawi currently discharging at the sediment base in the rift basin, mixing with shallow groundwater and contaminating drinking water locally with excess dissolved fluoride. Geochemical proxy indicators can be used to screen incomplete groundwater quality data to locate hidden hot springs in the unconsolidated basin sediments of Malawi's Rift Valley. A Piper plot analysis of model endmember and experimental groundwater data with complete geochemical profiles supported the use of basic geochemical proxy indicators and showed them to be at least 75% effective (i.e., three out of four boreholes) at identifying boreholes connected to hidden hot springs from geochemical data. The remaining borehole is potentially connected to the same hidden hot spring identified at Dedza (Figure 10). If proven, those four boreholes would represent three hidden hot springs which would indicate the method is 100% effective at identifying hidden hot springs. Future analysis of incomplete groundwater data in Malawi should screen geochemical data for proxy indicators of hot spring activity and cross-check with dental data to corroborate. This work has additionally shown that locations with increased incidence of severe dental fluorosis, confirmed by dentists, are simple and useful primary proxy indicators for locating hidden hot spring activity, particularly schools as they represent pupils from a variety of nearby locations. Identification of locations in that manner allows subsequent groundwater sampling efforts investigating the causes of severe dental fluorosis to be targeted. Similarly, dental studies investigating dental fluorosis (mild or severe) can be targeted in areas predicted to have elevated groundwater fluoride levels, such as our previous work predicting generic lithological groundwater fluoride risk zones, site-specific sources of particularly elevated groundwater fluoride (known hot springs) [15], and hidden hot springs identified by this study. Conversely, dental caries preventative interventions may be necessary in areas predicted to have low groundwater fluoride (<0.5 mg/L). The pioneering geoscientist-dentist collaborative efforts have proved to be substantially productive for both disciplines, where data and results significantly enhance the ability for both to target respective sampling work. This work illustrates the substantial benefits of cross-discipline collaborations and project that such efforts will become increasingly important as Malawi works toward achieving Sustainable Development Goal (SDG) targets for drinking water and health within the 2030 deadline.

3.6 Recommendations

This study has shown that the drinking water fluoride standard in Malawi (from boreholes and shallow wells) of 6 mg/L [13] is too high as it is not aligned with observed oral health risks. It is recommended in the first instance that the Malawi fluoride standard is updated to the globally accepted WHO fluoride standard of 1.5

mg/L [12] to mitigate oral health risks posed by hidden hot springs. The update was recommended in our previous work via stepped progression where the standard would reduce initially to 4 mg/L and then to 1.5 mg/L over time [15]. Only two hidden hot springs have fluoride concentrations >4 mg/L and would benefit from the first phase of stepped progression. The remaining 11 would still be considered 'safe' until the final phase of stepped progression which would align their fluoride standard with the WHO. Until the fluoride standard is updated, fluoride-contaminated water points such as hidden hot springs will continue to pose significant health concerns where they are used for drinking purposes as they cannot be decommissioned. Each hidden hot spring represents a borehole supply of untreated groundwater and may provide daily domestic water supply for a large number of people; therefore, the need for replacement water supplies for hidden hot springs is immediate. Hot springs are associated with additional geogenic contaminants harmful to human health such as arsenic [34], so updating drinking water standards to align with geogenic health risks is both essential and urgent in Malawi.

Dental sampling to examine oral health risks is recommended at and immediately surrounding the locations identified as hidden hot springs (1 – 9: Figure 7) for severe dental fluorosis. Those locations were identified solely from groundwater quality data so severe dental fluorosis incidence associated with those water points is probable but remains unknown. It is likely people regularly use those water points for drinking purposes and are particularly vulnerable to the condition due to observed excess fluoride concentrations. This further underpins the need for swift review of the Malawi drinking water fluoride standard [15], followed by decommissioning of the affected water points and acquisition of replacement water supplies where possible.

Investigation of the lateral extent of fluoride contamination of shallow groundwater from hot springs (known or hidden) is recommended for each known hot spring and hidden hot spring location identified by this study. It is likely that contamination extent will vary from source to source, depending on degree of mixing, aquifer porosity/permeability, hydraulic gradient, dilution (with recharging water) and/or discharge rate of hydrothermal groundwater. A geochemical and/or oral health investigation of water points immediately surrounding hot springs and hidden hot springs may identify additional groundwater fluoride contamination sources which pose oral health risks.

PHREEQ geochemical modelling of groundwater evolution within Malawi's Rift Valley is recommended to better understand mixing behaviour of hydrothermal groundwater with shallow groundwater in the unconsolidated sediments of the rift basin. A regional groundwater quality data set utilised to model groundwater geochemistry in an area with a hidden hot spring(s), may help to better describe the extent of contamination and the plume behaviour of specific hidden hot springs in the unconsolidated aquifers of Malawi's Rift Valley.

It is recommended that both the Ministry of Health and Population, and the Ministry of Forestry and Natural Resources (responsible for water affairs) in Malawi work more collaboratively so that they each may refine and target national sampling efforts where their interests coincide, specifically updating groundwater standards (for fluoride—a requirement of the SDGs) and oral health (dental fluorosis and dental caries). Working together in this manner will reduce time spent assessing two very different areas of research which we have shown to be intrinsically linked.

4. Conclusions

Hot springs are linked to localised endemic severe dental fluorosis due to particularly elevated fluoride concentrations from hydrothermal groundwater contaminating rural drinking water supplies. We coin the term 'hidden hot springs' to describe hot springs which do not occur at the surface as springs per se, but rather are buried beneath the unconsolidated sediments of Malawi's rift basin discharging hydrothermal water from depth to shallow groundwater. The buried nature of hidden hot springs presented a key challenge to identify. Archive groundwater data were too incomplete for standard geochemical modelling techniques (a common issue in Malawi), so a creative alternative was developed which synthesised multi-faceted proxy indicators for hot spring activity and used them to predict the locations of possible hidden hot springs in the southern part of Malawi. Basic geochemical proxy indicators (fluoride, sodium, calcium, magnesium) identified to be indicative of Malawi hot springs were used to identify nine hidden hot springs from a regional groundwater quality data set. Incidence of severe dental fluorosis was used to predict an additional three hidden hot springs where the condition was observed in school children. Locations were subsequently corroborated with geochemical proxy indicators from groundwater data collected reactively to support dental data which revealed an additional hidden hot spring.

Overall, thirteen hidden hot springs in Malawi were identified which are contaminating rural groundwater supplies with excess fluoride. A hidden hot spring vulnerability prediction map was developed for the region which is the first of its kind in Malawi. This study has shown that collaboration between geoscientists and dentists (an apparently unlikely combination), working together and sharing data in the same geographical areas, can significantly enhance respective research out-puts due to the linked nature of both disciplines with respect to fluoride and dental fluorosis. Future geoscientist groundwater sampling for fluoride prediction can be targeted using dental data indicating severe dental fluorosis locations. Dentists on the other hand can better recognise local geological control over observed community oral health and studies investigating fluorosis or dental caries can be targeted using our groundwater fluoride prediction methods.

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

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Institutional Review Board Statement: Smileawi/University of Glasgow Dental School Oral Health Survey: The study (Reference P.09/19/2788) was approved by the University of Malawi College of Medicine Research and Ethics Committee (COMREC).

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study. Consent for each child to participate was through a 'negative consent' process. Parents received a letter and were asked to return the letter to the school if they did not want their child to participate.

Data Availability Statement: Data available on request due to restrictions. The data presented in this study are available on request from the corresponding author. The data are not publicly available due to institutional ownership re-strictions.

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

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7.3 Further Analysis

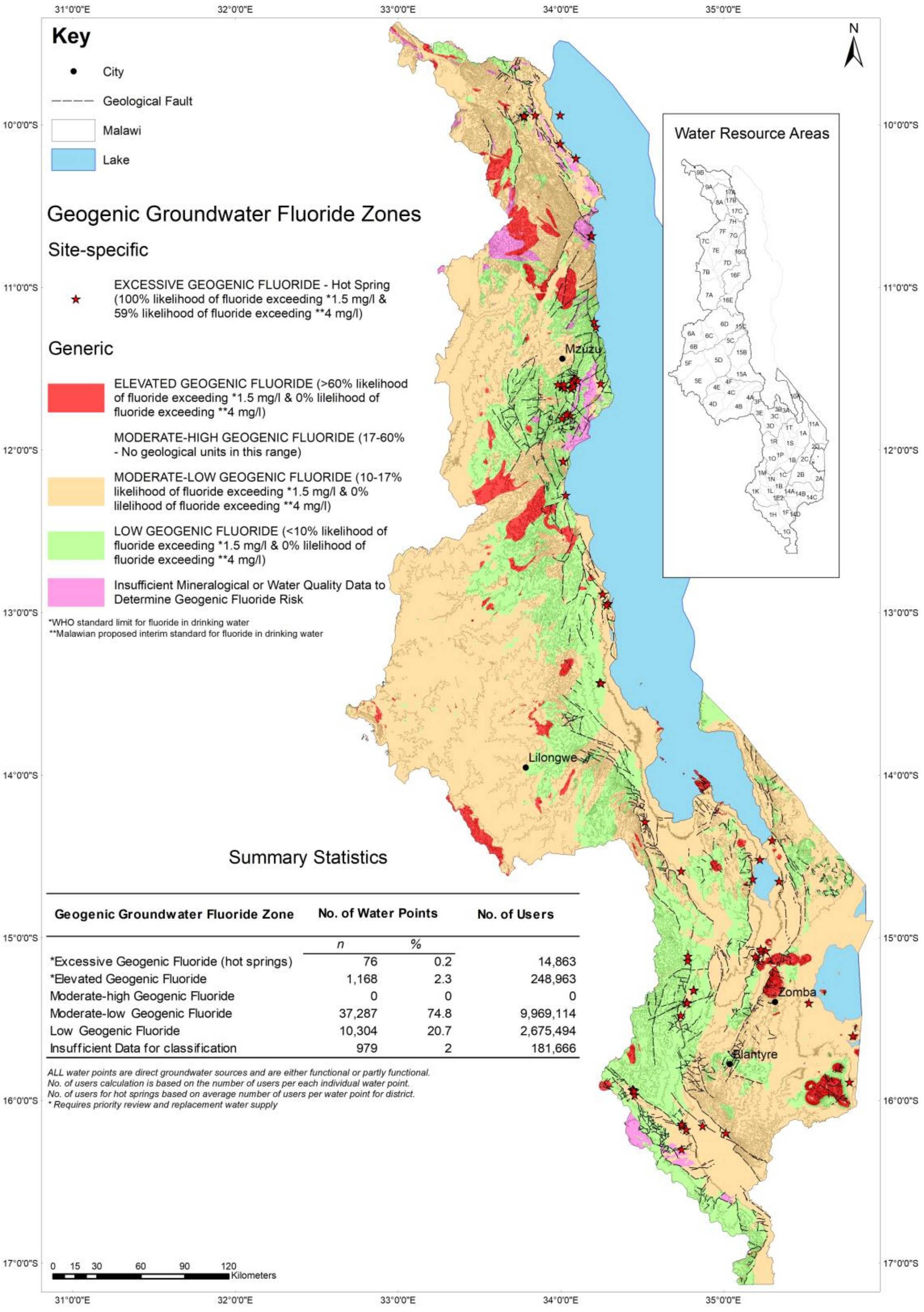
The results of the above paper provided additional groundwater data for inclusion into the prediction method. The same groundwater data set used to identify hidden hot springs was used to develop risk statistics for the groundwater fluoride prediction map in chapter 6. Separation of water points from that data set within the unconsolidated sediments lithology which were associated with hidden hot springs, plus the addition of new data from reactive groundwater sampling following the dental survey resulted in updates to the chapter 6 groundwater fluoride prediction statistics, which refined prediction confidence.

A total of 13 new locations were identified as site-specific ‘excessive geogenic fluoride’ water points and were added onto the groundwater fluoride prediction map developed in chapter 6. Nine water points from unconsolidated sediments were identified as hidden hot springs and were thus removed from that generic category and incorporated into the hot springs risk category. Four new (hidden) hot springs identified by reactive groundwater sampling were also incorporated into the hot springs category, increasing the number of site-specific geogenic sources of groundwater fluoride on the Malawi groundwater fluoride prediction map from 63 to 76 (Figure 7.3.1). Addition of those new locations updated groundwater fluoride prediction statistics (likelihood of encountering groundwater fluoride >4 mg/L from those sources) from 75% to 59%. All new hot spring locations contained groundwater fluoride concentrations >1.5 m/L so the ‘excessive geogenic fluoride’ risk factor for hot springs remains unchanged (Figure 7.3.1). The addition of new hot spring locations resulted in the estimated number of water point users at risk from groundwater fluoride >1.5 mg/L nationally to increase by 3834 from 11,029 to 14,863 (Figure 7.3.1). Estimations for water point users at risk from site-specific (hot spring) sources was based on the average number of people per functional and partly functional water point in each district (Table 7.3.1). Delineation of those hidden hot spring water points from unconsolidated sediments has increased prediction confidence for the 'Excessive Geogenic Fluoride' risk category significantly by identifying new locations with people at risk where previously no risk was predicted (Chapter 6).

Table 7.3.1. Summary statistics for number of water point users at risk from hidden hot spring locations identified. Estimations are based on the average number of users per water point for the district in which it occurs.

Hidden Hot Spring	Malawi District	Malawi WRA	Catchment	Average users per WP (for district)
1	Chikwawa	1	Middle Shire	175
2	Chikwawa	2	Middle Shire	175
3	Neno	1	Middle Shire	276
4	Ntcheu	3	SW Lakeshore	348
5	Mangochi	1	Upper Shire	263
6	Mangochi	1	Upper Shire	263
7	Mangochi	10	SE Lakeshore	263
8	Mangochi	1	Upper Shire	263
9	Phalombe	2	Lake Chilwa	154
10	Machinga	1	Upper Shire	424
11	Machinga	1	Upper Shire	424
12	Dedza	3	SW Lakeshore	403
13	Dedza	3	SW Lakeshore	403
Total				3834

The original groundwater sample size for unconsolidated sediments used to develop the groundwater fluoride prediction map (Chapter 6), was 678. The separation of nine hidden hot springs from that data set reduced the sample size to 669. The addition of 15 new data points from reactive groundwater sampling following the dental survey increased the final sample size to 684. The removal of nine groundwater fluoride concentrations >1.5 mg/L and the subsequent addition of 15 groundwater fluoride concentrations <1.5 mg/L resulted in the (generic) geogenic risk factor for groundwater fluoride (i.e. likelihood of encountering groundwater fluoride >1.5 mg/L) within unconsolidated sediments to reduce from 14% to 12%. The reduction in risk factor illustrates that the hypothesis: 'delineation of water points associated with hidden hot springs in the rift basin will result in increased prediction confidence for unconsolidated sediments' was correct and the prediction method has been refined as a result. Whilst the reduction in risk factor for unconsolidated sediments (within 'Moderate-Low Geogenic Fluoride' risk category) was successful, the new 12% groundwater fluoride risk factor remains within the same 'Moderate-Low Geogenic Fluoride' risk classification range of 10-17%, meaning that risk statistics for number of water points and water point users at risk from groundwater fluoride >1.5 mg/L within 'Moderate-Low Geogenic Fluoride' zones remain the same (Figure 7.3.1).



Summary Statistics

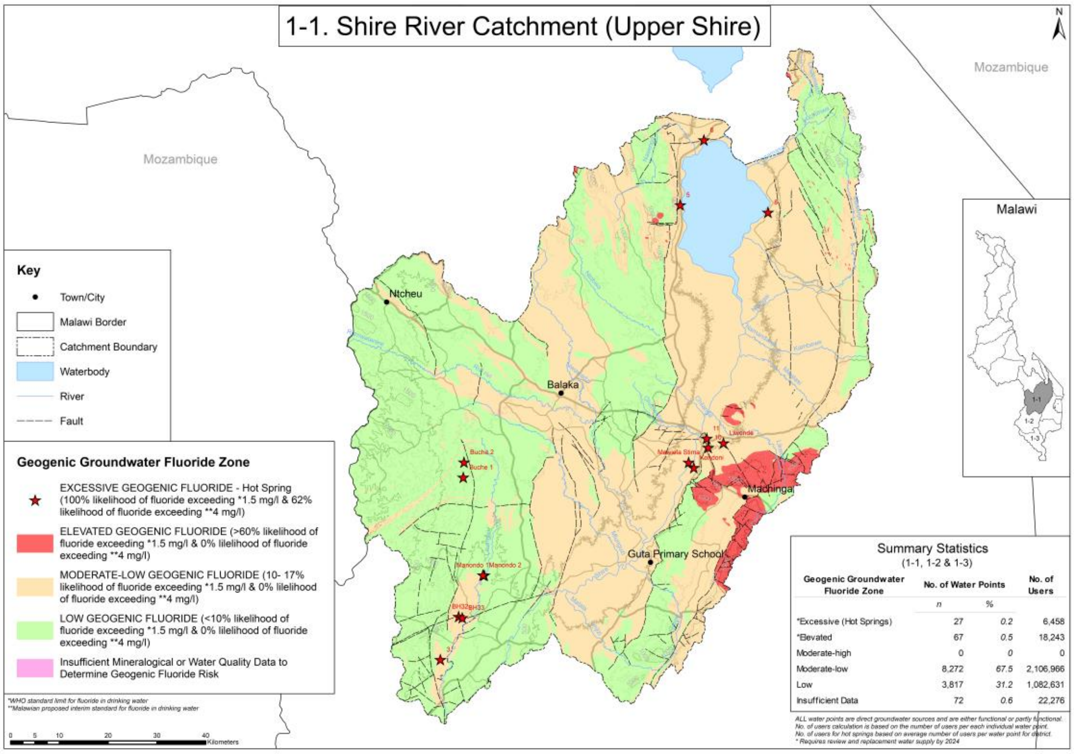
Geogenic Groundwater Fluoride Zone	No. of Water Points		No. of Users
	n	%	
*Excessive Geogenic Fluoride (hot springs)	76	0.2	14,863
*Elevated Geogenic Fluoride	1,168	2.3	248,963
Moderate-high Geogenic Fluoride	0	0	0
Moderate-low Geogenic Fluoride	37,287	74.8	9,969,114
Low Geogenic Fluoride	10,304	20.7	2,675,494
Insufficient Data for classification	979	2	181,666

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires priority review and replacement water supply*

Figure 7.3.1. Groundwater fluoride prediction map for Malawi. Map has been updated with data from chapter 7 (paper 4). Updates include - number of hot springs has been increased from 63 to 76 to include hidden hot springs, no. of users at risk from hot springs has increased from 11,029 to 14,863 and hot spring locations have been updated to include hidden hot springs.

Updates to prediction confidence from this chapter resulted in changes not only to the national groundwater fluoride prediction map (Figure 7.3.1), but additionally to six of the WRA (catchment) maps which were included in the supplementary materials of the published paper in chapter 6 (Addison et al., 2020c). Those updates include the addition of all new hot springs (incl. hidden hot springs) as site-specific 'Excessive Geogenic Fluoride' locations, including updated 'water point' and 'water point users at risk' estimations for each WRA. Updated WRA maps are included below (Figure 7.3.2) and comprise:

- WRA 1 – Shire River Basin (large river basin, divided into three separate maps)
    - *1-1 Upper Shire* (a)
    - *1-2 Middle Shire* (b)
    - *1-3 Lower Shire* (c)
- WRA 2 – Lake Chilwa Basin (d)
- WRA 3 – SW Lakeshore Basin (e)
- WRA 10 – SE Lakeshore Basin (f)

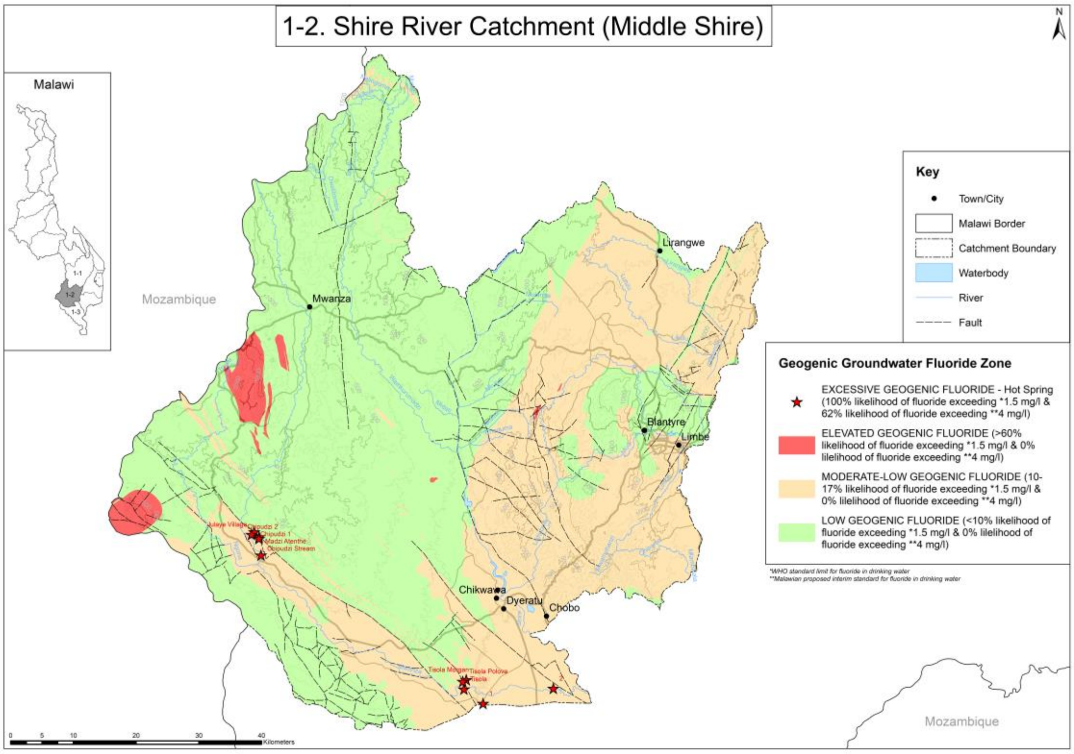


Summary Statistics
(1-1, 1-2 & 1-3)

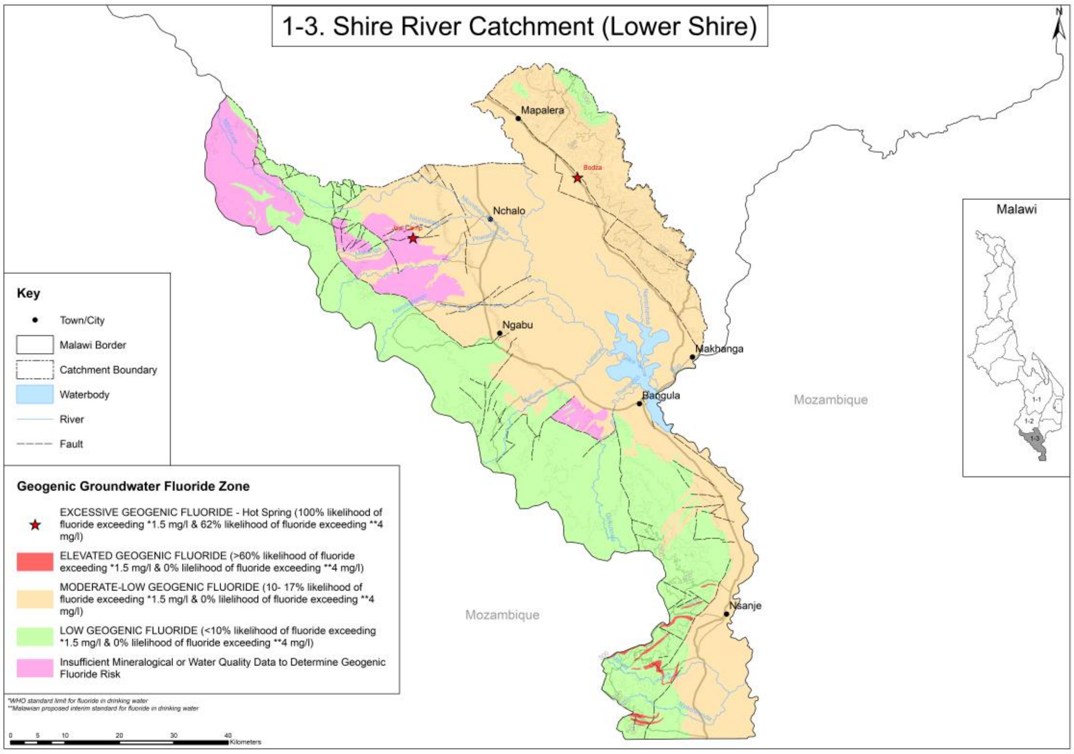
Geogenic Groundwater Fluoride Zone	No. of Water Points		No. of Users
	n	*%*	
*Excessive (Hot Springs)	27	0.2	6,458
*Elevated	67	0.5	18,243
Moderate-high	0	0	0
Moderate-low	8,272	67.5	2,106,966
Low	3,817	31.2	1,082,631
Insufficient Data	72	0.6	22,276

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires review and replacement water supply by 2024*

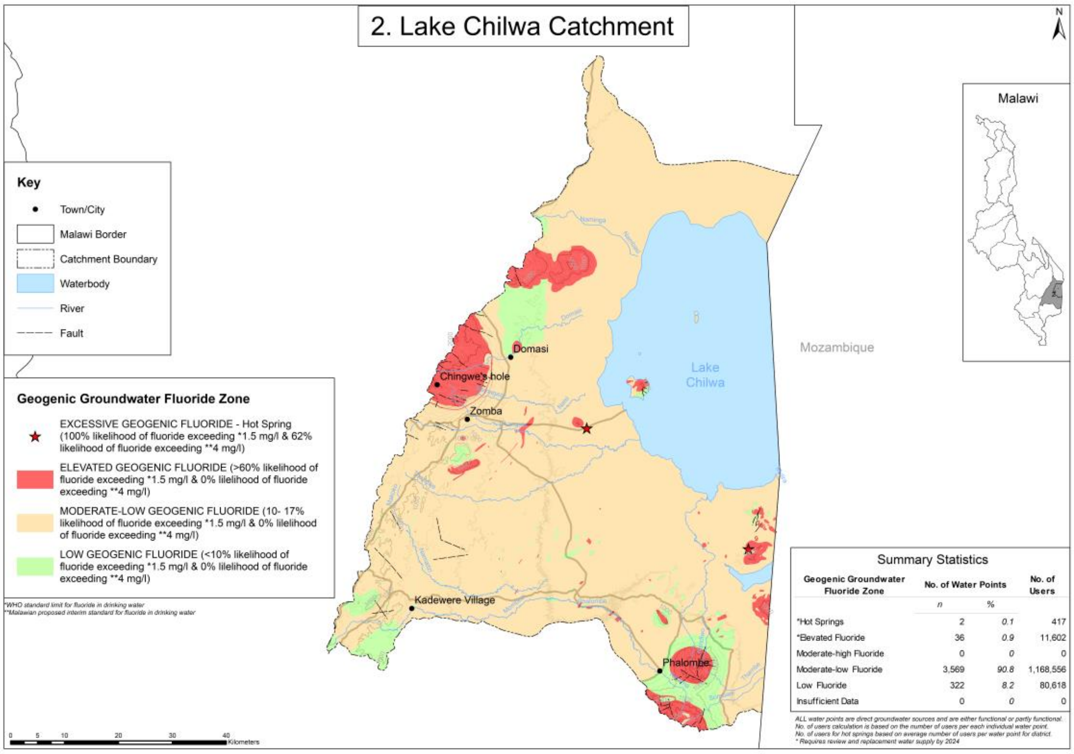
(a)


1-2. Shire River Catchment (Middle Shire)
N
Malawi
1-1
1-2
1-3
Mozambique
Mwanza
Lirangwe
Blantyre
Limbe
Chikwawa
Dyeratu
Chobo
Julaye Village
Chipudzi 2
Chipudzi 1
Madzi Atenthe
Chipudzi Stream
Tisola Morgan
Tisola Polova
Tisola
Key
Town/City
Malawi Border
Catchment Boundary
Waterbody
River
Fault
Geogenic Groundwater Fluoride Zone
EXCESSIVE GEOGENIC FLUORIDE - Hot Spring (100% likelihood of fluoride exceeding *1.5 mg/l & 62% likelihood of fluoride exceeding **4 mg/l)
ELEVATED GEOGENIC FLUORIDE (>60% likelihood of fluoride exceeding *1.5 mg/l & 0% lilelihood of fluoride exceeding **4 mg/l)
MODERATE-LOW GEOGENIC FLUORIDE (10-17% likelihood of fluoride exceeding *1.5 mg/l & 0% lilelihood of fluoride exceeding **4 mg/l)
LOW GEOGENIC FLUORIDE (<10% likelihood of fluoride exceeding *1.5 mg/l & 0% lilelihood of fluoride exceeding **4 mg/l)
*WHO standard limit for fluoride in drinking water
**Malawian proposed interim standard for fluoride in drinking water
0 5 10 20 30 40
Kilometers

(b)


1-3. Shire River Catchment (Lower Shire)
N
Malawi
1-1
1-2
1-3
Mapalera
Bodza
Nchalo
Jali Camp
Ngabu
Makhanga
Bangula
Nsanje
Mozambique
Mozambique
Key
Town/City
Malawi Border
Catchment Boundary
Waterbody
River
Fault
Geogenic Groundwater Fluoride Zone
EXCESSIVE GEOGENIC FLUORIDE - Hot Spring (100% likelihood of fluoride exceeding *1.5 mg/l & 62% likelihood of fluoride exceeding **4 mg/l)
ELEVATED GEOGENIC FLUORIDE (>60% likelihood of fluoride exceeding *1.5 mg/l & 0% lilelihood of fluoride exceeding **4 mg/l)
MODERATE-LOW GEOGENIC FLUORIDE (10- 17% likelihood of fluoride exceeding *1.5 mg/l & 0% lilelihood of fluoride exceeding **4 mg/l)
LOW GEOGENIC FLUORIDE (<10% likelihood of fluoride exceeding *1.5 mg/l & 0% lilelihood of fluoride exceeding **4 mg/l)
Insufficient Mineralogical or Water Quality Data to Determine Geogenic Fluoride Risk
*WHO standard limit for fluoride in drinking water
**Malawian proposed interim standard for fluoride in drinking water
0 5 10 20 30 40
Kilometers

(c)

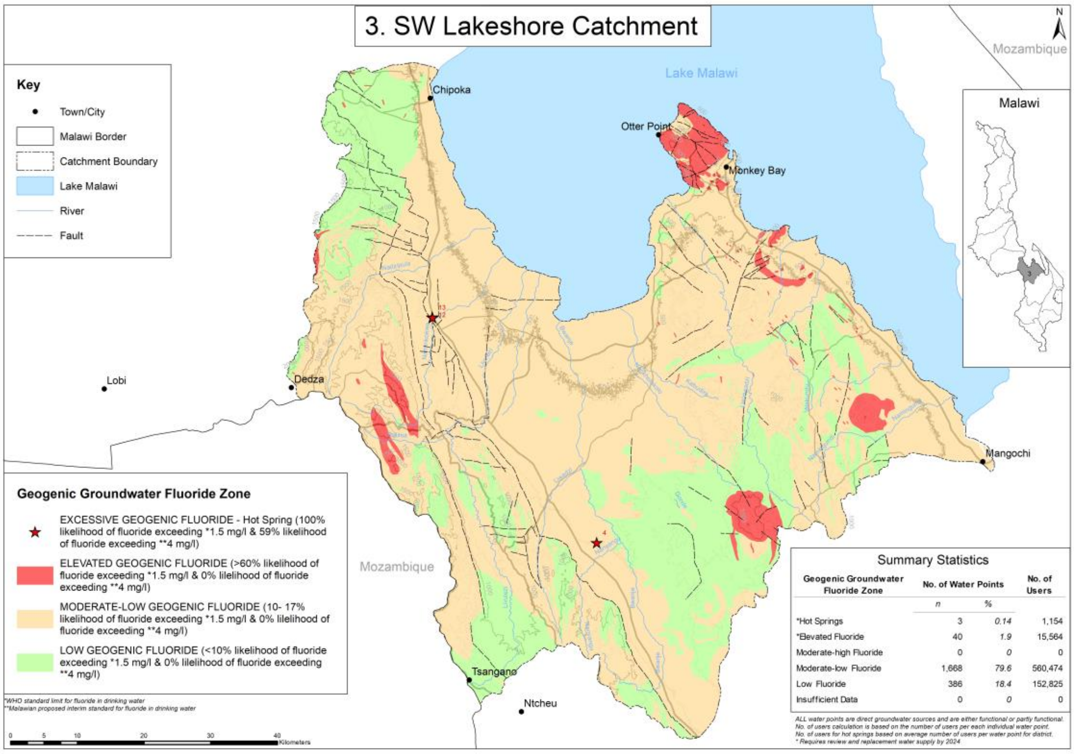


Summary Statistics

Geogenic Groundwater Fluoride Zone	No. of Water Points		No. of Users
	n	*%*	
*Hot Springs	2	*0.1*	417
*Elevated Fluoride	36	*0.9*	11,602
Moderate-high Fluoride	0	*0*	0
Moderate-low Fluoride	3,569	*90.8*	1,168,556
Low Fluoride	322	*8.2*	80,618
Insufficient Data	0	*0*	0

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires review and replacement water supply by 2024*

(d)

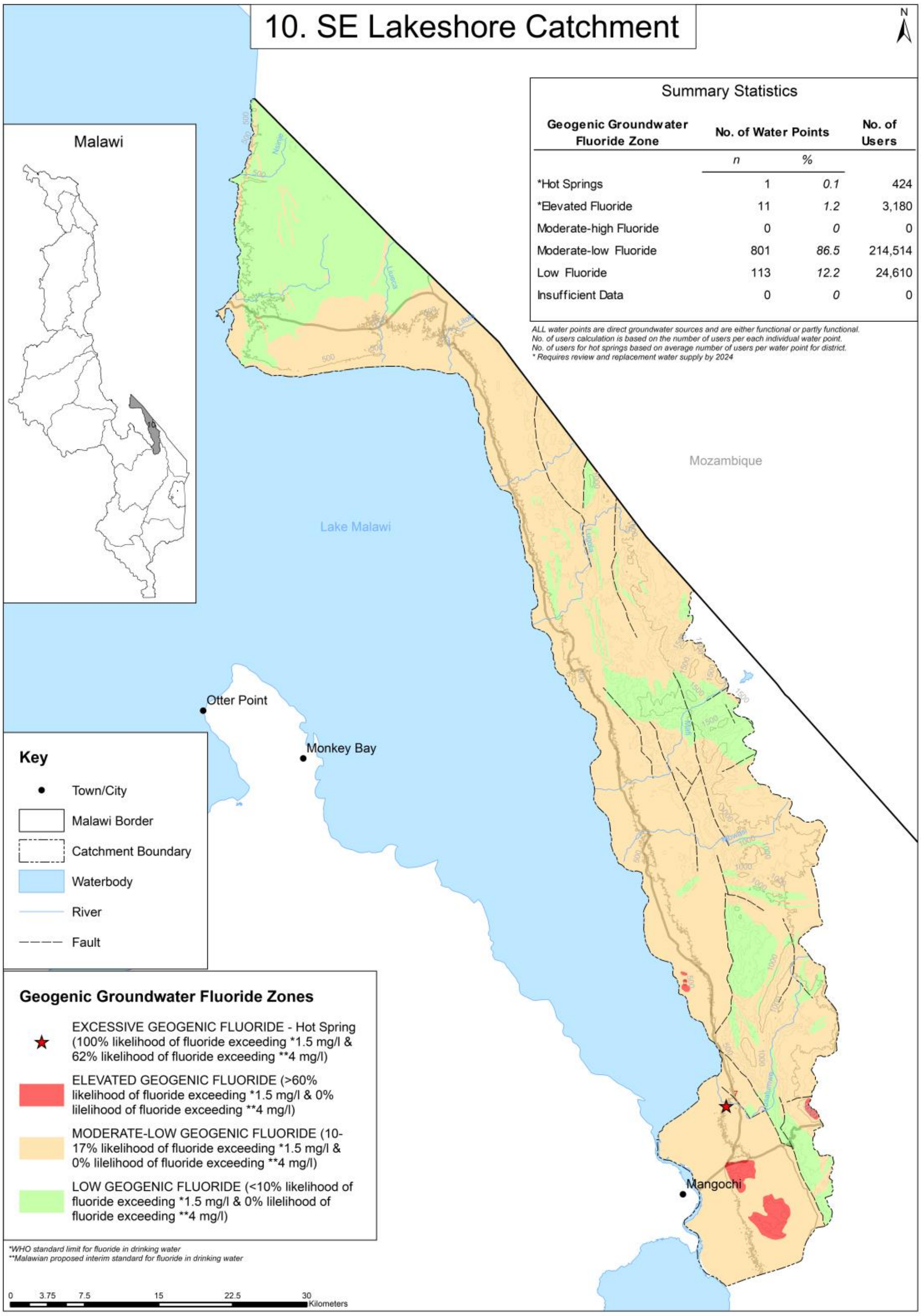


Summary Statistics

Geogenic Groundwater Fluoride Zone	No. of Water Points		No. of Users
	n	*%*	
*Hot Springs	3	*0.14*	1,154
*Elevated Fluoride	40	*1.9*	15,564
Moderate-high Fluoride	0	*0*	0
Moderate-low Fluoride	1,668	*79.6*	560,474
Low Fluoride	386	*18.4*	152,825
Insufficient Data	0	*0*	0

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires review and replacement water supply by 2024*

(e)



Summary Statistics

Geogenic Groundwater Fluoride Zone	No. of Water Points *n*	%	No. of Users
*Hot Springs	1	*0.1*	424
*Elevated Fluoride	11	*1.2*	3,180
Moderate-high Fluoride	0	*0*	0
Moderate-low Fluoride	801	*86.5*	214,514
Low Fluoride	113	*12.2*	24,610
Insufficient Data	0	*0*	0

ALL water points are direct groundwater sources and are either functional or partly functional.
No. of users calculation is based on the number of users per each individual water point.
No. of users for hot springs based on average number of users per water point for district.
** Requires review and replacement water supply by 2024*

(f)

Figure 7.3.2 a-f. Groundwater fluoride prediction maps for Malawi WRAs which were updated as a result of refining the groundwater fluoride prediction method within this chapter. Maps were originally published within the supplementary materials of paper 3 (Chapter 6) prior to update within this chapter.

7.4 Summary and Context

This chapter set out to refine and validate the groundwater fluoride prediction method developed in the previous chapter by addressing RQ. 5: 'Can the groundwater fluoride prediction method developed be refined to delineate hot spring influence from unconsolidated sediments?'. The key area for refinement identified by the previous chapter was anomalous elevated groundwater fluoride concentrations in the unconsolidated sediments of the rift basin. It was hypothesised that some may be associated with hidden hot springs which discharge at the sediment base and contaminate shallow groundwater with elevated groundwater fluoride, interfering with risk statistics for the unconsolidated sediments lithology. RO. 5.1: 'Investigate and identify hidden hot spring locations within unconsolidated sediments using proxy indicators, including a collaboration with dentists to use dental data as additional proxy indicator locations where severe dental fluorosis occurs.' was fulfilled by identification of those water points within the archive groundwater data set associated with hidden hot springs via the development of various proxy indicators. RO. 5.2: 'Separate hidden hot spring-influenced water points from unconsolidated sediments in the risk model and recalculate accurate statistics for both hot springs and unconsolidated sediments.' was fulfilled by separation of hidden hot springs from unconsolidated sediments and recalculation of risk statistics for both hot springs and unconsolidated sediments to provide updates to the National and WRA groundwater fluoride prediction maps developed in the previous chapter. New maps were developed and presented to illustrate the successful refinement of the prediction method.

The Government of Malawi has now acknowledged the need for proactive management of groundwater assets for fluoride as a direct result of continuous dialogue and collaboration with this work. They have released (internally) a public service reforms document which contains various key reform areas which must be addressed by 2026. Policy reform area 14: 'Accreditation of the water quality testing methods for Sustainable Development Goals (SDGs) chemical contaminants in water and sanitation' relates specifically to fluoride and states that 80% of households in fluoride-prone areas will be protected from tooth decay by that deadline. Malawi simply did not possess the knowledge required to propose such a target until the outcomes from this research were made available. They now have the ability to identify every household in fluoride-prone areas and can even prioritise those most at risk. A prediction method with immediate and significant implications such as this one requires ongoing refinement. This chapter presented one example of how the method can be successfully refined to produce more accurate results, further recommendations for refinement (case studies) will be presented in the next chapter.

Each results chapter in this thesis comprised a published journal paper, each containing an individual results and discussion section. The next chapter provides a general discussion of the main aim, research questions (RQ) and research objectives (RO) for the whole thesis.

Chapter 8 DISCUSSION, RECOMMENDATIONS AND CONCLUSIONS

8.1 Introduction

Chapter 1 presented a background to the broad research topic and described the issues being investigated. Chapter 1 additionally outlined the framework of the research in the form of an overall research aim, five research questions to be answered to achieve the aim and 10 specific research objectives designed to answer each of the research questions. Chapter 2 critically discussed published literature related to the research topic and provided context for the research gaps identified and the research questions. Chapter 3 described the various methods involved in the research process. Chapter 4 was an extensive Malawi-specific literature review and data collation designed to gather all published knowledge of fluoride occurrence in Malawi and draw preliminary conclusions on geogenic sources of fluoride. Chapter 5 presented a 'source-extent' investigation of the relationship between lithological sources of fluoride and groundwater, and the development of a geology-based screening method that could be used to predict groundwater vulnerability to geogenic fluoride. Chapter 5 additionally provided a quantification of the direct human health risk from elevated groundwater fluoride in Malawi and a preliminary investigation into fluoride-relevant groundwater policy. Chapter 6 adapted the screening method for predicting groundwater fluoride developed in chapter 5 and scaled it nationally for Malawi. Chapter 6 further investigated fluoride-relevant groundwater policy in Malawi with recommendations to update drinking water standards that are aligned with observed health risks. Chapter 7 refined the prediction method for screening groundwater fluoride in Malawi by delineating anomalous elevated groundwater fluoride associated with hidden hot springs from the unconsolidated sediments of the rift basin. The thesis structure is summarised in Figure 8.1.1.

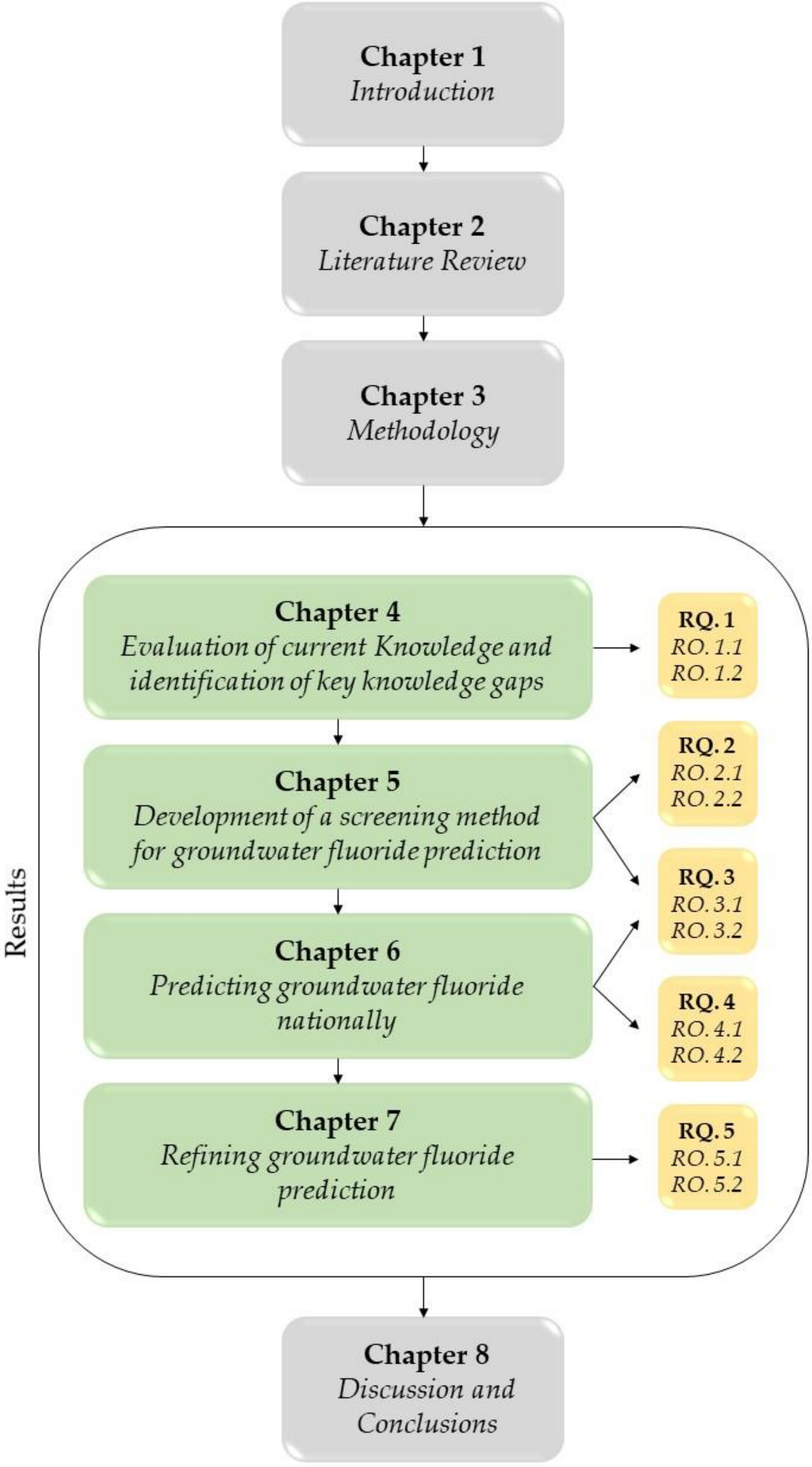


Figure 8.1.1. Flow diagram of the structure of the thesis.

This chapter will discuss the overall results of the research against the aim, research questions and objectives, and investigate the strengths and limitations of the prediction method for groundwater fluoride developed within the thesis. Impact of the research is discussed in detail in each of the papers published, however this chapter presents a discussion of the overall implications of the research.

8.2 Discussion

8.2.1 Restatement of aim and objectives

The aim of this research was to develop a national groundwater fluoride prediction method using limited groundwater data which can be applied nationally in Malawi (and the wider developing world), increasing Malawi's ability to achieve SDG 6.1, provide an evidence-based framework for redefining fluoride policy and assess current water supplies nationally.

Five research questions (RQ) were developed to achieve the overall aim of this research. Those research questions and associated research objectives (RO) are detailed below:

RQ. 1: What is the current understanding/knowledge gaps with respect to groundwater fluoride in Malawi? (Paper 1).

- **RO. 1.1:** Collate all existing data and knowledge pertaining to fluoride occurrence in Malawi via an extensive literature review and data collation.
- **RO. 1.2:** Augment archive data with recent groundwater data and conduct preliminary geological and geochemical analyses to investigate main sources and controls on occurrence in Malawi's groundwater.

RQ. 2: Can groundwater fluoride risk be mapped using geology and limited groundwater data? (Paper 2).

- **RO. 2.1**: Conduct a case study to investigate 'source-extent' relationship between geology and groundwater fluoride.
- **RO. 2.2**: Develop method for predicting and mapping geology-based groundwater fluoride risk using groundwater data.

RQ. 3: What is the direct link between geogenic groundwater fluoride and human health risk in Malawi and is the current fluoride standard for drinking water aligned with health risks? (Papers 2 & 3).

- **RO. 3.1**: Quantify key link between geogenic fluoride and risk to human health via a human health risk assessment case study.
- **RO. 3.2**: Investigate difference between current Malawi and global fluoride standards and advocate policy review via stepped progression for fluoride in drinking water in Malawi.

RQ. 4: Can the groundwater fluoride prediction method developed be scaled nationally to cover all lithologies using existing data? (Paper 3).

- **RO. 4.1**: Create high resolution digitised map of Malawi's geology.
- **RO. 4.2**: Scale methodology for mapping geological fluoride nationally using existing statistical 'fluoride-lithology' correlations where present, and extrapolations where data are absent.

RQ. 5: Can the groundwater fluoride prediction method developed be refined to delineate hot spring influence from unconsolidated sediments? (Paper 4).

- **RO. 5.1**: Investigate and identify hidden hot spring locations within unconsolidated sediments using proxy indicators, including a collaboration with dentists to use dental data as additional proxy indicator locations where severe dental fluorosis occurs.
- **RO. 5.2**: Separate hidden hot spring-influenced water points from unconsolidated sediments in the risk model and recalculate accurate statistics for both hot springs and unconsolidated sediments.

Fulfilment of the research questions and objectives are discussed in the next section.

8.2.2 Fulfilment of research questions and objectives

RQ. 1.

Research question (RQ) 1 was addressed within chapter 4 using Malawi as a case study. Research Objective (RO) 1.1 was fulfilled by conducting a desk study to collate all available data and literature to evaluate current understanding of groundwater fluoride occurrence in the southern periphery of an active continental rift valley. The task was performed to identify key knowledge gaps that would benefit from added knowledge from further study. Key knowledge gaps identified were:

- No national-scale documentation of groundwater fluoride occurrence.
- No available national groundwater data set.

- No comprehensive understanding of geological control on groundwater fluoride from various key geogenic sources.
- No understanding of hydrochemical control on groundwater fluoride occurrence.
- No national understanding of direct health links (fluorosis).
- No prediction method for groundwater vulnerability to geogenic fluoride, either published or within the government.

RO. 1.2 was fulfilled by augmenting collated historical groundwater data sets with recent groundwater data, collected by the CJF from hot springs and rural hand pumped borehole supplies in southern Malawi between 2016 – 2018. Historical and recent groundwater data were analysed in parallel to assess both geological and hydrochemical controls on fluoride occurrence in groundwater samples for southern Malawi. Data were not available for central and northern Malawi. Key findings from the preliminary data analysis were:

- Fluoride correlation with calcium confirmed the presence of fluorite (CaF_2) equilibration processes in most samples.
- Correlation with groundwater temperature and pH confirmed the influence of hydrothermal processes on elevated fluoride in Malawi’s rift valley.
- Diffuse “troublesome” groundwater fluoride concentrations in the range 1.5 – 6 mg/L (between WHO and current Malawi guideline standards for fluoride in drinking water) were shown to be significantly more extensive and associated with shallow rock weathering of lithological sources.

Results showed two main geogenic fluoride sources were responsible for southern Malawi’s highly varied groundwater fluoride occurrence: shallow weathering of aquifer rock (generic lithological source) and, hot springs (site-specific hydrothermal source). Hydrothermal sources were associated with the most elevated fluoride concentrations (>6 mg/L) but were identified to be relatively straightforward to locate, predict and manage due to their site-specific nature. Generic lithological sources were identified as the key management challenge due to the association with extensive diffuse concentrations between the WHO and Malawian guideline standards for fluoride in drinking water (1.5 – 6mg/L).

The key research gap identified by RO 1.1 was the lack of a prediction method for groundwater vulnerability from geogenic fluoride sources. The recent (2017) JMP classification of fluoride as a global priority chemical contaminant means that the ability to predict groundwater vulnerability to geogenic fluoride sources will be key to managing national groundwater assets within the SDG 6 umbrella. The key management challenge identified by RO 1.2 was diffuse groundwater fluoride concentrations associated with shallow rock weathering of lithological sources. The need to predict groundwater vulnerability from geogenic fluoride within generic lithological sources was a trigger for the second research question.

RQ. 2.

Research question 2 was addressed within chapter 5 using TA Mazengera, Malawi as a local-scale case study. The research question was developed based on the key research gap identified by RO 1.1 and the key management challenge identified by RO 1.2. The need to develop a prediction method for groundwater fluoride from generic lithological sources which can be applicable in the developing world (where limited and often sporadic groundwater data are common) was a key driver for RQ. 2.

RO. 2.1 was fulfilled by conducting a 'source-extent' investigation of groundwater fluoride with specific lithological sources. It was identified that lateral extent of fluoride contamination from lithological sources was limited and groundwater geochemical signatures from boreholes, wells, and springs reflected the composition of lithologies within which they occurred. Each specific lithology produced unique groundwater fluoride signatures reflective of lithological composition. Alkaline igneous rocks were linked to particularly elevated groundwater fluoride concentrations relative to other rocks.

RO. 2.2. was fulfilled by spatially analysing groundwater fluoride data with geology in ArcGIS to determine statistical relationships between each lithology and groundwater fluoride concentrations. Augen gneiss in TA Mazengera (alkaline meta-igneous lithology) presented the highest risk of groundwater fluoride and was thus mapped as a generic zone of increased groundwater vulnerability (or risk) of geogenic fluoride. The remaining two lithologies were presented in the same manner. The use of ArcGIS facilitated the development of a geology-based groundwater fluoride risk map of the area, built upon on fluoride-lithology statistics from sporadic groundwater data. For example: >60 % of groundwater samples collected from Augen gneiss displayed a fluoride concentration >1.5 mg/L, therefore the entire augen gneiss lithology was mapped as a zone of >60 % statistical risk of encountering groundwater with fluoride concentrations >1.5 mg/L (i.e., elevated enough to cause dental fluorosis). Calculating risk in this manner allowed an entire lithology (which may contain many hundreds of water points) to be mapped as a zone of statistical risk, based only on 16 initial groundwater samples. Prediction confidence would naturally increase with sample size, however the method allowed large areas (lithologies) to be assigned groundwater fluoride risk factors based on statistical relationships from sporadic experimental data.

RQ. 3.

Research question 3 was addressed in the chapter 5 case study. The direct link to human health risks from consumption of groundwater with elevated fluoride concentrations was quantified via a human health risk assessment. Each borehole sampled for groundwater chemistry was additionally assessed for a non-carcinogenic risk index, also known as a 'hazard quotient' (HQ) value which indicates degree of risk of fluorosis from each water point. Unsurprisingly, the water points carrying the most risk of dental fluorosis from the human health risk assessment coincided with the lithology with the highest statistical risk of groundwater fluoride >1.5 mg/L (alkaline igneous). This was the first time a direct link to dental fluorosis from groundwater fluoride had been quantified for Malawi and was pivotal to advocation of groundwater policy reform for fluoride in drinking water.

RO. 3.2. was fulfilled via a preliminary review of global (WHO) and local (Malawi) fluoride in drinking water policy in chapter 5, followed by a more detailed review in chapter 6. The WHO set a maximum global standard of 1.5 mg/L which is aligned with health risks as concentrations >1.5 mg/L are associated with causing dental fluorosis. Malawi's standard (specifically for raw groundwater supplies) is significantly higher at 6 mg/L. The Malawian standard acknowledges site-specific hydrothermal fluoride as a health risk (groundwater fluoride concentrations >6 mg/L in Malawi are associated with hot springs), however concentrations in the range 1.5 – 6 mg/L are currently assumed to be safe. The results from chapter 5 show that concentrations within that range cause dental fluorosis and mostly reflect generic lithological sources (the most extensive geogenic fluoride source), presenting risk to the greatest number of people nationally. Policy reform was thus advocated, specifically the 6 mg/L standard for raw groundwater in Malawi to align drinking water fluoride policy with observed health risks and bring their standard in line with the WHO.

RQ. 4.

Research question 4 was addressed within chapter 6. Some countries have developed complex geostatistical prediction models for fluoride using extensive national groundwater data sets. Many developing countries do not have access to extensive data sets and instead rely on limited, sporadic, and spatially inconsistent groundwater data making the development of complex risk models problematic. An innovative solution to mapping national groundwater fluoride risk was required where developing countries could make best use of existing data. Chapter 6 represented the first attempt to predict groundwater fluoride nationally for Malawi. The groundwater fluoride prediction method developed in chapter 5 was adapted to cover the entire country. The method was dependent on digital geological data with which to spatially analyse groundwater data (relative to geology), and subsequently develop risk factors based on fluoride-lithology statistics. Digital geological data was unavailable for Malawi so had to be digitised manually. RO. 4.1 was fulfilled by digitising 10, high-resolution scanned 1:250,000-scale geological maps which covered the entire country.

RO. 4.2. was also fulfilled in chapter 6. The method for predicting groundwater fluoride developed in chapter 5 was adapted and scaled to cover all of Malawi. Historical and recent CJF groundwater data were combined to calculate fluoride-lithology statistics for every lithology in the country which had corresponding fluoride concentrations. Groundwater data was extensive for southern Malawi (chapter 4), only local data was available for central Malawi (chapter 5) and none were available for northern Malawi leaving many lithologies across the latter two regions with no corresponding groundwater data from which to calculate fluoride-lithology statistical relationships. Geogenic fluoride risk factors were thus extrapolated for those lithologies using mineralogical composition of each lithology. A risk factor was applied where dominant mineralogy was similar to a lithology which had a calculated fluoride-lithology statistical relationship. For example: three alkaline igneous lithologies possessed calculated fluoride-lithology statistical relationships, each had a similar mineralogy and each presented a similar groundwater fluoride risk classification (>60 % risk of groundwater fluoride >1.5 mg/L), so other alkaline igneous lithologies which had no corresponding groundwater data, but displayed a similar mineralogical composition to those three (where such compositions could be supported by data), were assigned the same fluoride risk factor. Extrapolation in that manner was performed nationally to cover all lithologies where there were reasonable justifications on mineralogy. The result was a high-resolution, geology-based, national groundwater fluoride risk map. Site-specific hydrothermal fluoride sources were displayed as hot spring locations with 100% risk of groundwater fluoride concentrations > 1.5 mg/L. Generic lithological sources were displayed as geology-based zones, each reflecting a predicted risk factor which reflected projected statistical risk of groundwater fluoride >1.5 mg/L. Risk factors developed were as follows:

Excessive Geogenic Fluoride	100 % risk of groundwater fluoride >1.5 mg/L
Elevated Geogenic Fluoride	>60 % risk of groundwater fluoride >1.5 mg/L
Mod-high Geogenic Fluoride	17-60 % risk of groundwater fluoride >1.5 mg/L
Mod-low Geogenic Fluoride	10-17 % risk of groundwater fluoride >1.5 mg/L
Low Geogenic Fluoride	<10 % risk of groundwater fluoride >1.5 mg/L
Insufficient data for classification (unknown risk)	

The method developed in chapter 6 was based on all available groundwater data for Malawi which as discussed was limited, sporadic and spatially inconsistent. The method was successful in creating a prediction method which could be used to effectively screen for groundwater fluoride nationally. The method was designed to be dynamic so that the addition of new data improves prediction accuracy for each lithology. The risk developed map can be continually updated where new groundwater data is acquired, gradually increasing prediction confidence over time. The method will be an invaluable tool for many developing nations working towards achieving SDG 6 targets as only digital geological data and (sporadic) spatially referenced groundwater data (with at least a fluoride concentration) is required.

RQ. 5.

Research question 5 was addressed in chapter 7. Prediction confidence was inconsistent within 'Unconsolidated sediments' due to complexities arising from hydrothermal influence in the sediments of the rift basin. Unconsolidated sediments were associated with moderate-low groundwater fluoride risk (14 %) and represented the only unconsolidated lithology group in Malawi. Numerous particularly elevated groundwater fluoride concentrations therefore appeared anomalous, and it was hypothesised in chapter 6 that they may be linked to hidden hot springs, discharging hydrothermal groundwater at the sediment base of the rift basin along active rift faults. RO. 5.1. was fulfilled by developing multi-faceted proxy indicators for hot springs in Malawi and using them to identify water points within the rift basin's unconsolidated sediments that were predicted to be associated with hidden hydrothermal activity. The objective was achieved by utilising regional archive groundwater data used in chapters 4 and 6, and via a collaborative effort with dental health professionals. Historical data were further augmented by reactive groundwater sampling at locations identified as hidden hot spring locations using dental data. The result was a hidden hot spring vulnerability prediction map for southern Malawi containing 13 locations predicted to be directly connected to hidden hot springs in the rift basin.

RO. 5.2. was fulfilled by updating the prediction method (and map) developed in chapter 6 with results and new data from chapter 7. Nine water points were separated from the generic unconsolidated sediments category and added to the site-specific hydrothermal fluoride category, along with four new (hidden) hot springs sampled by the CJF. Update resulted in increased prediction confidence for 'Excessive Geogenic Fluoride' category which comprised all known hydrothermal fluoride sources. The number of site-specific locations on the risk map increased from 63 to 76 nationally. The risk factor for 'Excessive Geogenic Fluoride' category remained at 100 % risk of groundwater fluoride >1.5 mg/L.

Removal of nine water points from unconsolidated sediments to hydrothermal fluoride, plus the addition of 15 new boreholes sampled reactively by the CJF (in unconsolidated sediments) resulted in update for unconsolidated sediments. Update from chapter 7 resulted in a decrease to the groundwater fluoride risk factor for unconsolidated sediments from 14% to 12% (risk of groundwater fluoride >1.5 mg/L.). The 'Moderate-low Geogenic Fluoride' risk category (which contains unconsolidated sediments) remained unchanged as the overall updated fluoride risk factor for that risk category remained within the same range (i.e., 10 – 17 % risk of groundwater fluoride >1.5 mg/L). If update to unconsolidated sediments (the most extensive lithology within the moderate-low category – chapter 6) had decreased the overall risk factor below 10 %, then the 'Moderate-low Geogenic Fluoride' risk category would have reduced to 'Low Geogenic Fluoride'. That change would have resulted in update to the prediction map where all 'Moderate-low' zones would have switched to 'Low'. Decrease in risk factor for unconsolidated sediments represented increased prediction confidence, demonstrating that prediction accuracy within the method has successfully been refined via delineation of water points influenced by hydrothermal activity, and also by the addition of new data.

8.2.3 Strengths

Widespread groundwater fluoride prediction using limited data and resources

The screening method developed within this research allows groundwater fluoride prediction to be developed at national scales, even in countries where limited access to data and resources abound. The ability to assign statistical groundwater fluoride risk factors to entire lithologies based on sporadic groundwater data is powerful as it allows large areas to be classified where limited or sometimes no groundwater data occur. Digital geological data can be modified and presented to serve as prediction maps for groundwater fluoride. This research used the GIS platform

ArcGIS which can be an expensive subscription, however all analyses performed within this thesis can also be performed in the GIS platform QGIS, which is open source and free to download and use. Countries without access to national digital geological data can use a GIS platform to digitise scanned versions of paper maps as was achieved in this research. The screening method for predicting groundwater fluoride is therefore applicable in countries (particularly developing nations) where access to expensive software and complete groundwater data sets are limited.

Adaptable method

The prediction method is highly adaptable and can be applied at any scale. The method was originally developed at local scale, producing a groundwater fluoride prediction map for a Traditional Authority area in Malawi. The method was then adapted to perform the same function at the national scale. That adaptivity is a powerful tool which can be applied to any location. The ability to continually adapt the method with new data allows for gradual increase in prediction confidence over time. The method was developed for predicting the occurrence of one geogenic contaminant, however it could be adapted to predict any geogenic groundwater contaminant where dissolution of aquifer material is the source, for example: salinity or arsenic.

Targeted investment

The 2017 JMP classification of fluoride as a global contaminant of concern, and one now included in SDG 6 indicators, means that countries globally must review and manage groundwater assets for fluoride if they are to achieve SDG 6 targets. This presents a significant challenge in developing countries where the fiscal burden on the government is greatest and access to funds most limited. Limited access to financial resources means that efforts to manage groundwater assets for fluoride (and providing replacement water supplies where required) without a national solution to predicting it is unrealistic without a means to target investment. The prediction method developed within this research can be easily implemented by governments in developing countries to target investment by screening for groundwater fluoride nationally. Site-specific ‘Excessive Geogenic Fluoride’ water points (hydrothermal fluoride) can be targeted first as they pose the greatest risk to human health and are the most straightforward sources to identify. Warnings can be placed at water points and replacement water supplies acquired. Water points within generic ‘Elevated Geogenic fluoride’ zones can be targeted next, groundwater testing for fluoride can begin within those zones and replacement water supplies acquired where concentrations exceed 1.5 mg/L. A tiered approach to managing groundwater assets in that manner will maximise national investment by prioritising those water points most at risk.

Policy review

The outputs of this research can be used as a tool for a review of drinking water policy in countries where the drinking water standard for fluoride is not aligned with observed health risks. Malawi is currently working towards a reduction of its 6 mg/L standard for fluoride in raw groundwater to the globally accepted WHO standard of 1.5 mg/L via stepped progression (chapter 6). The groundwater fluoride prediction maps (national and catchment) produced in this thesis are currently being utilised by the Malawian Government to both manage groundwater assets for fluoride and as an evidence-based tool for their review of policy. The Ministry of Forestry and Natural Resources (responsible for water – formerly the Ministry of Agriculture, Irrigation and Water Development) have actively engaged with this research since the preliminary results in chapter 4 so that decisions made regarding fluoride policy update are informed with the most up-to-date science available.

8.2.4 Limitations

Limitations arise from decisions made during the research process. Whilst decisions are made to strengthen the method or research outputs, each decision to set new parameters ultimately creates limitations which are important to acknowledge and discuss.

Data

The primary and most obvious limitation of the method is the decision to use sporadic and incomplete data. The accuracy of fluoride-lithology statistical relationships calculated within the method are dependent on the volume of data used for each lithology which is highly variable. The resulting groundwater fluoride risk factors associated with each lithology had highly variable prediction confidence between lithologies. That limitation was highlighted in Chapter 6 where unconsolidated sediments had an initial sample size of 678 while basic igneous rocks had a sample size of only three. Risk factors (% likelihood of encountering groundwater fluoride >1.5 mg/L) based on fluoride-lithology statistical relationships were calculated for each of those lithological categories using the same method, however, prediction confidence was higher for unconsolidated sediments than it was for basic igneous rocks due to the difference in initial sample size. The sporadic nature of the data used was also a limitation. Many lithologies were extrapolated a risk factor for groundwater fluoride due to an absence of corresponding groundwater fluoride data from which to calculate statistical relationships. Whilst effective for covering large areas, that process may have produced inaccurate results for some lithologies. Data limitations are balanced by the method's adaptability where continuous addition new data will gradually increase the accuracy, therefore prediction confidence for each lithology over time as national groundwater testing continues.

Simplicity

The simplicity of the method is one of its greatest strengths as it allows screening for groundwater fluoride at national scales using limited resources within a developing world context. That simplicity may also be a limitation due to the fact that many heterogeneous hydrogeological complexities which may affect the results at different scales and at different locations were not considered. The method was largely based on the results of chapter 5 where relationships between source and extent of groundwater fluoride contamination were investigated. The weathered basement aquifer was chosen as it is the most extensive aquifer type in Malawi and allowed for specific lithologies to be examined with respect to groundwater fluoride concentrations. The weathered saprolite layer of the weathered basement aquifer provided additional insight into the extent of influence exerted by a lithological fluoride source (i.e., how far does fluoride travel in groundwater from source), which was shown to be minimal using experimental data. The weathered basement aquifer type was assumed to represent of the whole country within the method. More complex aquifer systems may produce different results at different scales, for example: a hydrogeological scenario similar to that investigated at TA Mazengera in chapter 5, but with an additional layer of alluvium and steeper topography may transport fluoride from a lithological source over greater distances due to a steeper hydrogeological gradient and higher conductivity and transmissivity values in the unconsolidated layer. That would result in increasing inaccuracy of fluoride-lithology statistical relationships as groundwater fluoride measured from one borehole may be associated with another lithological source some distance away. That limitation is why the method is intended as a preliminary screening tool for predicting groundwater fluoride that is effective at national scale to allow the government to target investment. This method should not replace testing.

8.2.5 Research contribution

This research sought to make several contributions to knowledge with both global and local context. These comprise:

Global Novelty

- A new research approach for predicting groundwater vulnerability to geogenic fluoride was developed which is applicable in lesser developed countries where limited hydrochemical data prevents the development of comprehensive risk models.
- A screening method for groundwater fluoride prediction was developed which can be easily applied at national scale in any country.
- A new understanding of groundwater fluoride occurrence has been generated for peripheral locations within active continental rift systems, where magmatic activity has ceased but hydrothermal processes are still present.

Local Novelty

- National groundwater fluoride occurrence has been documented for the first time in Malawi providing a master data set of groundwater fluoride spanning 50 years.
- New knowledge and an integrated understanding of hydrogeological processes responsible for fluoride occurrence has been generated for Malawi for the first time. That includes specific geogenic sources and their corresponding fluoride risk factors.
- Tiered groundwater fluoride prediction maps have been generated for Malawi, including areas with no groundwater fluoride data.
- An evidence-based platform has been developed for redefining fluoride-relevant groundwater policy and updating fluoride standards in Malawi where there was none previously.

8.2.6 Filling of research knowledge gaps

Key knowledge gaps were identified during the initial stage of the research process. Each knowledge gap is detailed below along with a description of how each was addressed by this thesis.

- **Knowledge Gap 1 (Local)**: There is very little data available for groundwater fluoride or knowledge of its occurrence for Malawi compared to other EARS countries, highlighting an immediate need for groundwater fluoride research. It was suggested that a national geological assessment was required to fill the knowledge gap due to groundwater fluoride being geogenic in origin.

Sporadic, local-scale studies investigating general groundwater quality with only brief mentions of fluoride and limited published data were discovered but no national-scale documentation of fluoride occurrence was found. The closest was the 'Hydrogeology Atlas' (Government of Malawi, 2018), published internally within the Government of Malawi which contained catchment maps for the country displaying various hydrochemical elements and compounds of concern, including fluoride. Fluoride maps displayed locations of water points with fluoride concentrations either above or below the Malawian drinking water standard for raw water of 6 mg/L. More detail was unavailable, and no data were published. This research collated all available sources of fluoride data from Malawi from published or grey literature reports, data provided by the Government of Malawi and recent studies conducted by the CJF into one master data set. The data were subsequently analysed nationally and published as a peer-reviewed journal article (chapter 4) as the first comprehensive national documentation of groundwater fluoride occurrence in Malawi.

The most comprehensive explanation for fluoride occurrence in groundwater in Malawi was attributed simply to 'dissolution of basement rock'. Some studies mentioned hot springs as a source of fluoride but more detailed information beyond that was not available. This thesis added considerable knowledge and understanding to fluoride occurrence in Malawi, and indeed peripheral locations on active continental rift systems. Local-scale (chapter 5) and a national-scale (chapter 6) fluoride-lithology analyses determined which specific lithologies and thus lithological groups pose the highest risk of groundwater fluoride. A similar statistical analysis was performed for hydrothermal fluoride resulting in hot springs being identified as the source of the most excessive fluoride concentrations.

Fluoride occurrence is well documented in other EARS countries north of Malawi (Tanzania, Kenya, and Ethiopia) with many published studies available. That may be attributed to more active continental rifting and volcanism within those countries attracting the majority of geoscientific research. In contrast, Malawi has had very little research on fluoride and its occurrence was little understood. Malawi's location on the EARS periphery is unique in that active rifting occurs, associated hydrothermal activity occurs but is non-magmatic, and no active volcanism is present anywhere in the country. In that respect rifting in the Malawi Rift is less extreme than other parts of the EARS. This thesis sought to fill the knowledge gap with a comprehensive national understanding of groundwater fluoride occurrence at this unique location on the rift periphery. Data collation and preliminary analyses were conducted in chapter 4, local-scale fluoride-lithological analysis was conducted to determine specific relationships between groundwater fluoride and specific rocks in chapter 5, those analyses were then performed nationally in chapter 6 and hydrothermal fluoride was investigated in chapter 7.

- **Knowledge Gap 2 (Local)**: Very little data is available and even less is understood of the health implications of Malawi's groundwater fluoride. There is a need to quantify the direct link from geogenic groundwater fluoride sources and human health so that policy reform (for fluoride) can be advocated.

Very little understanding was available on the direct relationship between groundwater fluoride occurrence and human health (fluorosis). Only one published study presented data on the subject and made an attempt to designate an area as an endemic fluorosis area, based solely on the occurrence of fluorosis in school children and elevated fluoride in groundwater in some boreholes in the study area. No attempt had been made to quantify the risk locally or nationally. This thesis sought to fill that gap in knowledge via a human health risk assessment case study. The method adopted was initially developed by the United States Environmental Protection Agency to assign risk factors to water points based on their 'non-carcinogenic risk index' (otherwise known as HQ values) (USEPA., 2019). The results were successful in quantifying the direct human health risk (fluorosis) from groundwater fluoride for 39 water points in central Malawi where 74% of children under six were shown to be vulnerable.

- **Knowledge Gap 3 (Global)**: There is a need for an innovative method to screen for groundwater fluoride risk from geogenic sources in developing countries which makes the best use of existing sporadic groundwater data and can be deployed with minimal resources.

Lack of knowledge of fluoride occurrence in Malawi resulted in no available method of predicting its occurrence. The JMP classification of fluoride as a global contaminant of concern meant that countries globally must review their groundwater assets for fluoride and find replacement water supplies for those with harmful concentrations. This posed a significant challenge for developing countries such as

Malawi where groundwater data is often sporadic or even non-existent. This thesis sought to fill the gap in knowledge by developing a prediction method to screen for groundwater fluoride which was applicable at national scales in developing countries with limited resources, making the best use of existing data. Statistical relationships between specific lithologies and groundwater fluoride concentrations (proxy for relative fluoride content of source rock) facilitated the development of a tiered system of risk factors for generic lithological sources nationally. A collation of hot spring data facilitated quantification of site-specific hydrothermal fluoride risk in the same manner, resulting in the identification of hot springs as the highest risk of the most excessive fluoride concentrations. Detailed risk maps were subsequently developed at national and catchment-scales. The prediction method was designed to be adaptive, allowing prediction confidence to increase with each addition of new data. That adaptivity was demonstrated in chapter 7 where new data was added, increasing prediction confidence (and updating risk factors) for hydrothermal fluoride and unconsolidated sediments.

8.2.7 Implications of the research

There are local and global implications of this research. The local (Malawi) implications are significant and are evidenced by a recent addition to the Government of Malawi human health and policy reform in support of the Sustainable Development Goals. Following this thesis, the Government of Malawi (Nov 2020) has specifically identified the risk of geogenic fluoride as a Key Reform Agenda item for action by the Ministry of Forestry and Natural Resources in the planning cycle 2020 to 2026 (Government of Malawi, 2020), a direct result of the work contained within this thesis and continuous, ongoing collaboration with key stakeholders in the Government. Malawi is now in a position to assess its groundwater assets for fluoride using the risk maps contained within this thesis. Their plan to identify and acquire replacement water supplies for 80% of households with harmful fluoride concentrations by 2026 can now be conducted in a targeted manner by prioritising the highest risk water points.

The published papers from chapters 4, 5 and 6 attracted the attention of an international, cross-disciplinary funding application which is being submitted and managed by the University of Exeter's Camborne School of Mines. I was personally approached by one of the Primary Investigators (PI) who had read those papers and wanted to integrate my fluoride hydrogeological work within their funding proposal. They are primarily a deep drilling project investigating the geology of carbonatite cores (alkaline plugs) in southern Malawi and required the addition of hydrogeological research which would benefit from the opportunity to investigate deep boreholes (up to 1 Km). The proposal has since been submitted and once accepted will provide a unique opportunity for a new branch of refinement for this research by investigating fluoride-lithology behaviour in deeper groundwater in a lithology previously identified as an ‘elevated geogenic fluoride’ lithology (chapter 6).

The global implication of this research is the application of the method for predicting groundwater fluoride in other countries with limited groundwater data and resources. The method developed will work for any country which has access to (at least) sporadic groundwater fluoride data, GIS software and geological data. A screening method to identify and prioritise groundwater assets for fluoride may be all that is required to manage groundwater fluoride within the SDG timeframe.

8.3 Research recommendations

This thesis provides a platform for various areas of further research. Recommendations are summarised below.

8.3.1 Recommendations for Malawi

Ongoing refinement of the prediction method in Malawi

Two case studies are recommended to refine the prediction method, based on the outcomes of this thesis. The first is in TA Mazengera where the original local-scale study to develop the prediction method (chapter 5) was conducted. 39 water points were sampled for the case study which were evenly distributed and chosen to represent the three main lithological units. A more comprehensive study which samples all 120+ water points in the study area would provide an opportunity to test the accuracy of the prediction method by comparing predicted groundwater fluoride risk from chapter 5 (which used sporadic groundwater data) to statistics calculated using groundwater data from every water point. A comparison of results from both studies may provide an opportunity to quantify the accuracy of the prediction method using a case study.

Another recommended case study is a comprehensive groundwater sampling campaign in Dedza district within the 6 Km prediction radius identified in chapter 7. Medical data confirms Mua Primary School as an endemic dental fluorosis area, however the groundwater source(s) with excess fluoride concentrations responsible for observed incidence of the condition has not yet been identified. It was hypothesised in chapter 7 that at least one water point within 6 Km radius of the school would produce groundwater fluoride >1.5 mg/L due to the presence of a (hypothesised) hidden hot spring. Identification of the fluoride source will support chapter 7 outcomes by: supporting the use of dental data as a useful proxy indicator for locating excess fluoride sources, and; refine the prediction method further by the addition of new data and the identification of a new site-specific ‘Excessive Geogenic Fluoride’ source(s).

Groundwater sampling in zones with ‘Insufficient Mineralogical or Water Quality Data to Determine Geogenic Fluoride Risk’

Lithologies on the groundwater fluoride risk map for Malawi which were classified as ‘Insufficient Mineralogical or Water Quality Data to Determine Geogenic Fluoride Risk’ will require sampling for groundwater fluoride. Those zones pose the greatest uncertainty on the risk map. Sporadic groundwater sampling initially will be sufficient to establish fluoride risk factors for each lithology. Those lithologies can thus be assigned a generic risk category on the risk map and can be included into prioritised groundwater asset management plans depending on their risk classification.

Utilisation of the prediction method for screening groundwater fluoride to prioritise national groundwater asset management

The method developed within this thesis and the risk maps produced as a result provide a tool for targeted groundwater sampling for fluoride (to support SDG 6.1 targets) which prioritises those water points most at risk from geogenic sources, a task which would not have been possible previously. The ability to target and prioritise fluorosis risk is invaluable with over 120,000 water points nationally, allowing those water points most at risk to be assessed first. Hot springs should be the primary target for asset management as they pose the greatest risk to human health from fluorosis. It is recommended that signage be installed at those sites in both English and Chichewa warning users of the risk associated with drinking water from those sources and replacement water supplies acquired immediately. Water points within ‘Elevated Geogenic Fluoride’ zones (which represent alkaline igneous lithologies) number 1168 nationally affecting an estimated 249,000 water points users and should be the next priority for groundwater fluoride asset management. Groundwater from water points in those zones should be sampled and tested for total chemistry (including fluoride) in a laboratory. Any water points producing groundwater fluoride concentrations >1.5 mg/L should be decommissioned, and replacement water supplies acquired. The above work will remove the worst risk of fluorosis from the population, significantly improve SDG 6.1 attainment within the deadline of 2030, and achieve the Government of Malawi’s key reform agenda item for the Ministry of Forestry and Natural Resources (80% of fluoride-prone households must be assessed by 2026). The remaining water points within ‘Moderate-low Geogenic Fluoride’ and ‘Low Geogenic Fluoride’ zones which contain the vast majority of water points nationally can then be sampled in order of decreasing risk.

Hot spring groundwater study

This research discovered 76 hot spring locations in Malawi which pose excessive risk of fluorosis for people who use them for drinking purposes. Further study to investigate the radius of influence in shallow groundwater from hot springs is recommended. Most hot springs in Malawi experience some degree of mixing with shallower groundwater so an investigation into the lateral extent of contamination by sampling water points immediately adjacent to hot springs may reveal additional groundwater sources in the ‘Excessive Geogenic Fluoride’ risk category. It has been shown previously that hot springs contaminate local shallow groundwater to a radius of around 1 Km (Kundu et al., 2002) so an initial testing radius of 1 Km would be recommended in the first instance. Local aquifer systems may vary in composition and porosity/permeability so groundwater sampling for fluoride may reveal a larger or smaller radius of influence for different locations in Malawi. If the study reveals groundwater fluoride contamination of shallow groundwater surrounding hot springs, a new generic zone of ‘Excessive Geogenic Fluoride’ from hydrothermal sources may be added to the risk map surrounding hot spring sites, thus updating the method, and increasing prediction confidence.

Further collaboration with health professionals

This thesis has shown that collaborative efforts with health professionals can be mutually beneficial. It is recommended that groundwater scientists within the Government of Malawi work with dentists operating in the country to identify locations with severe dental fluorosis. Those locations can be used to identify locations of hidden hot springs in the northern and central regions where there are significantly less groundwater fluoride data available. Rift basin unconsolidated sediments occur along the lakeshore of Lake Malawi in those regions and may contain many hidden hot springs which are contaminating drinking water with excess fluoride concentrations causing severe dental fluorosis. Working collaboratively with dentists may help to refine the search for undiscovered excess fluoride water points within more extensive generic (lithological source) zones, as increased incidence of dental fluorosis indicates a water source with elevated fluoride concentrations. The approach works in reverse as groundwater fluoride risk maps can assist dentists to locate and prioritise areas likely to contain endemic dental fluorosis. Almost nothing is known about the occurrence of skeletal or crippling fluorosis in Malawi therefore collaboration between groundwater scientists and local health centres nearest to hot spring locations is recommended to assess the extent of those conditions and their relation to drinking hydrothermal groundwater.

Redefinition of groundwater policy for fluoride

This thesis has shown that the current Malawian guideline standard for fluoride in drinking (raw) water of 6 mg/L (Malawi Bureau of Standards, 2005) is too high and is not aligned with observed health risks. It is recommended that the standard be aligned with the WHO's standard of 1.5 mg/L (WHO and UNICEF, 2017) via stepped progression. Detail on this plan is outlined in chapter 6 and is currently under discussion within the Government of Malawi. The fluoride-relevant sections of the Malawi standard documents for raw water must be redefined to include geogenic sources of fluoride contamination including detail on how such contamination should be remediated.

8.3.2 Recommendations for the research approach

Global screening for groundwater fluoride in the developing world

It is recommended that countries globally adopt this groundwater fluoride prediction method to screen for excess concentrations which may be causing fluorosis, and to prioritise groundwater asset management for fluoride towards SDG 6. Any country which cannot develop comprehensive risk models due to sporadic national groundwater data can adopt this method for very little expense using existing data and free, open-source GIS software. Countries can subsequently save time and money by prioritising remediation efforts and boost their chances of achieving SDG 6.1 before the 2030 deadline, a task which may not have been possible previously.

How well does the method work in different aquifer types?

The method developed within this thesis assumed the weathered basement aquifer type for the whole country. That decision was made because the weathered basement aquifer was the most dominant and extensive aquifer in the country. Further studies similar to the local-scale study in TA Mazengera (chapter 5) in different aquifer types may reveal complexities surrounding shallow groundwater transport of fluoride from lithological sources which are not accounted for in the current method. Incorporation of results from such studies would improve the overall accuracy of the method, increasing prediction confidence and allowing it to be adapted to locations with a wide range of aquifer types.

8.4 General conclusions

The research aim was substantially achieved in this thesis via five research questions and 10 research objectives. Each was fulfilled via four journal papers which were published in international journals. In that regard, this thesis is underpinned by peer-reviewed scientific research. Key general conclusions are summarised below:

- First ever collation of national data set for groundwater fluoride in Malawi.
- Groundwater fluoride in Malawi occurs from 2 main geogenic sources: lithological and hydrothermal. Hydrothermal and lithologies of alkaline igneous composition are associated with the most excessive concentrations.
- Groundwater fluoride concentrations from boreholes, wells and springs reflect fluoride content of the host lithology due to low hydraulic conductivity and transmissivity values in weathered basement aquifers.
- The direct link between groundwater fluoride and human health (fluorosis) in Malawi was quantified via a human health risk assessment case study.
- Malawi standard for fluoride in raw drinking water at 6 mg/L is not aligned with observed health risks and needs to be reduced to 1.5 mg/L via stepped progression to align with the World Health Organisation (WHO). Drinking water standard documents must be redefined to include geogenic contamination sources with remediation techniques.
- A groundwater fluoride prediction method was developed along with a national risk map which can be used to screen groundwater sources nationally for excess fluoride. Prioritising management of groundwater infrastructure assets for fluoride using the method will boost chances of achieving SDG 6 in Malawi.
- Previously hidden hot springs were identified in the unconsolidated sediments of the rift basin in southern Malawi via multiple proxy indicators and a collaboration with dentists.
- New data from hidden hot spring study facilitated update of the method, improving prediction accuracy and updated groundwater fluoride risk factors for hot springs and unconsolidated sediments. Update showed that the method is adaptable and prediction confidence increases with the addition of new data.

This thesis was built upon the belief that innovative and creative solutions are required to build resilience to global challenges. That has never been more evident in the developing world due to pressures created by the approaching sustainable development goal (SDG) deadline and more recently by the impact of the Covid-19 pandemic. The United Nations' (UN) Joint Monitoring Programme (JMP) classification of two primary chemical contaminants of concern (which includes fluoride) has triggered a global drive for update of SDG-led groundwater targets to identify populations vulnerable from fluoride in drinking water. International investment and innovative research will be key to tackling the challenge in the developing world. The method developed in this thesis to predict and screen for fluoride in groundwater is innovative and can be applied at any scale in any country for little expense. It will be particularly effective in developing countries where limited access to data and resources are a hinderance to risk models and may be what is required to achieve SGD 6.1 before 2030. The scientific and social implications (both global and local) of this method will be significant where it is applied.

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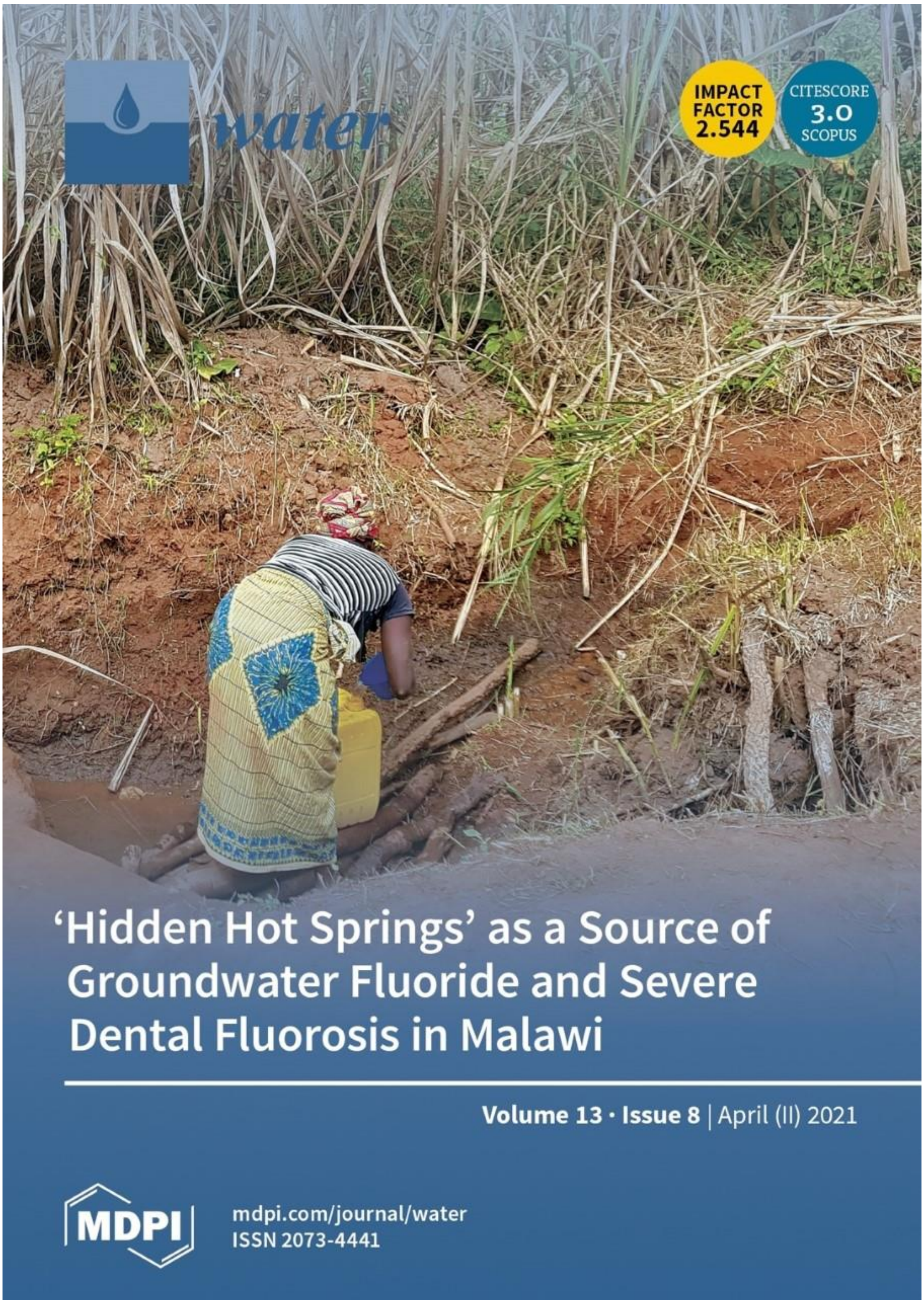
APPENDIX

Cover for Water MDPI journal volume 13, issue 8 (Chapter 7).



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‘Hidden Hot Springs’ as a Source of Groundwater Fluoride and Severe Dental Fluorosis in Malawi

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ISSN 2073-4441

Ethics approval from University of Glasgow/Smileawi dental survey (Chapter 7).

CERTIFICATE OF ETHICS APPROVAL

This is to certify that the College of Medicine Research and Ethics Committee (COMREC) has reviewed and approved a study entitled:

P.09/19/2788 - A Pilot Study of the Prevalence of Dental Caries in A Cohort of 5-12 Year Old Children in Malawi by Jeremy Bagg

On 17-Sep-19

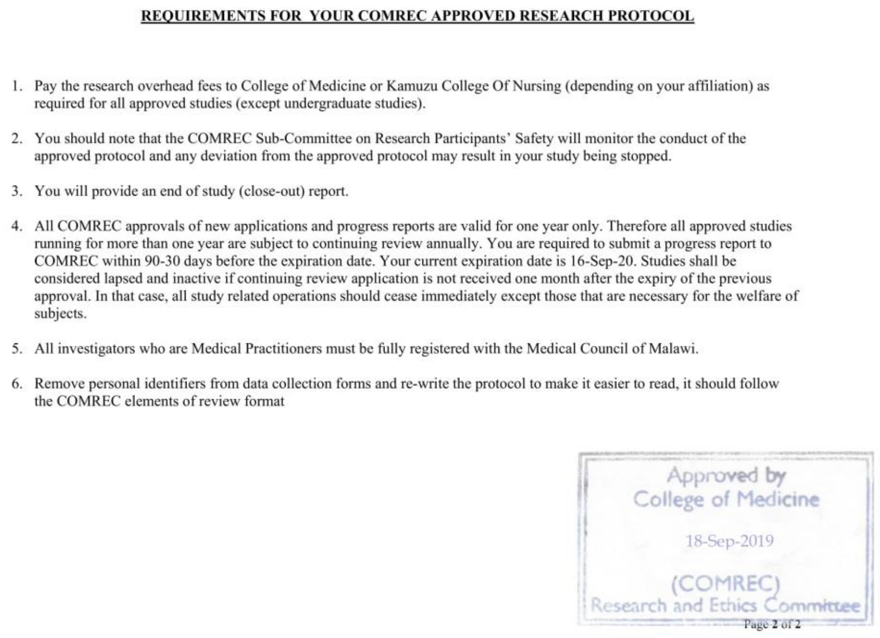
As you proceed with the implementation of your study, we would like you to adhere to international ethical guidelines, national guidelines and all requirements by COMREC some of which are indicated on the next page for your study

17-Sep-19

Dr. YB. Mlombe - Chairperson (COMREC)

Date

Approved by
College of Medicine
18-Sep-2019
(COMREC)
Research and Ethics Committee



REQUIREMENTS FOR YOUR COMREC APPROVED RESEARCH PROTOCOL

1. Pay the research overhead fees to College of Medicine or Kamuzu College Of Nursing (depending on your affiliation) as required for all approved studies (except undergraduate studies).

2. You should note that the COMREC Sub-Committee on Research Participants' Safety will monitor the conduct of the approved protocol and any deviation from the approved protocol may result in your study being stopped.

3. You will provide an end of study (close-out) report.

4. All COMREC approvals of new applications and progress reports are valid for one year only. Therefore all approved studies running for more than one year are subject to continuing review annually. You are required to submit a progress report to COMREC within 90-30 days before the expiration date. Your current expiration date is 16-Sep-20. Studies shall be considered lapsed and inactive if continuing review application is not received one month after the expiry of the previous approval. In that case, all study related operations should cease immediately except those that are necessary for the welfare of subjects.

5. All investigators who are Medical Practitioners must be fully registered with the Medical Council of Malawi.

6. Remove personal identifiers from data collection forms and re-write the protocol to make it easier to read, it should follow the COMREC elements of review format

Approved by
College of Medicine
18-Sep-2019
(COMREC)
Research and Ethics Committee

Page **2** of **2**