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

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: fluoride control, calcium, pH and temperature sensitivity
• Troublesome >1.5–6 mg/l fluoride of diffuse occurrence a key management challenge

GRAPHICAL ABSTRACT

Fluoride in the lower East African Rift System, Southern Malawi

Hydrothermal groundwater provenance control

Increased fluoride in proximity to faulted areas

A B S T R A C T

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

Abbreviations: SB, Shire Basin; LSB, Lower Shire Basin.
⁎ Corresponding author at: Department of Civil & Environmental Engineering, University of Strathclyde, Glasgow, Scotland, G1 1XJ.
E-mail address: Marc.addison@strath.ac.uk (M.J. Addison).

https://doi.org/10.1016/j.scitotenv.2019.136260
0048-9697/© 2020 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
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, compliant 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 fluoride (CaF\textsubscript{2}) may arise; upon groundwater calcium increase, fluoride may precipitate on sediments, fault surfaces or in caves, to later re-dissolve upon the return of suitable hydrochemical conditions (Maltsve 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 (Kalina 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 Fatii, 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,
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.

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 metagneous 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, fragmented 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 fluoride 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.

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

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., 2007) 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 fluoride 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.


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, Namambolo 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);

<table>
<thead>
<tr>
<th>Classification</th>
<th>Fluoride Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>0–1.5</td>
</tr>
<tr>
<td>Slightly elevated (S. elevated)</td>
<td>1.5–2</td>
</tr>
<tr>
<td>Elevated</td>
<td>2–6</td>
</tr>
<tr>
<td>Excessive</td>
<td>6+</td>
</tr>
</tbody>
</table>
• 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 fluoride effective solubility to increase with salinity;
• Prime targets for suspected high fluoride are those groundwaters of low calcium, i.e. Na-HCO3 and Na—Cl 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.

The MoAIWD archive data, whilst fragmented, does provide some opportunity to assess hydrochemical controls. For example, under fluoride 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 fluorate (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.

3.4. Cijf 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).

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 fluoride 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 fluoride 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, 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 favourable 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, 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 fluorite 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 fluorite 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 range is commonly found in samples with fluorite both above and below these concentrations. Very low fluorite though, below 0.5 mg/l, is frequently, but not always, characterised by low pH, c. 5.8–6.6.

Our 2016–2018 survey data provides good opportunity to revisit the fluorite – 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 fluorite concentrations with low calcium and where calcium concentrations are elevated fluorite 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.

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 fluorite 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 fluorite 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 fluorite 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 fluorite with calcium displayed. We concur that those archive data attract the most caution and potential qualification in the data interpretation.

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 fluorite 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 fluorite spatial distributions – all data

Geological controls upon the spatial distribution of all fluorite 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.

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

---

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

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
Key

- Known Dental Fluorosis Area
- Hot Spring (2016-2018 survey)
- Hot Spring (Kaonga et al, 2014)
- Hot Spring (Kirkpatrick, 1969) estimate
- Excessive F (6+ mg/l) 2016-2018 Survey
- Elevated F (2-<6 mg/l) 2016-2018 Survey
- S. Elevated F (1.5-<2 mg/l) 2016-2018 Survey
- Low F (0-<1.5 mg/l) 2016-2018 Survey
- Excessive F (6+ mg/l) Pritchard et al, 2008
- Elevated F (2-<6 mg/l) Pritchard et al, 2008
- Low F (0-<1.5 mg/l) Pritchard et al, 2008
- Excessive F (6+ mg/l) 2018 Atlas
- Elevated F (2-<6 mg/l) 1980-2014 Archive
- S. Elevated F (1.5-<2 mg/l) 1980-2014 Archive
- Low F (0-<1.5 mg/l) 1980-2014 Archive
- City

- Shire River
- Main Geological Fault
- Basement Complex
- Chilwa Alkaline Province
- Igneous rocks of unknown affiliation
- Karoo Supergroup
- Lake Malawi Granitic Province
- Lupata Series
- Minor Intrusions
- Superficial deposits

Legend:
- Lake Malawi
- Lake Chilwa
- Mulanje Massif
- Gneiss quality

Map: Geology of the region showing key geological features and known dental fluorosis areas.
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, 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 fluorotic 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 (Gighieri 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 (Gighieri 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 (Figs. 5 & 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 fluoride occurrences around carbonatite cores in the Southern Region, particularly around Chiwla 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 fluorite. 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 (Gighieri 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
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                 | 0.45                   | 0.9            | 85.7%        | 1.43%      |
| Central       | 10 | 3.6                  | 0.5                    | 0.6            | 70%          | 0%         |
| Southern      | 1285 | 1.22               | 0.81                   | 1.23           | 82.88%       | 9.26%      |
| All           | 1365 | 1.23               | 0.48                   | 0.8            | 82.93%       | 8.79%      |

5. Conclusions

This study found that limited research has been undertaken to understand 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 better understood, as do the probable control of fluoride 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 low calcium, high pH conditions as more conclusively shown herein.

The authors gratefully acknowledge the Scottish Government, via the ‘Climate Justice Fund: Water Futures Programme’ for funding this research. This research was funded under research grant HR-CJF-03 awarded to the University of Strathclyde (R.M. Kalin). Further thanks are due to Adrian Bath for insightful discussions around the detail in his early work in Malawi.

Acknowledgements


Fraser, A., 2016. Exploring the Origin of High Salinity Groundwater Using Cl Br. Department of Civil and Environmental Engineering, University of Strathclyde (MSc hydrogeology thesis (unpublished)).


