



Arsenic occurrence in Malawi groundwater

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ABSTRACT: Despite an estimated 90,000 groundwater points, mostly hand-pumped boreholes, being used for drinking-water supply in Malawi, evaluation of groundwater arsenic has been limited. Here we review the literature and collate archive data on groundwater arsenic occurrence in Malawi; add to these data, by surveying occurrence in hand-pumped boreholes in susceptible aquifers; and, conclude on risks to water supply. Published literature is sparse with two of the three studies reporting arsenic data in passing, with concentrations below detection limits. The third study of 25 alluvial aquifer boreholes found arsenic mostly at 1-10 µg/l concentration, but with four sites above the World Health Organisation (WHO) 10 µg/l drinking-water guideline, up to 15 µg/l; the study also discerned hydrochemical controls. Archive data from non-governmental organisation (NGO) borehole testing (two datasets) exhibited below detection results. Our surveys in 2014-18 of hand-pumped supplies in alluvial and bedrock aquifers tested 310 groundwater sites (78% alluvial, 22% bedrock) and found below test-kit detection (<10 µg/l) arsenic throughout, except possible traces at two boreholes containing geothermal-groundwater contributions. Our subsequent survey of 15 geothermal groundwater boreholes/springs found four sites with arsenic detected at 4-12 µg/l concentration. These sites displayed the highest temperatures, supporting increased arsenic being related to a geothermal groundwater influence. Our 919 sample dataset overall indicates arsenic in Malawian groundwater appears low, and well within Malawi's drinking-water standard of 50 µg/l (MS733:2005). Still, however, troublesome concentrations above the WHO drinking-water guideline occur. Continued research is needed to confirm that human-health risks are low; including, increased monitoring of the great many hand-pumped supplies, and assessing hydro-biogeochemical controls on the higher arsenic concentrations found.

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Arsenic in groundwater is a global concern due to its potential to impact human-health when contaminated groundwater is used for drinking-water supply. Cases of widespread contamination have emerged in South/North America, Europe, South-East Asia, and Bangladesh-India where 40 million people were affected (Ahmed *et al.*, 2004; Smedley and Kinniburgh, 2013). Exposure in water is generally due to toxic trivalent arsenite As (III) and has been linked to skin, bladder and lung cancers, skin lesions, cardiovascular disease and infant development (George *et al.*, 2012). European and US regulations implement standards equivalent to the WHO drinking-water guideline, 10 µg/l (WHO, 2011). However, many developing nations still adopt the pre-1993 WHO drinking-water guideline of 50 µg/l, including Malawi (Malawi Standards (2005) for waters delivered from boreholes and protected shallow wells). This may be due to a lack of analytical facilities to test

for low concentrations, or compliance issues with realistically meeting lower standards (Smedley and Kinniburgh, 2013). Arsenic is, however, now designated a global level priority chemical to monitor in assessing performance against the Sustainable Development Goal (SDG) target 6.1 indicator of population proportion using safely managed drinking water (WHO and UNICEF, 2017).

Widespread groundwater contamination usually arises from desorption/dissolution of host rock arsenic naturally present. Concentrations range from <0.5 to 15,000 µg/l depending upon the mineralogy and fluid-rock interaction occurring. Elevated concentrations, above 10 µg/l, are the exception rather than rule (Smedley and Kinniburgh, 2013). Many minerals contain arsenic with sulphide minerals such as arsenian pyrite (Fe(SAs)₂) and arsenopyrites (FeAsS) forming key geogenic sources. Although solid-phase

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arsenic contents influence groundwater contamination, aquifer material in some of the most prominent cases may not be that high in arsenic, possibly containing from as low as 1-20 mg/kg (Smedley and Kinniburgh, 2002). Solution conditions favouring arsenic release are hence often key with a complex range of possible biogeochemical reactions influencing release (Hoque *et al.*, 2017). Generalising though, mobilisation of rock-formation arsenic into groundwater is most favourable under oxidising conditions at high pH, or else, perhaps more commonly, strongly reducing conditions (Smedley and Kinniburgh, 2013). For instance, dissolution of arsenic bearing iron-oxides may occur upon reducing conditions where the presence (and lability) of organic matter and sulfates are important. Reduction of the latter to sulfide may remove arsenic from solution due to insoluble arsenic sulfide formation, or else sorption to iron sulfides (Rowland *et al.*, 2011).

Groundwater arsenic assessment at national levels is not always comprehensive. It could be perceived an unlikely issue in the prevalent rock types, a country may have insufficient analytical resources, or there is an absence of obvious health impacts - a potential false security. The global case map of Smedley and Kinniburgh (2013) does not identify any African arsenic-affected aquifers, with only four instances of (mining related) occurrence. This may arise from African hydrochemical conditions being less prone, however, monitoring may often be inadequate (Ravenscroft *et al.*, 2009). The recent review of arsenic in African waters by Ahoulé *et al.* (2015) echoes and exemplifies, in detail, confirming there appears limited assessment of arsenic in Malawi (Ahoulé *et al.*, 2015). The British Geological Survey (BGS) (having long-term hydrogeological experience in Malawi and significant arsenic experience globally (Smedley and Kinniburgh, 2013)) in 2004 anticipated arsenic in Malawi's main aquifers to be low: below 50 µg/l and possibly 10 µg/l, in most groundwater from the Basement rock and Mesozoic (Karoo and Cretaceous) sediments (BGS, 2004). They caution, however, this anticipation required assessment, in conjunction with testing of alluvial aquifer where concentrations may be locally higher. Mapoma and Xie (2014) likewise perceive arsenic problems to be low, albeit still based upon sparse data. Our study hence aims to: review the available literature and assemble archive data on groundwater arsenic occurrence in Malawi; add to this knowledge base, by surveying occurrence in drinking-water supply boreholes in susceptible aquifer types; and, conclude upon the current understanding of risks posed to Malawi's drinking-water supply and its future needs.

MATERIALS AND METHODS

Description of study area: Malawi is a low-income country in Southern Africa. Rural communities account for around 85% of its >17 million population who largely depend upon groundwater. Access to groundwater continues to increase with hand-pumped borehole community supply 'water-points' pivotal to Water and Sanitation Hygiene (WaSH) programmes and SDG 6 attainment. Water-point mapping under our Climate Justice Fund: Water Futures Programme (CJF) (www.cjwaterfuturesprogramme.com) has so far mapped 61,000 water points, and it is projected around 90,000 points may exist across Malawi.

Malawi is positioned on an elongate plateau towards the southern extreme of the western branch of the East-African Rift System (EARS). Its Miocene-recent structural geology (Fig. 1a) is mainly influenced by the EARS and bound by many faults. Ground elevations decline from 3000 m in the highlands to 30 m in the southern valley plains around the Shire River, the sole outflow from Lake Malawi. The deeper geology is largely influenced by the basement-forming Pre-Cambrian metamorphic lithologies arising from events associated with the formation of the Cape Fold Belt and the now largely eroded Falkland Mountain Range (Catuneanu *et al.*, 2005). The Pre-Cambrian or Lower Palaeozoic crystalline 'Basement' rocks comprising gneiss, granulite and some granite are hence extensive. Down sagging of mountain belt forelands is where much of the younger Karoo (Jurassic) sediments accumulated (Catuneanu *et al.*, 2005). Weather-resistant Karoo alkaline granitic and syenitic intrusions form the elevated south-east uplands (BGS, 2004). Karoo igneous rocks occur locally in Southern Malawi as basaltic intrusions. Thick Karoo sediments (mainly Permo-Triassic), comprising mainly sandstones, marls and conglomerates with some coal seams, occur in the north and south with younger Cretaceous to Pleistocene age sediments locally present. Recent Quaternary alluvium, colluvium and lacustrine deposits occupy the plains; significant alluvium arises from erosion of rift escarpment material (BGS, 2004). Groundwater supplies are mostly hand-pumped from the Quaternary alluvial aquifer that can be high yielding (up to 15 l/s), or Basement/bedrock where yields are sensitive to the distribution of overlying colluvium, the degree of weathering and frequency of faults, joints and bedrock fractures (Upton *et al.*, 2016). Yields of 0.5 l/s, sufficient for hand-pumps, are viable where saturated weathered thicknesses are >10 m (Smith-Carington and Chilton, 1983). Some groundwater resources also exist in: Mesozoic alkaline and basaltic intrusions in the south-east uplands that are poorly permeable, but largely freshwater; Karoo sediments, usually well

cemented with low porosity, but where fractured may allow groundwater flow; and, Cretaceous sediments, where less well-indurated (BGS, 2004).

Review of Malawi literature and archive data: A literature review was undertaken to collate Malawian groundwater arsenic occurrence data. Archive groundwater quality data held by the regulator, the Ministry of Agriculture, Irrigation and Water Development (MoAIWD), were also reviewed,

covering electronic databases on groundwater quality collated under various initiatives. The data span 1980 to 2017 and cover the early 1990s onset of growing international awareness of groundwater arsenic. Collation, of these records into a single management information system, however, remains an on-going MoAIWD effort. Additional to these data sets, a non-exhaustive review was made of other known ‘ad-hoc’ MoAIWD paper records, or third party, for example non-governmental organisation (NGO), reports held.

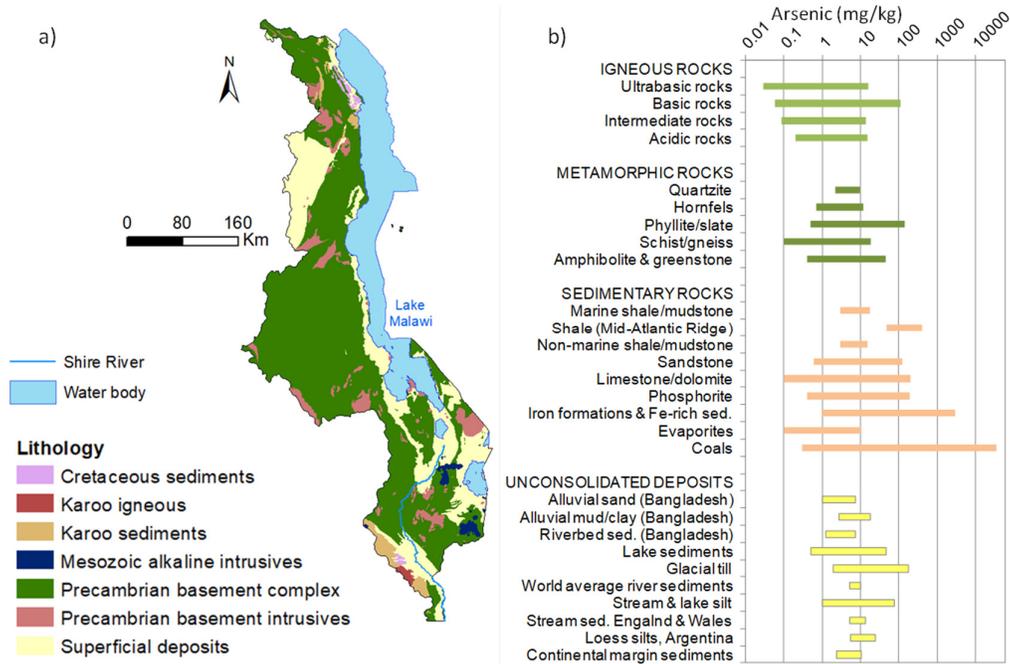


Fig. 1. a) Geology of Malawi; and, b) typical ranges of arsenic in rocks and sediments, based on Smedley and Kinniburgh (2013).

Field surveys – design rationale: Groundwater-quality surveys were conducted in 2014-16 of hand-pumped boreholes widely used for rural community drinking-water - domestic supply, or by schools and hospitals. Surveys were targeted in possible areas of increased arsenic susceptibility. Although archive groundwater data with sporadically elevated iron in Maseya, Katunga and Ngabu Traditional Authorities (TAs) in Chikwawa District could signify reducing conditions conducive to arsenic release, data paucity precluded such occurrences being that useful in guiding area selection. Anticipated rock arsenic content was considered by comparing to the international tabulation of Smedley and Kinniburgh (2013), summarised in Fig. 1b. For example, biotite-hornblende gneisses are unlikely to be greatly impacted by weathering with solid-phase arsenic expected to be low (<20 mg/kg, per Fig. 1b). Coal shales in Lengwe National Park could pose high risk

(up to 35,000 mg/kg arsenic in coals, per Fig. 1b), however, boreholes were absent due to Park restrictions. Arsenic contamination may be connected with pyrite presence (data limited) and reduced conditions within igneous rocks such as basalt (up to 113 mg/kg, per Fig. 1b). TA Ngabu was hence selected as an area with higher arsenic risk in that weathering could be high in the Karoo basaltic bedrock. Alluvial deposits there are also partly derived from basalts known to contain elevated iron-bearing magnetite and arsenic within the range of 3-41 mg/kg (Smedley and Kinniburgh, 2002).

Groundwater-quality field surveys: Locations of all sites sampled in our various surveys conducted over 2014-18 are shown in Fig. 2. All surveys were undertaken during June, within the hot-dry season and onset of declining water tables. Surveys in 2014 comprised: 42 boreholes within the basaltic bedrock

aquifer in TA Ngabu (Wild, 2014); and, 55 boreholes (43 in TA Ngabu, 12 in Kakoma, Mwanza Valley, TA Chapananga) within the Shire River Basin alluvial aquifer (Melville, 2014). In 2015, a higher resolution survey was made of 93 boreholes in the Mwanza Valley alluvial aquifer at Kakoma (McGrath, 2015). In 2016, a re-survey of the TA Ngabu area comprised

sampling of 98 additional boreholes in similar areas to the 2014 surveys (Flink, 2016). The 2016 survey also sampled two 'geothermal boreholes' in the Neno District thought to contain, possibly arsenic-rich, geothermal groundwater contributions arising from upward groundwater discharge (via faults etc.) from depth.

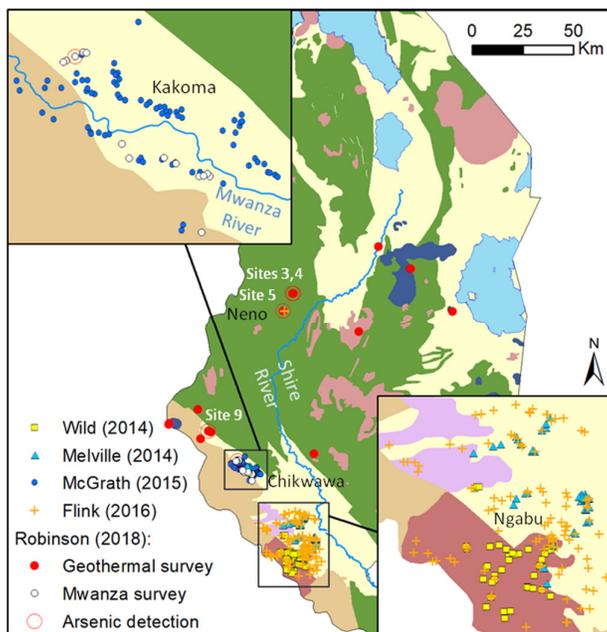


Fig. 2. Borehole locations sampled during surveys of groundwater quality – arsenic occurrence in Southern Malawi during 2014-18 by the CJF programme.

Survey work in 2018 comprised two components (Fig. 2): further examination of arsenic occurrence associated with known or suspected geothermal groundwater discharges at springs or boreholes in Southern Malawi, within the Districts of Blantyre, Chikwawa, Machinga, Ntcheu and Zomba (Robinson, 2018); and, further study of the Mwanza Valley alluvial aquifer, primarily to assess vertical variation in salinity, with arsenic data also being obtained (MacLeod, 2018). The geothermal survey examined 15 sites at 230 to 860 m ground elevation that were located near faults or geological/intrusion features, comprising 10 springs and 5 boreholes (3 'artesian' naturally flowing boreholes). These comprised 4 sites in the alluvium/colluvium underlain by Karoo sediments, 8 Basement sites, 2 igneous-rock sites, and 1 site in faulted Karoo sediments. The Mwanza Valley study obtained 20 samples, comprising 9 samples from nested (different-depth) piezometer sites at three localities (Manjolo, Kampomo and Chabwedzeka), and the remaining 11 samples from hand-pump supplies in the vicinity.

Chemical analysis: Arsenic for the 2014-16 surveys was screened with the Hach® EZ Arsenic Test Kit (Hach, 2015). Similar to other kits, it is based upon the Gutzeit method (George *et al.*, 2012). Any sample hydrogen sulphide is oxidised to sulfate. Addition of sulfamic acid and zinc then reduces arsenic to arsine gas that reacts with test-strip mercuric bromide to form arsenic-mercury halogenides (e.g., AsH_2HgBr) that yield different strip colour grades depending upon sample amounts of arsenic. Concentration thresholds of 0, 10, 30, 50, 100, 300, 500 $\mu\text{g/l}$ are identified with the colour chart, but concentrations are not determined. George *et al.* (2012) confirms the Hach® EZ kit offered high reliability with 97-100% of waters tested being correctly identified relative to 10 or 50 $\mu\text{g/l}$ thresholds.

For the 2018 survey, total arsenic was quantified to a detection limit of 3.0 $\mu\text{g/l}$ using Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis on 0.45 μm filtered samples preserved at site (20% nitric acid) and shipped for analysis to the Univ. of Strathclyde laboratory, Scotland (Robinson, 2018).

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Supporting data for major ions, iron, pH, electrical conductivity (EC), total dissolved solids (TDS) and temperature were obtained using field probes or wet-chemistry methods (Rivett *et al.*, 2018; Robinson 2018) using MoAIWD laboratories for all 2014-16 survey samples; and, for the 2018 survey, modern (IC, ICP-OES) methods on shipped samples.

RESULTS AND DISCUSSION

Review of literature studies: Data from known Malawian surveys by other authors reporting arsenic in groundwater are summarised in Fig. 3. Two of the three surveys reported arsenic data in passing. The earliest published case appears to be Pritchard *et al.*

(2007, 2008) and Mkandawire (2008) who undertook dry-season (August and October 2006) and wet-season (February and April 2007) surveys of 52 hand-dug shallow (<15 m deep) wide-diameter (>1 m) wells across six districts in Southern Malawi (Fig. 3). Their rationale was to examine supplies vulnerable to anthropogenic contamination. Gross microbiological contamination proved to be particularly apparent in the wet season. Arsenic analysis was undertaken in Malawi via wet-chemistry - photometer analysis, or the Rapid arsenic test kit (Quick Econo II). For all 225 samples tested, arsenic was reported below the 2-3 µg/l detection limit applicable. Reporting did not comment upon factors controlling arsenic absence.

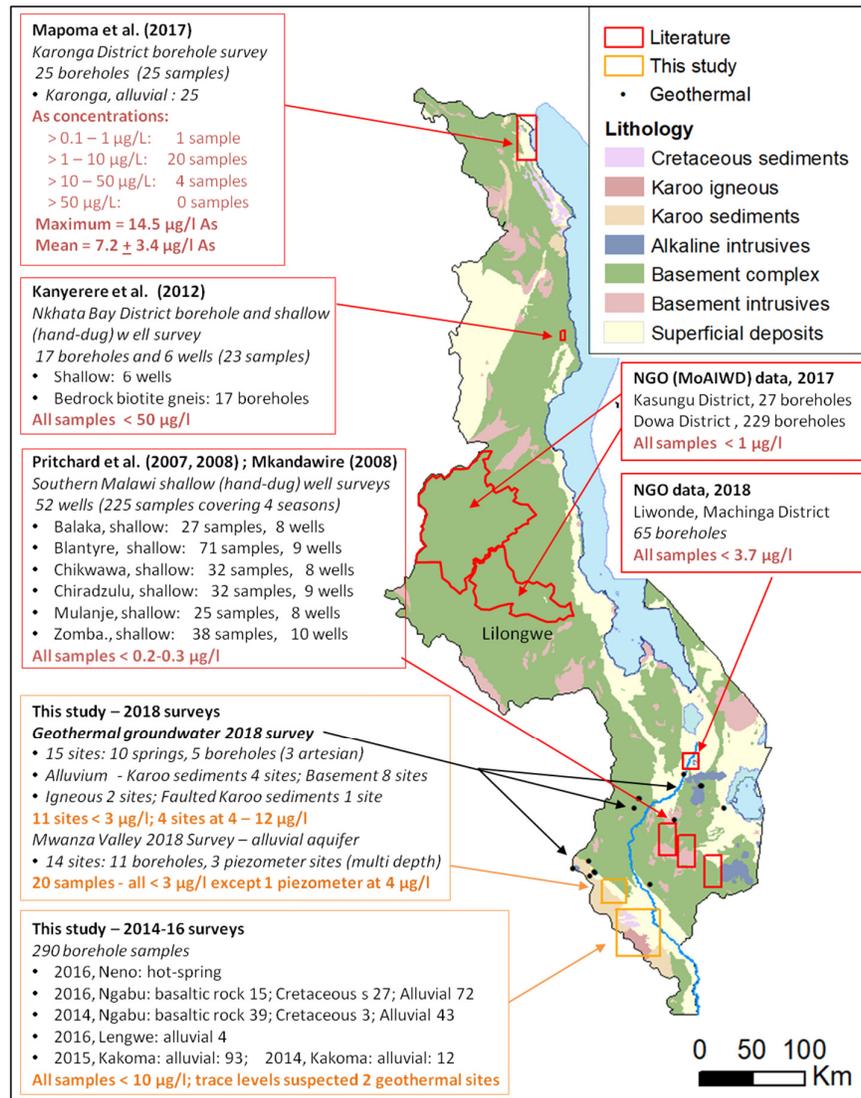


Fig. 3. Summary of arsenic occurrence in Malawian groundwater based on review of literature archive studies and our 2014–18 surveys.

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The study by Kanyerere *et al.* (2012) likewise focused upon microbiological risks. The authors surveyed 17 boreholes in bedrock biotite gneiss units and 6 (hand-dug) shallow wells in the rural Nkhata Bay District, Northern Malawi. Arsenic for all samples was below Malawi's Maximum Permissible Limit of 50 µg/l (Malawi Standards, 2005). Further comments on arsenic were not made. Analysis was via ICP-OES in South Africa; as such, detection limits were potentially in the low µg/l range, however, quantified concentration data below 50 µg/l were not reported. Mapoma *et al.* (2017) present a 2015 survey of groundwater-quality constraints upon drinking-water and irrigation use (for rice growing), sampling 25 boreholes of 35-60 m depth in the Karonga District alluvial plain aquifer that borders northern Lake Malawi. Arsenic analysis was conducted in China using ICP-OES. Most boreholes tested were in the 1-10 µg/l range, with four just exceeding the WHO 10 µg/l drinking-water guideline, up to 14.5 µg/l. The arsenic mean of 7.2 ± 3.4 µg/l is indicative though of concentrations frequently approaching the WHO drinking-water guideline. Mapoma *et al.* (2017) emphasise the need for follow-up investigations in the district to clarify that the situation is not hazardous to human health, noting elevated arsenic is synonymous with hard water and high fluoride occurrence. Increased arsenic also correlates with more reducing conditions, although not that reducing compared to globally significant arsenic cases. They suggested that arsenic is perhaps mobilized by changes in groundwater redox coupled to fluid-rock interactions and pH change leading to dissolution of Arsenic-bearing minerals. They conducted some geochemical (PHREEQC) modelling substantiating this possibility. The study represents Malawi's most detailed consideration of hydrochemical controls upon local arsenic occurrence.

Ministry (MoAIWD) archive data: The MoAIWD laboratory does not include arsenic analysis within its current routine groundwater quality monitoring suite of 20-23 parameters, nor within any suites used previously (MoAIWD, 2017). Much of this analysis is conducted at the request of clients, mainly NGOs assessing (new) water-point quality. Inspection of the electronic archive groundwater quality concentration data within all available databases collated from 1980 to 2017 failed to reveal any arsenic concentration data. Detailed in MoAIWD (2017), and commented upon in Rivett *et al.* (2019), the MoAIWD's laboratories require significant investment. Whilst wet-chemistry-photometry methods or test kit methods for arsenic could be implemented, reagent kit costs largely prevent their routine use (in the absence of obvious health concerns). Although an atomic absorption

spectrophotometry (AAS) instrument is housed by the laboratory in Blantyre, and capable of low µg/l arsenic detection, the near obsolete instrument is reported as faulty and not used (MoAIWD, 2017). Facility investment is, however, being made with the recent acquisition of an AAS for the headquarter Central Water Laboratory and an ICP-OES (or MS) is proposed within the National Water Resources Master Plan (MoAIWD, 2017).

A trawl of data held by the MoAIWD arising from third-party (e.g., NGO) activity found two datasets. An NGO's dataset from a 2016-17 survey revealed below detection limit, <1 µg/l, arsenic for all 229 borehole samples taken from the Dowa District, with similar results for 27 borehole samples from the Kasungu District, both located north of Lilongwe in Basement rock (Fig. 3). Significantly, arsenic analysis was a condition imposed upon the NGOs by their funders to ensure water delivered from installed water points was safe for human consumption. The MoAIWD laboratory undertook analysis for most determinants, but out-sourced arsenic analysis via AAS to the ARET (Agricultural Research and Extension Trust) laboratory in Malawi. A second dataset held by the MoAIWD from a different NGO contained results from sampling in 2018 of 65 boreholes around Liwonde in Machinga District (Fig. 3). The area is close to the Shire River and overlies alluvial or Basement rock units. Analysis was via AAS with all samples below the <3.7 µg/l detection limit.

Potentially some further arsenic data could exist. Mapoma and Xie (2014) comment "Arsenic is not a problem currently based on spot checks carried out by the ministry"; however, these data were not found in the MoAIWD archive collated. It is possible that further unpublished data may be held by NGOs, or perhaps other visiting international research bodies and/or their collaborating universities in Malawi.

2014-18 Survey Results: Our survey results for 2014-16 and 2018 are summarised in Fig. 3. Sample-point locations exhibiting detectable arsenic are circled in Fig. 2. None of the 2014 surveys covering the TA Ngabu basaltic bedrock, the alluvial aquifer to the immediate east and Kakoma - Mwanza Valley exhibited detectable concentrations of arsenic registering 'zero' concentration using the test kit. It was concluded arsenic throughout was below the kit minimum 10 µg/l positive detection threshold. Similar, below detection, results were obtained for the more spatially intensive survey of the Kakoma alluvial aquifer in 2015. The 2016 re-survey of the TA Ngabu basaltic bedrock and alluvial aquifer systems also reconfirmed below 10 µg/l detection threshold

concentrations across these areas. Quantified arsenic concentrations in the Mwanza Valley survey in 2018 near Kakoma were all below 3 µg/l with the exception of one piezometer sample at 4 µg/l. It was therefore concluded arsenic throughout the sampled regions of these aquifer was consistently below the WHO drinking-water guideline of 10 µg/l, and comfortably within the Malawi drinking-water Standard of 50 µg/l. These results were observed despite our targeting of geological systems in Southern Malawi thought to be at higher risk of arsenic contamination based on rock-type characteristics. It remains unclear if the low arsenic relates to an absence of hydrochemical solution (groundwater) conditions favouring arsenic release from sediments, or an absence of potentially available arsenic within the aquifer sediment itself, or both. Our supporting hydrochemical data endorse conceptualisation of a typical alluvial valley – escarpment bedrock/Basement system (Rivett *et al.*, 2018, 2019). This comprises a lower TDS recent recharge Ca/Mg–HCO₃ type groundwater in shallow fractured escarpment and valley margin alluvial units developing to medium TDS, ion-exchange influenced, Na–HCO₃ groundwater mid-plain, to highest TDS, potentially brackish, Na–Cl (SO₄) groundwater towards groundwater discharge areas around the Shire River lowlands. The lack of quantified arsenic concentrations in the 0.1-10 µg/l range and adequate definition of reducing (redox) conditions limits analysis of controls upon the expected heterogeneous occurrence of low (<10 µg/l) arsenic concentrations and correlations with arsenic presence (as developed by Mapoma *et al.* (2017) for Karonga District, per above). Partial insight though was achieved by using iron data to infer redox conditions, and with observed pH, assess potential arsenic mobilisation. Preliminary geochemical modelling with reference to arsenic (and iron) pH-E_H phase diagrams and use of the 2014 basaltic rock survey groundwater pH (6.02-8.11 range, mean 6.93 ±0.47) and total iron (0.05-0.8 mg/l, mean 0.20 ± 0.17 mg/l) and 2014 alluvial survey pH (6.37-8.02, mean 7.20 ±0.43) and total iron (0.02-0.77 mg/l, mean 0.30 ±0.18) data (Melville, 2014; Wild, 2014), soluble arsenic species were predicted over the range of groundwater conditions sampled. This may infer a lack of arsenic-bearing minerals could account for the observed low arsenic.

Geothermal groundwater survey results: Test kit analysis of both boreholes surveyed in 2016 in Neno District (Fig. 2) containing geothermal groundwater, although below the first increment of positive detection of 10 µg/l, registered faint colouration above the typical ‘zero’ colour. Observed temperatures of 39°C and 50°C confirmed significant geothermal groundwater contributions.

The 2018 geothermal survey found 11 sites below the 3 µg/l detection limit, but with four sites detecting arsenic (Fig. 2). The Site 9 borehole (July Village) recorded 4 µg/l within the alluvium/colluvium underlain by Karoo sediments adjacent to the exposed Basement lithology of the Mwanza Fault footwall; Site 5 borehole (Mapundi Village) exhibited 9 µg/l within colluvium underlain by Basement with proximal faulting (intrusions absent); and, spring Sites 4 and 3 at 10 µg/l and 12 µg/l respectively, located 400 m apart at Manondo Village. The springs discharge from Pre-Cambrian Basement hornblende-biotite gneiss (with epidote) and are located along an E-W trending fault connected to a network of smaller faults and a nearby phonolite intrusion (Robinson, 2018). Both borehole sites are used for drinking-water - domestic supply and both springs for bathing and domestic activities (Robinson, 2018). Whilst solid-phase arsenic is expected to be low in the biotite-hornblende gneiss (Fig. 1), this lithology is common to these sites, hosting Site 3 and Site 4, underlying Site 5 beneath colluviums, and adjacent to Site 9. Despite the modest concentrations, a plot of arsenic versus groundwater temperature (Fig. 4a) confirms detectable arsenic was found in the warmest boreholes (both 49 °C) and springs (38°C and 41°C) and corroborates the significance of geothermal waters to arsenic occurrence in supplies. Several chemical parameters further endorse the importance of geothermal contributions by similarly exhibiting increased concentrations with sampled groundwater temperature. For instance, increased lithium with temperature (Fig. 4b) may be ascribed to its frequent occurrence in geothermal waters (Rowland *et al.*, 2011) and deep subsurface brines with elevated lithium (albeit tightly bound) found within granitic rocks. Lithium concentrations significantly exceeded the mean of 23±2 µg/l found in Irish shallow-granite groundwater (Kavanagh *et al.*, 2017). Increased fluoride with temperature (Fig. 4c) is likewise attributed to hydrothermal sources, common in the EARS. Malawian groundwaters in the eastern alluvial plain rift zone and Central Malawi Basement are likely to be most influenced by fluoride (BGS, 2004). Fluoride poses the most significant health risk of the parameters analysed, with concentrations approaching 10 mg/l, and 73% of samples above the WHO 1.5 mg/l drinking-water guideline. Sodium, considering multiple source and ion exchange influences possible, exhibits a particularly linear increase with temperature that could be attributed to the influence of deep geothermal brines (Fig. 4d). Arsenic in geothermal waters may arise from fluid-rock interactions of arsenic-bearing minerals such as pyrite in the thermal reservoir, or by migrating hot fluid scavenging of

arsenic from overlying aquifer rocks (Rowland *et al.*, 2011). The relative importance of these processes controlling arsenic occurrence and the hydrochemistry and energy resource value of geothermal groundwaters

are the subject of on-going work that is supported by stable isotope facilities recently developed in Malawi (Robinson, 2018).

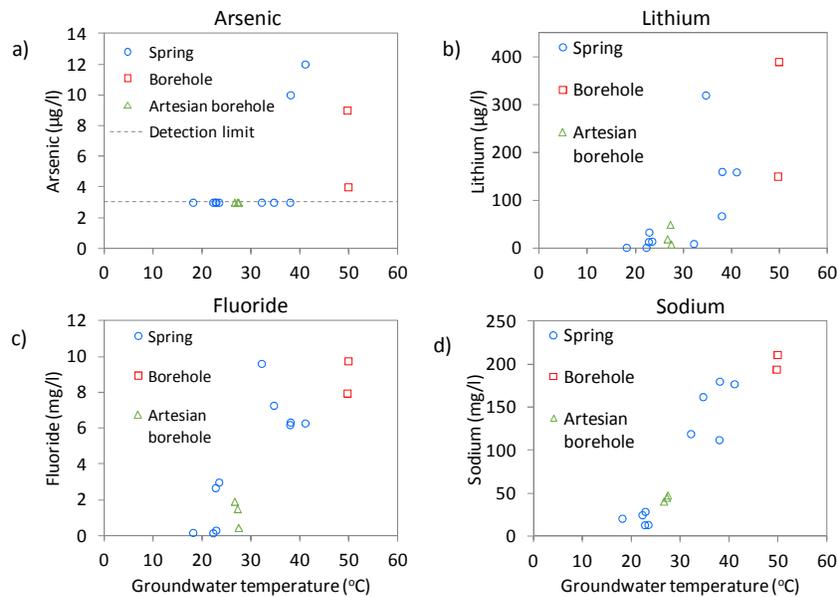


Fig. 4. Geothermal groundwater 2018 survey: plots of groundwater temperature versus: a) arsenic, b) lithium, c) fluoride, and d) sodium.

In summary, the geothermal survey data reinforce the significance of geothermal water components controlling observed water quality and arsenic occurrence. Arsenic concentrations detected in the geothermal groundwaters are the highest found in our surveys, but remain modest at $<15 \mu\text{g/l}$, and comparable to the archive Malawian literature survey maximum (Fig. 3). Hence, although maxima just exceed the WHO $10 \mu\text{g/l}$ drinking-water guideline and are thus somewhat troublesome, arsenic concentrations observed to date throughout Malawi still remain comfortably within the $50 \mu\text{g/l}$ limit applied for water delivered from boreholes and protected shallow wells (Malawi Standards, 2005). The findings overall affirm earlier expectations for the Malawian (hydro) geological circumstance that arsenic concentrations in groundwater may be generally low (BGS, 2004). The troublesome breaches of the current WHO drinking-water guideline though still point to the need for further investigations of areas prone to geothermal groundwater contributions and, or reducing conditions, especially in alluvial aquifer systems with natural or anthropogenic sources of organic matter. In total, 919 groundwater samples (Fig. 3 total) have been subjected to arsenic analysis, representing testing of just 1% of water points projected to now exist across Malawi. Hence there remains significant work to be done in the further

assurance of water supply quality. Given that arsenic concentrations detected to date are mainly in the $1 - 20 \mu\text{g/l}$ range, there is a parallel need for Malawi (the MoAIWD) to develop modern laboratory facilities and capacity to routinely determine concentrations within this range and possible variation in population exposures to groundwater arsenic.

Conclusions: Our surveys and sparse literature confirm arsenic in Malawian groundwater appears low, and well within the national $50 \mu\text{g/l}$ standard applied. Most groundwater supplies were below the $10 \mu\text{g/l}$ WHO drinking-water guideline, with marginal breaching in one alluvial-aquifer literature survey, and our survey samples containing geothermal groundwater contributions. Further research is needed to confirm human-health risks are low; including, increased monitoring of the great many hand-pumped supplies, and assessing hydro-biogeochemical controls on the higher arsenic concentrations found.

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