

Reconnaissance study of groundwater quality in the artisanal gold mining districts of Migori County, Kenya

BGS GLOBAL - EASTERN AFRICA ODA PLATFORM Open Report OR/21/012



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Front cover

Well in Kabobo, Migori, Kenya, with tailings reprocessing in cyanide vats in the background.

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B Palumbo-Roe, L Olaka, R Bell, C Mitchell, T Bide, C Odiwuor, T Barlow

Contributor/editor

A MacDonald, J Muluu & E Odada

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British Geological Survey offices

Nicker Hill, Keyworth,

Nottingham NG12 5GG Tel 0115 936 3100

BGS Central Enquiries Desk

Tel 0115 936 3143 email enquiries@bgs.ac.uk

BGS Sales

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The Lyell Centre, Research Avenue South, Edinburgh EH14 4AP

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Cardiff University, Main Building, Park Place, Cardiff CF10 3AT

Tel 029 2167 4280

Maclean Building, Crowmarsh Gifford, Wallingford OX10 8BB Tel 01491 838800

Geological Survey of Northern Ireland, Department of Enterprise, Trade & Investment, Dundonald House, Upper Newtownards Road, Ballymiscaw, Belfast, BT4 3SB

Tel 01232 666595 www.bgs.ac.uk/gsni/

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon SN2 1EU

Tel 01793 411500 Fax 01793 411501 www.nerc.ac.uk

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Foreword

This report summarises a groundwater quality reconnaissance study carried out in November 2019 in Migori, Kenya, by the British Geological Survey (BGS) in collaboration with the Department of Geology at the University of Nairobi (UoN), as part of the Integrated Research Project: "Small-scale Artisanal Gold Mining and Water Quality in Kenya", funded by the BGS Official Development Assistance (ODA) programme Geoscience for Sustainable Futures, RP1: Integrated Natural Resource Management in eastern Africa (NERC Grant ODA-NC NE/R000069/1). BGS staff were licensed to conduct research in Migori by the Kenyan National Commission for Science, Technology & Innovation under licence NACOSTI/P/19/2208.

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Summary

Information on groundwater quality in areas of artisanal and small-scale gold mining assists in the sustainable development, use and protection of groundwater resources. Groundwater contamination associated with mining may occur for different reasons: from pumping of mineralised and acidic mine water due to oxidation of previously reduced ore; from point or diffuse sources of contamination, mostly represented by leaks and runoff from mine tailings; and from leaks of spent water from processing plants. The extent of groundwater contamination is also influenced by many variables besides mining practices, including climatic conditions, geology and geomorphology, and their interaction.

The British Geological Survey (BGS) collaborated with the University of Nairobi to carry out a groundwater quality reconnaissance and mine drainage characterisation in Migori County, Kenya. Migori County is a major artisanal and small-scale gold mining (ASGM) centre located near Lake Victoria, in southwest Kenya, close to the Tanzanian border. Gold is produced from quartz–carbonate veins within the meta-volcano-sedimentary rocks of the Precambrian Migori Greenstone Belt.

This report describes the sampling and chemical analysis results of baseline water samples collected from twenty-one boreholes, dug wells or springs and seven mine shafts and panning ponds during the rainy season in November 2019. Samples were analysed for inorganic chemistry composition.

The analysed inorganic constituents of waters from the boreholes, dug wells, and springs reveal that most parameters are within the acceptable limits of the World Health Organization drinking water standards (WHO, 2017). Nevertheless, there are a number of WHO exceedances of the permissible drinking water limits. These are summarised below.

The nutrient nitrate (NO₃) content is generally low and only found above the WHO drinking water standard of 50 mg/l in one dug well and one spring, which may be impacted by contamination from domestic wastewaters, household septic tanks and pit latrines.

The fluoride (F) content is generally less than the WHO drinking water standard of 1.5 mg/l, with three exceedances out of twenty-one groundwater samples, all deep (>50 m) groundwater and with F less than 2 mg/l.

Arsenic (As) shows more exceedances of the WHO drinking water quality guideline of 10 μ g/l, in five of the twenty-one groundwater samples (values from 13.7 μ g/l to 129 μ g/l). Although high arsenic in groundwater has not previously been recorded in the area, these new findings are comparable to values already known from neighbouring mining areas in the Lake Victoria Basin in Tanzania. The primary source of As is likely to be the As mineral arsenopyrite (FeAsS), which constitutes an important part of the ore assemblage in the gold-quartz veins. The relative importance of anthropogenic and geogenic sources and the processes affecting high concentrations of arsenic in groundwater require further research.

Other trace elements (e.g. Cd, Co, Cu, Ni, Pb, Sb, Zn) also potentially linked to the quartz-gold vein ore mined in the area are found in low concentrations and, for those elements of health-based concerns, are below the relevant drinking water quality standards in all the groundwater samples.

Mercury (Hg) data have been reported, although all values should be taken as a minimum due to a problem with field preservation during sampling. Mercury presence in ASGM areas is due to its use to extract gold from ore as an amalgam, and is a major human health concern. Provisional total mercury concentrations were well below the WHO standard for drinking water of 6 μ g/l (for inorganic mercury) in all groundwater samples, with a median value of 0.016 μ g/l. A relatively high value of dissolved Hg of 0.16 μ g/l was found in a dug well water in the proximity of an ASGM site. At this site gold is extracted from tailings via tank leaching using cyanide solution and spent tailings heaps accumulate. This single sample may indicate the potential environmental threat that the cyanide gold leaching practice of mercury-laden tailings poses to groundwater, due to the formation of water-soluble cyanide-mercury complexes which enhance mercury mobility. Additional sampling and analysis of mine waters was done, as they are a potential source of contamination and also, in some cases, may be used for domestic water supply. The mine water was sampled from shafts at four sites where gold-quartz veins are mined. The mine waters, sampled from shafts mining the gold-quartz veins at four different sites, show wide variation in the concentrations of total dissolved elements, but none of them are acid, with a range of near-neutral pH values from 6.19 to 7.75. They are all bicarbonate waters and their conductivity (SEC) increases with mine shaft depth (SEC 164 to 1733 μ S/cm). Fluoride and arsenic are the only elements that exceed WHO drinking water standards. Fluoride is above the WHO of 1.5 mg/l in one deep mine. Arsenic is above the WHO standard of 10 μ g/l in all four mine waters and greatly exceeds the limit in two of them (178 and 190 μ g/l).

The chemistry of water from two panning ponds and tailings leachate confirms previous findings, being highly mineralised, with sulphate as major ion. There is variable composition in terms of potential hazardous elements, which is likely to reflect the different ore type processed at each mine: i) very acid (pH 3) metal-rich waters at Macalder, associated with the reprocessing of past tailings from mining of the Macalder poly-metallic Volcanogenic Massive Sulphide ore deposit; and ii) pH neutral waters with low hazardous element content at Osiri mine. Mercury was detected at concentration of 1 μ g/l in the Osiri mine pond.

1 Introduction

Migori County is a major artisanal and small-scale gold mining (ASGM) centre located near Lake Victoria, in southwest Kenya, close to the Tanzanian border. Gold is produced from quartz–carbonate veins within the meta-volcano-sedimentary rocks of the Precambrian Migori Greenstone Belt. The local economy is strongly tied to ASGM, which provides the main source of livelihood for approximately 10,000 residents and takes place at sites in Nyatike, Rongo, Suna East, Suna West, Kuria East, and Kuria West Sub-counties (Barreto et al., 2018). However, as well as economic benefits, mining operations can have an adverse effect on the environment, including contamination of soil, sediments, waters, and the ecosystems they sustain. There is previous evidence of widespread contamination of harmful elements, including mercury, in soil, sediments in Migori (Odumo et al., 2014, Ngure, 2014); however, there have been no comprehensive studies of groundwater quality in relation to on-going mining activities. Given the importance of groundwater for water supplies in rural Kenya (Lapworth et al., 2017), information on groundwater quality in areas of artisanal and small-scale gold mining is essential to assist in the sustainable development, use and protection of groundwater resources, so that drinking water can be adequately treated and the contamination can be prevented.

The British Geological Survey (BGS) collaborated with the University of Nairobi to carry out a groundwater quality reconnaissance in Migori County in November 2019. This report describes the sampling and chemical analysis results of twenty-eight water samples which were collected from boreholes, dug wells, springs, mine shafts and panning ponds during the rainy season (November 2019) in Migori County, Kenya.

1.1 PROJECT AIM

The purpose of the groundwater reconnaissance in the present study was to carry out a baseline characterisation of the groundwater quality in the area and a characterisation of the mine water. The definition adopted in this study of "baseline" refers to the actual content of an element in the environment at the time of measurement (Nordstrom, 2015; Salminen and Gregorauskiene, 2000). In an area of heavy anthropogenic impact, such as mining areas, the geochemical baseline includes the geogenic natural content (background) and the potential anthropogenic diffuse contribution.

The new data are used to identify the presence or absence of particular quality concerns and to assess the present suitability of groundwater inorganic chemistry for drinking purposes. The mine waters were included in the study both because they represent a potential source of contamination and also, in some cases, a household water supply.

The number of sites sampled and the range of chemical substances analysed should not be considered a comprehensive environmental survey. The results reported here refer only to the sites sampled at the time of the survey, and the absence of evidence for contamination by particular substances at these sites should not be used to assume contamination is not present at other sites in Migori County or elsewhere in the region. These results reflect the level of resources available for the study: the accuracy of the conclusions on groundwater quality will be improved if more samples are analysed.

1.2 SAMPLING STRATEGY

There is significant artisanal and small-scale mining in Migori County. Aerial photography from Google Maps® indicates numerous shafts and clustered surface mining operations, and heaps of tailings scattered across the rural landscape. Sampling areas were selected to cover known present and past mining areas. The distribution of existing boreholes, wells and springs was the main control on potential sites for groundwater sampling. Permissions and the accessibility of some boreholes (for example inaccessible wells in school premises during the national school exam period) influenced the sampling locations. Sampling strategy was designed to target all these water supply types: shallow hand-dug wells (generally <10 m deep); hand-pumped boreholes, (generally <30 m deep); deep boreholes with mechanical pumps (generally >50 m deep); springs; and mine shafts. Additional mine processing waters and mine waste leachates

were collected from mine sites to gain an indication of contaminant sources from mining activities, which could infiltrate to groundwater through the unsaturated zone.

Water sampling was carried out during the period 15th to 20th November 2019.

1.3 STUDY AREA

Migori County is located south of the Winam Gulf in western Kenya, close to the Tanzanian border (Figure 1); subcounties are Nyatike, Rongo, Awendo, Uriri, Suna east, Suna west, Kuria west, and Kuria east

Migori has a tropical climate, and the average annual temperature is 21.2 °C, with annual precipitation about 1369 mm. Rainfall is bimodal, with rains in March to May and September to November. The driest months are between December and February.

The main rivers in the county are the Kuja, also known as Gucha, River, Migori River and Riana River, all of which originate in the highland region of Kisii and Narok counties.



Figure 1 Study area: Google map of Migori area (retrieved December 15, 2021 from https://www.google.com/maps/place/Migori,+Kenya/).

1.4 GEOLOGY AND MINERALISATION

The regional geology is represented by the Precambrian Migori Greenstone Belt of south western Kenya, which is dominated by Nyanzian and Kavirondian rocks that form the Nyanza Craton. The Migori Greenstone Belt is 20 km wide north-south and extends for 80 km along a northwest-southeast strike from the Tanzanian border to the Winam Gulf. It is responsible for most of Kenya's gold production. The Nyanzian and Kavirondian rocks are among the oldest in Kenya, approximately 2.8 billion years old. The Nyanzian system comprises a metamorphosed volcanosedimentary succession, with a series of extrusive volcanic rocks (e.g. lavas and tuffs) alternating with sediments and banded ironstones. The Kavirondian, which rests uncomfortably on the Nyanzian, consists of grits, sandstones, mudstones, greywackes and conglomerates.

In the study area the 'Migori Gold Belt' comprises the southernmost section of the greenstone belt. It consists of a Nyanzian meta-volcano-sedimentary succession of turbidites, shales, tuffs, basalts, dacites, dolerites, andesites and rhyolites (Shackleton, 1946), which were deposited in a sedimentary basin with major volcanic centres at Macalder and Lolgorien. Both the Nyanzian and Kavirondian systems are isoclinally folded about axes that have an east-westerly trend. The Kavirondian system is only slightly younger than the Nyanzian, but folding in the two systems has

similar orientation. The Gold Belt is bounded by the Migori granite to the south and the younger Archean Kitere and Kilgoris granites to the north (Shackleton, 1946).

Gold mineralisation occurs within banded iron formations, tuffaceous rocks and most commonly in steeply dipping, strike parallel, quartz veins often associated with steeply dipping strike slip faults (Ichang'I, 1993; Ogola, 1987; Ogola, 1993; Sanders, 1964; Shackleton, 1946).

Gold is mainly associated with sulphide mineralisation and consists of fine-grained, granular aggregate of pyrite, pyrrhotite, chalcopyrite, magnetite, arsenopyrite, sphalerite and galena (Du Bois and Walsh, 1970). It is most commonly found along microfractures within pyrite and inclusions in arsenopyrite (Ogola, 1993).

The highest concentrations of gold are found within the steeply dipping veins within turbidites, andesites and tuffs, in close proximity to the contact with the Migori Granite to the south west of the belt. Auriferous veins generally occur parallel or sub-parallel to the strike of host rocks and dip towards the granite contact. The orientations and spatial relationship of these veins to the granite suggest mineralisation was related to fluids generated by the granitic intrusion circulating through the metal rich volcano-sedimentary succession post deformation and metamorphism of the greenstone belt (Ogola, 1987; Ogola et al., 2002). Of lesser importance are laterally persistent quartz veins controlled by major strike-slip faults oblique to the strike of host rocks, these occur more widely spread than the strike-parallel veins, but gold grades are generally lower (Ichang'i, 1993).

Banded iron formations (BIF), which are found throughout the belt associated with tuffs and breccias proximal to volcanic centres, often contain sulphide related gold mineralisation. It is not well understood if this mineralisation is syngeneic, related to circulation of fluids during emplacement or epigenetic related to later granitic magmatism or possibly a combination of both with late stage fluids re-mobilising sulphides (Henckel et al., 2016). Gold bearing banded iron formations occur in the Macalder deposits (but not the main host for gold here) and, as the main host for gold, in the Kilimapesa mine, further east at the opposing end of the belt to Macalder.

Also of note are Cu-Au-Ag deposits around the Macalder area, which have been worked for copper, zinc and silver, and are currently worked for gold by small scale operations. The relationship of the sulphide orebody and nearby volcanic centres possibly suggest a VMS Kuroko style massive sulphide (Ichang'i and MacLean, 1991). Similar deposits are seen in equivalent Archean greenstone belts in the Canadian Shield. Much like the banded iron formations, however, there is some uncertainty as to the mineralisation processes. The stratabound, stratiform morphology of the orebody, lack of alteration pipe and stockwork zone and relationship to nearby lithological units suggest syngenetic origins (Ichang'i and MacLean, 1991). However, there has been some suggestion that the brecciated volcanic rocks associated with subaqueous eruptive centres may have acted as traps for later stage metasomatic replacement by gold bearing fluids in an epigenetic setting (Ogola, 1987; Ogola et al., 2002). It has been noted that gold concentrations in the Macalder deposit are much lower than other confirmed VMS deposits from elsewhere in the Tanzanian Craton and are more within the range of more typical Archaean base metal massive sulphide deposits (Henckel et al., 2016).

1.5 HYDROGEOLOGY

Limited hydrogeological information is available for this region of Kenya. No new detailed hydrogeological investigations were carried out as part of this study. This assessment is, therefore, based on previously available information.

The variable lithology, in combination with the steeply dipping, complex structure, means that the local hydrogeology is both laterally and vertically heterogeneous. It is also complicated by the presence of a shallow weathered lateritic zone (laterite is an iron- and aluminium-rich tropical weathering soil) and variable overlying alluvial sediments. Simplified maps of aquifer characteristics (Africa Groundwater Atlas, 2019) show the area is dominated by basement rocks with low-moderate yields, with unconsolidated sediments (alluvium) in the north-west that typically have moderate yields.

The main source of information on groundwater in the area is the Migori-Kihancha Regional Master Plan (1974), which documents water and land uses in the region and assesses the

potential for water supply development. The Plan covers the Gucha and Migori catchments and reports that the lack of any extensive groundwater resource and development is due to the limited potential of the igneous and metamorphic rocks to transmit water. Additional hydrogeological reports were collected for this project from the Water Resources Authority (WRA) in Kisii Town, Regional Office for Lake Victoria South Catchment Area for the villages of Masara (NP/MGR/WRG-2018), and Mukuro (NP/MIG/WRG-2011). The aquifer properties of similar igneous and metamorphic rocks have also been studied elsewhere in Africa (e.g. Ofterdinger et al., 2019, MacDonald et al., 2008), providing useful analogues for probable groundwater flow mechanisms in this region.

The complex geology of the area can be split into:

- a shallow, unconfined superficial alluvial aquifer, in the north-west of the study area;
- shallow (10–50 m) laterite with variable permeability, found across the area;
- a deeper bedrock (80–200 m), semi-confined aquifer comprised of Nyanzian metamorphosed volcano- sedimentary rocks. To the south the study area is bounded by the Migori Granite. In the north the Nyanzian sediments are overlain by younger Kavirondian metasediments.

The superficial alluvial sediments are only found locally below the confluence between the Gucha and Migori rivers. The texture of these sediments is largely unknown, but the Regional Master Plan indicates it is composed of layers of silt, gravel and lava fragments. The potential yield of this unconsolidated aquifer is likely to be ~ 3 l/sec, based on data collected from boreholes in similar alluvial aquifers in the region. Groundwater stored in the alluvial aquifer is likely to provide some recharge to the underlying Nyanzian bedrock aquifer, although this may be complicated by the complex, multi-layered nature of the bedrock aquifer.

The groundwater potential of the highly variable shallow laterite is largely unknown. The Regional Master Plan states that the Nyanzian bedrock aquifer is confined by a relatively impermeable layer of weathering products. However, hand-dug wells in the study area are likely to be installed into the laterite layer which, from field observations, reaches a thickness of a few metres. No yield data is available for the aquifer in this area, but previous work in Nigeria (Bonsor et al., 2014), which looked at the vertical variations in hydraulic conductivity (K) of laterite soils, showed that yields are likely to be highest close to the surface (K 100–400 m/d) and decrease with depth (up to 6 m below ground level) where weathering is less developed (K 0.03–0.1 m/d). The laterite is likely to be in variable hydraulic continuity with the underlying bedrock aquifer.

The Nyanzian bedrock is the main aquifer in the study area, with a complex sequence of steeply dipping volcano-sedimentary rocks, including tuffs, lavas, shales and banded ironstones. The complex regional geology may have created a compartmentalised aquifer, which is bounded to the south by the Migori Granite and overlain in the north by younger Kavirondian age rocks. The fracture and fissure system in the Nyanzian aquifer occurs at various depths, the main supply of water often being struck at about 50–60 m and rest groundwater levels varying between 5 and 50 m below ground level (Regional Master Plan, 1974).

Estimated yield data given by the Regional Master Plan for the Nyanzian aquifer is ~1.36 l/s from borehole tests. From tests in the same Nyanzian aquifer outside the Migori region, yield estimates are <1 l/s. These yields are lower than typical from volcano-sedimentary rocks (Macdonald et al., 2008), and indicate the impact of metamorphism on the aquifer, which has reduced the aquifer productivity so that yields are more comparable to those in Basement aquifers.

Recharge patterns and volumes to the aquifer are uncertain; the Regional Master Plan suggests that recharge is limited to direct infiltration of rainfall into the fracture systems and through alluvial sediments in the north-west. Groundwater flow and storage in this Nyanzian bedrock aquifer are likely to be, preferentially, at the boundaries of individual lava and tuff layers; in fractures; and in solution cavities in tuffs and along fault zones (Regional Master Plan, 1974). Previous research into the storage and transport of groundwater in complex metamorphic aquifers (MacDonald et al., 2008) suggests that the top and bottom of lava flows are often highly fractured and weathered, allowing for horizontal groundwater flows, while faults and fractures allow vertical flows. However, overall the permeability and porosity of the Nyanzian aquifer is likely to be low, due to the impact

of metamorphism. Regional groundwater flow directions in the Nyanzian aquifer have been identified as being towards the north-west and Lake Victoria (Regional Master Plan, 1974).

The majority of springs occur in dissected landscapes of the Migori Granite (Figure 4), where rainfall is higher than across the rest of the region. The presence of both vertical and horizontal joints in the Migori Granite is favourable both for infiltration of recharge to boreholes and outflow of groundwater via springs.

Borehole records and geophysical data used to estimate the thickness of underlying layers and their potential as aquifers, from available WRA reports, indicate that there are generally two aquifers, a shallow aquifer with low groundwater potential between 10 and 50 m depth, within the lateritic formation and/or the uppermost, partially weathered bedrock, and a second aquifer, considered to be productive even though the yield differs from place to place. This aquifer is estimated between 80-200 m within moderate to highly weathered and or fractured intrusive igneous rocks. A maximum borehole depth of about 200 m is recoded in the study area, below which the Nyanzian rocks are massive and largely unfractured, and contain very little or no groundwater.

1.6 PAST AND PRESENT MINING

Gold was discovered in the Migori Gold Belt in 1920. An overview of historic mining and current prospects across the entire region is given in Henckel et al. (2016). There were large scale mining activities in the area between 1930 and 1966 (Ogola, 1987, Ogola et al., 2002). The largest mine was Macalder, opened in 1941, which initially extracted gold from the oxidised zone of the massive sulphide orebody; once the primary ore was reached, copper and zinc were mined, with gold and silver as by products. The primary sulphide ore was a fine-grained streaky aggregate of pyrite, pyrrhotite, chalcopyrite, magnetite, arsenopyrite, zincblende and galena with interstitial calcite. Chlorite was often abundant in vein margins. Gold was present as electrum and a small percentage of cobalt was detected.

A detailed outline of operations and mineral occurrences at the Macalder mine is given in Du Bois and Walsh (1970) and Shackleton (1946). The mine ceased operations in 1966. The Migori-Kihancha Regional Master Plan reported that at the time of the survey (1974) Macalder mine was producing copper only, employing a process called solution mining. Solution mining was carried out by pumping dilute sulphuric acid into a pipe network with nozzles in the ground and in old mining shafts. After about 3 months, the resulting copper sulphate solution was pumped out of the mine into precipitation tanks with scrap metal, which becomes coated with metallic copper through a redox reaction. The copper was then washed, dried and bagged as copper cement for refinement. It was reported that, although water was re-circulated in the process, there was a more or less constant overflow of water from the precipitation tanks at a rate of about 0.3 l/s, discharging into a small tributary of the Gucha river. Effluent stream showed a pH of 3, a copper content of 50 mg/l and zinc content of 12 mg/l (Migori-Kihancha Regional Master Plan, 1974). A "moonlike" landscape has been left by the past large-scale mining at Macalder, consisting of unstable piles of waste, abandoned excavations and large stretches of barren land.

As well as Macalder mine, many other companies carried out smaller gold mining operations that exploited relatively small, but rich auriferous quartz "reef" veins. By the time of closure of the mines, a total of 4,284 kg of gold, 1,210 kg of silver and 20,000 tonnes of copper had been recovered from the Migori Gold Belt (Ogola et al., 2002). Small placer deposits have also been worked from the Migori River in the past, but there are currently no operations exploiting this type of deposit and they are thought to be exhausted.

Artisanal gold mining has continued to date in various parts of the county, including in Masara, Macalder, Masaba, Kehancha, Kitere, Kamwango (Rongo), Migori, Osiri, Mikeyi, Carlos mines in Kehancha and Prancis mines in the Kuria-Transmara border. All current operations are small scale, working drifts, pits or shafts of varying depths throughout the Gold Belt. The largest hubs appear to be located near significant quartz veins near the Migori Granite contact, except the Kilimapesa mine, operated by Goldplat, which works gold hosted in banded iron formations at the eastern end of the gold belt (Goldplat, 2020), and notably includes numerous cyanidation facilities.

1.6.1 Field observations of ASGM in Migori

Field visit observations of the ASGM areas showed that gold mining and processing are carried out via underground extraction, crushing, milling, sluicing, and amalgamation using mercury, followed by amalgam burning and recovery of the gold (Mitchel et al., 2019). During sluicing and amalgamation, small basins/ponds next to the sluices provide water for slowly pouring milled ore mixed with process water over the wooden sluice box, which is lined with a mat (Figure 2, Figure 3). The same panning ponds are then used for amalgamation, where mercury is added to the concentrate recovered from the mats, and mixed by hand, resulting in the formation of a mercury gold amalgam. The amalgam is squeezed through cloth and taken for burning and sale to nearby traders. Throughout the process, tailings collect in the small basin at the end of the sluice and are periodically removed with a shovel and stacked in adjacent piles. They are re-processed multiple times through the sluice boxes to recover as much gold as possible.

The spent tailings are sold to the operators of cyanidation plants, which use cyanide to recover residual gold. Numerous large but seemingly informal cyanidation facilities were noted during field visits. No access to these sites was possible and the details of the operations are unclear.



Figure 2 ASGM ore processing units: sluice boxes used to concentrate gold from the other minerals in the milled ore, and tailings ponds.



Figure 3 ASGM ore processing units: sluice boxes and tailings ponds (top left); tailings dried out before being sold for reprocessing (top right); tailings leaching plant (bottom left) and cyanidation tanks (bottom right).

1.7 GROUNDWATER QUALITY AND MINING IMPACT IN THE STUDY AREA

1.7.1 Mine drainage composition and geoenvironmental models

Geoenvironmental models are useful by providing predictions of potential environmental issues associated with particular types of deposits during mining and mineral processing, especially when specific site data are scarce. The following paragraphs describe the main controls and associated features of natural and mine waters draining the gold mineral deposits recognised in the study area. A comprehensive description of the relevant geoenvironmental models can be found in Plumlee et al. (1999). Volcanogenic massive sulphide (VMS) deposits have some of the greatest potential for adverse environmental impacts because of the high acid-generating potential of high sulphide content. The geology/mineralogy of the deposit exerts a major influence on both pre-mining background water compositions and on mine drainage chemistry. Increases in total dissolved metals (e.g. copper, zinc, lead, and cadmium) in groundwater/mine waters generally correlate with higher associated sulphide mineral (e.g. pyrite, chalcopyrite, galena) content, and decreases in acid-neutralizing capacity. Evidence of very low pH leachates described in Macalder mine (Section 1.6) fits the general environmental signature of a VMS ore deposit.

By contrast, in small "gold-quartz-carbonate vein" ore type deposits, like the ones largely exploited in Migori, the relatively disseminated sulphide mineral content of the ore and the acid-buffering capacity of carbonate alteration assemblages generally prevent significant acid mine drainage, and mine waters are likely to exhibit near-neutral pH ranges, and low to moderate concentrations of dissolved metals (Plumlee et al., 1999). Enhanced acid mine drainage may still occur where local, relatively high sulphide mineral concentrations are present in gold ore or in tailings material as a result of enrichment during processing, or where much of the ore is hosted by rocks that have relatively low acid-buffering capacity.

Banded iron formations (BIF) are also known to host gold mineralisation in the area. Similarly to the gold-quartz vein type, the low base-metal sulphide content inhibits the development of significantly metal-enriched water. Ferruginous water might be expected.

1.7.1.1 NEUTRAL PH MINE DRAINAGE WITH ENHANCED ARSENIC

Despite a general low level of base (i.e non-ferrous) metal concentrations in the near-neutral pH mine waters, arsenic concentrations can be high. Arsenopyrite constitutes an important part of the ore assemblage in the gold-quartz veins. The mineral will also accumulate in the mine tailings. Elevated concentrations of arsenic may be released into water either by natural water-rock interaction and sulphide oxidation processes or as a result of pollution from mining activity. Processes involved in the release of soluble arsenic species are affected by variations in redox potential, pH, bulk fluid chemistry, and by microbial activity (Bowell, 1994). The most common processes responsible for elevated concentrations of arsenic in groundwater are: arsenopyrite oxidation caused by dewatering during mining, followed by dissolution of the arsenic secondary minerals precipitates by post-mining groundwater rebound; oxidation of arsenic-bearing mine tailings; desorption of arsenate species from particulates at high pH in oxidized weathered regolith; and the high mobility of reduced arsenite species in reduced groundwaters (e.g. Smedley et al., 1996; Craw et al., 2015). Specific chemical analyses of Migori mine water samples were not available ahead of this study to complement the information above. Nevertheless, analogy with studies in Tanzania (Kassenga and Mato, 2008; Ligate et al., 2016), revealing arsenic contamination of water sources in relation to on-going mining activities, suggested arsenic concentrations may also exceed safe drinking water standards in Migori.

1.7.2 Additional environmental concerns associated with gold mineral processing: mercury and cyanide

Mercury and cyanide, both used to enhance gold extraction in ASGM, are additional elements of environmental and human health concern associated with mineral processing and poor waste management.

The Minamata Convention on Mercury (UNEP, 2013) obligates parties to take steps to reduce and, where feasible, eliminate mercury use in ASGM, as ASGM represents the largest global source of mercury emissions and releases. Nevertheless, mercury amalgamation is still being used to aid gold recovery.

Mercury is released to the atmosphere when the amalgam is burned in small charcoal fires. Mercury vapour, besides representing a major pathway for human intake, can thus be deposited downwind causing local enrichment of mercury in soils (Callahan et al., 1994, Appleton et al., 1999). Some mercury will also remain in the panning ponds' waters (predominantly in particulate form), some in the pond tailings which are often reprocessed several times. Odumo et al. (2011a) provide the composition of water from these ponds at ore processing sites of Mikei, Osiri, Masara and Macalder gold mines. Analysis using Energy Dispersive X-ray Fluorescence (ED-XRF) technique showed a wide range of dissolved base metal and metalloids concentrations up to very high levels, including copper (Cu) up to 15000 μ g/L; zinc (Zn) up to 690 μ g/l; arsenic (As) up to 18000 μ g/l and lead (Pb) up to 210 μ g/l in all the mine waters. However, mercury was not seen above the detection limit of Hg 2 mg/kg, which could be due to its high density, so that it settles at the bottom of the pond with other sediment, rather than being present in solution.

Adsorption of mercury onto iron oxyhydroxide, clays, and organic particles is an important process that limits the concentration of mercury in waters. As a result, transport of mercury from mine sites to watercourses occurs primarily in the particulate phase and the concentration of dissolved mercury species is generally very low in the water column, as a consequence of effective adsorption (Van Straaten, 2000). However, sediments contaminated with mercury, once entering the water environment, are a concern because they are a source of elemental mercury and ionic mercury that can be converted to methylmercury, the most toxic form, which bioaccumulates in organisms and is transferred through the food chain up to humans, primarily through fish consumption.

The rate of mercury methylation, and therefore the amount of methylmercury produced, is a complex process, varies greatly in time and space, and depends on numerous environmental factors, including temperature and the presence and amounts of oxygen, organic matter, and sulphate. Acid mine drainage can provide a favourable environment for methylation of mercury, because the high concentration of sulphate typically present in these low pH waters is microbially reduced and ionic mercury is methylated as part of a metabolic process carried out by sulphate-reducing bacteria (Rytuba, 2000).

Of additional concern is the reprocessing of the tailings containing mercury using cyanide. It can pose a major source of mercury pollution and a potential threat to groundwater, especially when the cyanide gold leaching practice can enhance mercury release into aquatic environment due to water-soluble cyanide-mercury complexes.

Most cyanide used for gold extraction is recovered and recycled, but some inevitably remains in tailings liquor and can leak into regional groundwater networks. Any loss of cyanide to the environment is a major concern because it is toxic to a wide variety of organisms.

1.7.3 Pathways to groundwater contamination

Based on the above information, groundwater contamination associated with mining may occur by pumping of mineralised and acidic mine water (which develops from oxidation of previously reduced ore); or rebound of abandoned mine workings; by leaching and runoff from mine waste dumps and tailings; or from spent water from processing plants. The extent of contamination is influenced by many variables as well as mining practices, including geology and geomorphology, climate (e.g. precipitation), and their interaction.

1.7.4 Existing groundwater quality data

Data on groundwater quality in the study area are scarce. The Regional Master Plan (1974) reported groundwater, based on limited data from a few boreholes, wells and numerous springs, to be of excellent physical and chemical quality. Samples showed soft to medium hard waters with a slightly acidic pH. Some groundwater showed a higher pH value of 8.2. The principal anion was bicarbonate (HCO₃ 22–370 mg/l), and cations were relatively equally distributed, with sodium and calcium as dominant cations. Nitrogen compounds, which are indicators of pollution by human or animal waste or fertiliser, were almost entirely absent. The silica content was 35–50 mg/l and fluoride was generally less than 0.5 mg/l.

The University of Nairobi has carried out a study of looking at groundwater quality and quantity levels in Migori town, mostly focused on urban pollution. The study used borehole log data from the Ministry of Water and topography maps from the Mines & Geology department. Groundwater quality was found to be soft and of NaHCO₃ type. The main issue for ground water quality was nitrate (NO₃) and fluoride (F). They suggested that anthropogenic pollution was mainly caused by poorly managed waste disposal and the use of pit latrines.

Additional available chemical data from PhD dissertations, although limited to few trace elements, suggest a general better quality of groundwater from drinking water boreholes and wells compared to the mine effluents and mining impacted streams recorded in Odumo et al. (2011b, 2014) and Ngure (2014). In one study, twenty-one boreholes were sampled by Mazira (2011) in the peak wet (May) and dry (December) seasons in the Nyatike-Karungu areas, within 0–20 km radius of Macalder mine. The range in mean metal concentration in groundwater across the area during the dry season, analysed by the flame atomic spectroscopic method (FAAS), was Zn 0.04–0.19 mg/l, Cu 0.01–0.04 mg/l, Pb 0.63–2.48 mg/l, and Fe 0.44–1.63 mg/l. During the wet season was the range was Zn 0.03–0.37 mg/l, Cu 0.01–0.05 mg/l, Pb 0.51–4.02 mg/l and Fe 0.44–2.43 mg/l (Mazira, 2011). These groundwaters were within the safe recommended concentrations for drinking water for Cu and Zn, but the Pb WHO safe drinking water level of 0.01 mg/L was greatly exceeded in borehole waters in Macalder, Akala, and Masara.

Another study showed that water samples obtained from household drinking water supplies (source not specified) around Macalder mine and analysed by TXRF (Total Reflection X-ray Fluorescence) had safe levels of lead (0.01 mg/l) and undetectable levels of arsenic (Nyamai, 2016).

The impact of mining on groundwater flow regimes in the area is poorly understood, but is likely to be highly complex. The fractures and other voids which dominate groundwater flow in the Nyanzian aquifer have the potential to create rapid flow paths which, if groundwater is polluted, could pose a risk to groundwater-sourced drinking water supplies. Groundwater levels were monitored by an NGO at a water supply borehole (installed by Engineers Without Borders) during 2017/2018, located between the Macalder Mines and Migori and most probably drilled into the Nyanzian aquifer, in order to observe any effect of nearby gold mining operations. This showed drawdown from regular daily pumping, and a fall in groundwater level during the dry season. Some recovery is seen during the rainy season, although interpretation of these third-party data is limited as no raw data is available for analysis.

2 Methods

2.1 FIELD SAMPLING PROCEDURE

Groundwater was sampled from hand-dug wells and boreholes using existing hand- or solar powered-pumps, rope and bucket, or water taps (from five boreholes water was pumped into tanks provided with taps from which a sample was obtained). Groundwater was collected in Teflon sampling jugs, which were rinsed three times with sample water and then filled. Samples from springs, stream water and mine effluents were collected using a Teflon jug in the same way. The sample locations were recorded using a Global Positioning System (GPS). No purging was carried out of the boreholes or wells, but all were in constant use, so we assumed that samples were of fresh groundwater. Measurements of specific electrical conductivity (SEC), pH, redox potential (Eh), dissolved oxygen and temperature were carried out immediately on site using a separate, rinsed beaker. Dissolved oxygen measurements were obtained in airtight sample tubes filled immediately to prevent air contamination. Field alkalinity was determined by titrating 50 ml filtered water sample against $1.6 \text{ N H}_2\text{SO}_4$, using a bromocresol green indicator solution. Field Eh measurements were reported after conversion to the standard hydrogen electrode (SHE).

Water was sampled from the sampling jug and filtered using a plastic syringe and 0.2 μ m cellulose nitrate filter with the Swinnex® filter holder into high-density polyethylene (HDPE) plastic bottles, rinsed three times with the sample water. Dedicated subsamples of 0.2 μ m filtered water were stored in 100 ml borosilicate glass laboratory reagent bottles for mercury chemical analysis. The un-acidified sampling bottles were carefully filled just to overflowing to ensure no air bubble was trapped inside the sample container. The samples were labelled, and stored in ice boxes until the return to the base camp and then at 4 °C to avoid any major chemical alteration prior to analysis.

Samples for cation analysis were acidified with 1% v/v Aristar nitric acid + 0.5% hydrochloric acid on return to the UK and prior to analysis. The subsamples for mercury analysis were preserved with 2% Aristar nitric acid.

A sample information sheet was created for each sample and used to record sample ID, date of sampling, time of sampling, location and name of sampling site (including GPS coordinates if available), borehole details, sampling method, weather conditions, field measurements, container pre-treatment and preservations added, colour, odour, sediment and any other observation that the sampler considered may affect the results of the analysis.

2.2 HEALTH AND SAFETY

The team carried out the activity safely, taking into consideration the issues identified in the risk assessment and complying with the BGS Guidance note: A safe system of fieldwork (2019).

2.3 CHEMICAL ANALYSIS

Determination of Cl⁻, SO₄²⁻, NO₃⁻, NO₂⁻, Br⁻, F⁻, HPO₄²⁻ was done by ion chromatography (IC).

Determination of major, minor and trace element cations, including mercury (Ca, Mg, Na, K, Si, Total P, Total S, Ba, Sr, Mn, Total Fe, Li, Be, B, Al, Ti, V, Cr, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W,

TI, Pb, Bi, Th, U, Hg) in groundwater samples was done by inductively-coupled plasma mass spectrometry (ICP-MS), using an Agilent 8900 series triple quadrupole ICP-MS-QQQ with an octopole reaction system (ORS), in combination with an autosampler. The system was controlled by a computer through dedicated software (Agilent MassHunter), which also controlled the autosampler. The instrument was calibrated at the beginning of every analytical run using at least three standards and a laboratory blank for each trace element cation and three standards and a laboratory blank for each trace element cation and three standards and a laboratory blank for each trace element cation (Sc), germanium (Ge), 0.5 and 1 μ g/L. A mixed internal standard solution containing scandium (Sc), germanium (Ge), rhodium (Rh), indium (In), tellurium (Te), rhenium (Re) and iridium (Ir) was added to the samples at a fixed ratio of approximately 1:10 via a T-piece. Any suppression of the instrument signal caused by the matrix is corrected by the software using the response of an internal standard.

The non-purgeable organic carbon (NPOC) content was determined using a Shimadzu TOC-V CPH analyser with an associated ASI-V auto-sampler. These tests are included in the UKAS Accreditation Schedule for the BGS Inorganic Chemistry laboratories.

2.4 DATA QUALITY CONTROL

Multi-element quality control (QC) check standards, containing the trace elements of interest (c. $0.25 \mu g/L$ for mercury) and separate major element standards at varying element concentration, were analysed at the start and end of each ICP-MS run and again repeatedly after no more than every 30 samples. Quality control data are assessed using Shewhart Charts. Accuracy was also monitored by regular participation in the Aquacheck inter-laboratory proficiency testing scheme for waters, in which approximately 350 laboratories participate worldwide.

Each analytical run was independently verified by a different analyst, including post processing of the data for drift, dilution and collation.

Mercury (Hg) (from ICP-MS) analyses were made of dedicated subsamples stored in glass bottles. The lack of sample acidification in the field means that the samples might have suffered loss of Hg through sorption on the container walls or volatilisation if head space was present in the bottles, and all analysed values should be taken as a minimum.

Whilst mercury analysis is not in scope of accreditation, the method used mirrors in house laboratory method AG 2.3.21, which is fully accredited for 56 elements by UKAS to the requirements of BS EN ISO/IEC 17025:2017. Run-specific detection limits were calculated as three times the standard deviation of the 1% nitric plus 0.5% hydrochloric acid laboratory blanks inserted at regular intervals during the analysis.

A duplicate sample obtained as a field data quality control (QC) was analysed to check on the robustness of the sampling method. The field duplicate sample was collected in exactly the same way as the primary sample from that location, but half an hour later.

As a further QC check, one field blank sample was analysed with the batch of samples. This consisted of deionised Millipore® water instead of sample water, but prepared in the field using the same method and equipment, to check on any contamination from the sampling method or equipment.

Results for field duplicate samples showed good robustness of the sampling method. Measurement uncertainty arising from sampling was estimated as the relative percent difference between field duplicates (D): RPD = (D1-D2)100/[(D1+D2)/2], with acceptable variability between sample pairs (RPD) being < 10%. RPD ≤ 1 % was obtained for Ca, Na, K, Cl, SO₄, Ba, Sr, Mn, Mg, 2.6% for NO₃, 5.3% for Si, 8.2% for F; 6.7% for Fe. Greater RPD was measured for NPOC (21%), P (39%) and Ti (34%). The remaining trace elements above detection limits have RPD < 8%, except for Zn (33%), Cd, Pr and Nd (10%) and Sm, Eu, Gd, Tb (21–28%).

Concentrations of major and trace elements determined in procedural field blanks were negligible when compared with the reported data. ICP-MS detection limits are reported in Table 3.

For six water samples ionic charge balance exceeds the usually acceptable range of $\pm 10\%$, but is less than $\pm 36\%$. Due to significant elevated concentrations present in two water samples, ionic charge concentrations for Mn, Al, Co, Cu and Zn were included in the total cationic concentration (meq/I). This was in addition to the routine ionic charge calculation from Ca, Mg, Na, Mg (major components) and Sr, Ba, Fe and Li (minor components).

The mercury data is reported for information only since the subsamples for mercury analysis were not preserved immediately after sampling and the inherent chemical instability of this element could mean the subsamples are not representative. Therefore, careful interpretation of the data is required.

3 Results

A total of twenty-eight waters were sampled from six hand-dug wells, twelve boreholes, three springs, four mine shafts, two panning ponds and one spoil leachate. Figure 4 shows their location and underlying geology.



Figure 4 Sampling location and geology. Adapted from Shackleton (1946), Ichang'i and MacLean (1991) and Huddelston (1951). Groundwater sample symbols are: "Deep boreholes" representing mechanically (solar/diesel/electric) pumped boreholes with an inferred depth >50 m; "Hand-pumped boreholes" with hand-pump with inferred depth <30m; "Dug wells" very shallow (<10 m) dug wells.

3.1 BOREHOLE AND SPRING WATERS

3.1.1 Water quality

The hydrochemistry of samples from all the boreholes, hand-dug wells and springs, but not the mine waters, is described here and summary statistics reported in Table 1 and Table 2.

We have divided the data on the basis of water supply type, which best reflects the groundwater depth given the uncertainty or absence of borehole data at the time of writing. The groups are: "Boreholes (BH)" (N=8), representing mechanically (solar/diesel/electric) pumped boreholes with an inferred depth >50 m; "Hand-pumped boreholes (BH/HP)" (N=4), with inferred depth <30 m; "Dug wells (DW)" (N=6), very shallow (<10 m) wells, and "Springs (SP)" (N=3). These categories may reflect aquifers at different depths, and reflect potentially different vulnerability to contaminants from surface, and/or secondary water quality effects controlled by Eh/pH/residence time conditions.

3.1.2 Physico-chemical parameters

The groundwater specific electrical conductance (SEC) is variable, ranging from 91 μ S/cm to 1255 μ S/cm, median 739 μ S/cm. It varies greatly within each water source type (Figure 5), but there is an increasing trend with depth from low to high SEC. The deep boreholes cluster at higher SEC values (median 887 μ S/cm, range 570 to 1255 μ S/cm) than the other types (Figure 5), while both the hand-pumped boreholes (range 173–1000 μ S/cm, median 486 μ S/cm) and the dug wells (range 91–800 μ S/cm, median 207 μ S/cm) have some of the lowest SEC values. The spring samples have a median SEC of 431 μ S/cm and a large range between 144 to 830 μ S/cm, with the highest salinity seen in the NDIWA spring.

Most groundwaters are oxidising (Eh 325 to 550 mV). Moderately reducing waters (Eh 195–265 mV) were measured in one spring, one dug well and two of the hand-pumped boreholes (Figure 5).

Dissolved oxygen (DO) across all samples ranges from 0 to 6.8 mg/l with a median value of 2.6 mg/l. Only one sample (NDIWA spring) was completely anoxic (DO <1.5 mg/l). The springs (median 2.2 mg/l, range 0–3 mg/l) and dug wells (median 2.2 mg/l range 1.7–4.2 mg/l) show the lowest median DO values. The hand-pumped boreholes show a smaller range (1.5–2.7 mg/l), but a slightly higher median of 2.5 mg/l. The waters from the deep boreholes show the largest range in DO concentrations (0.4 to 6.9 mg/l) with median 4.3 mg/l. It is possible that conditions and constraints during sampling, such as sampling from tanks and lack of borehole purging, meant that the DO measurements of samples are not always representative of the DO in the aquifer. Therefore, these DO measurements should be considered with caution.

The groundwaters display a wide range of pH from 5.6 to 7.8. All the deep boreholes and handpumped boreholes and most of the dug wells and springs show the optimum pH range 6.5–8.5 for water supply (WHO, 2017) (deep boreholes' range 6.74–7.82, median 7.10, hand-pumped boreholes' range 6.58–7.17, median 6.76). Two dug well and one spring samples have slightly lower pH (Figure 5).



Figure 5 Distribution of Eh, pH, and SEC in groundwater grouped by water supply type. BH – Deep borehole; BH/HP – shallow borehole with hand pump; DW – dug well; SP – spring (see text for details).

3.1.3 Major elements

Table 1 shows the summary statistics for the major cations and anions grouped by water supply type and Figure 7 shows their distribution across the types.

The waters from the deep boreholes and hand-pumped boreholes (N=12) are all of bicarbonate type, mostly Ca $-HCO_3$ with subordinate Na $-HCO_3$. Dug well waters (N=6) are either bicarbonate and chloride types, and Ca- or Na-rich. Of the three spring waters, one is Na $-HCO_3$ water type and two are Ca-Cl water types (Figure 6).

Calcium concentrations range greatly from 2.7 mg/l to 100 mg/l, median 54.6 mg/l, with the deep boreholes in the upper range, while the other groups have some of the lowest concentrations.

Magnesium concentrations range from 0.93 mg/l to 47.9 mg/l, median 17.6 mg/l, and show similar patterns to Ca: higher concentrations are measured in the deep boreholes, followed by the hand-pumped boreholes and the springs, with the lowest concentrations in the dug wells.

Sodium concentrations vary greatly within and across types with a minimum of 11 mg/l and a maximum of 119 mg/l, median 37.9 mg/l; the highest values are reported in two deep boreholes. No health-based guideline value has been derived for Na, as the contribution from drinking water to daily intake is small. At room temperature, the average taste threshold for sodium is about 200 mg/l, and this is often taken as an advisable upper threshold (WHO, 2017). None of the groundwaters exceeds the threshold.

Potassium concentrations are mostly below 10 mg/l in all types (range 1.34–20.8 mg/l, median 5.59 mg/l). Two deep boreholes have higher K concentrations of 17 mg/l and 21 mg/l.

Bicarbonate is generally the most abundant anion (overall range 36.6–788 mg/l, median 432 mg/l). It ranges from 432 to 727 mg/l in the deep boreholes, but is distinctly lower in the dug wells (37–170 mg/l). Samples from hand-pumped boreholes show a much wider range (73 –787 mg/l).

Chloride shows greatest variability among the dug wells (range 1.24–75.8 mg/l, median 11.1 mg/l). There are narrower ranges in the deep boreholes (1.24–32.8 mg/l, median 11.3 mg/l) and the springs (11.1–37.3 mg/l, median 15.8 mg/l). Concentrations of CI in all the hand-pumped boreholes are noticeably low (2.6–6.9 mg/l, median 5.33 mg/l). Chloride is considered to behave conservatively in natural waters. The low measured values are very close to rainfall concentrations. Anthropogenic inputs of CI can be important; they include agriculture, septic tank leakage, or the occasional well disinfection with chlorinated products. No health-based guideline value is available for chloride in drinking water (WHO, 2017), although chloride concentrations in excess of about 250 mg/l can give rise to detectable taste in water. None of the samples exceeds the 250 mg/l value.

Sulphate ranges from <5 mg/l to 80 mg/l, median 10.1 mg/l. Only two of the deep boreholes have relatively high concentrations of 52 and 80 mg/l; and one dug well sample has 48 mg/l. The presence of sulphate in drinking water can cause noticeable taste, and very high levels might cause a laxative effect in unaccustomed consumers. It is generally considered that taste impairment is minimal at levels below 250 mg/l. None of the samples exceeds this threshold.

The range of silicon concentration is from 12.7 to 42.8 mg/l, median 23.2 mg/l, with the shallow boreholes showing the widest range and highest concentrations.

3.1.3.1 NITRATE, DISSOLVED ORGANIC CARBON, IRON AND MANGANESE

Figure 8 shows the distribution of nitrate, non-purgeable organic carbon (NPOC), iron and manganese in the sample waters.

Nitrate concentrations range from 0.3 to 105 mg/l, median 11.9 mg/l, with two out of the 21 groundwater values above the 50 mg/l drinking water standard (WHO, 2017), in one dug well and one unprotected spring in Kehancha.

NPOC ranges from 0.5 to 8 mg/l, median 0.9 mg/l, with the lowest values in the deep boreholes.

Iron concentrations range from 0.5 to 1034 μ g/l, median 19.2 μ g/l. This low median value is characteristic of oxidising waters. The deep boreholes (median 8.1 μ g/l, range 1.4–156 μ g/l) show the lowest values. Iron concentrations >100 μ g/l are more common in the shallow hand-pumped boreholes and dug wells, and one water, from a hand-pumped boreholes, has a very high

concentration of 1034 μ g/l. No health-based guideline value is proposed for iron (WHO, 2017), but at levels above 0.3 mg/l (300 μ g/l), iron stains laundry and plumbing fixtures. There is usually no noticeable taste at iron concentrations below 0.3 mg/l, although turbidity and colour may develop.

Manganese is mostly below 50 μ g/l: (range 0.4–774 μ g/l, median 16.4 μ g/l), which is well below the WHO (2017) health-based value of 0.4 mg/l (400 μ g/l), and taste-based guideline of 0.1 mg/l (100 μ g/l). A single much higher concentration of 774 μ g/l was measured in one of the dug wells, which also showed a high Fe concentration.

3.1.4 Other trace elements

Figure 9 to Figure 12 show the distribution of selected other minor and trace elements, grouped by water supply type. Summary statistics for these are reported in Table 1 and Table 2.

Comparison with the guidelines for chemicals that are of health significance in drinking water shows the following:

All the waters from the deep and shallow boreholes, dug wells and springs are below the drinking quality standards for antimony (WHO standard 20 μ g/l), barium (WHO standard 1300 μ g/l), cadmium (WHO standard 3 μ g/l), chromium (WHO standard 50 μ g/l), lead (WHO standard 10 μ g/l), nickel (WHO standard 70 μ g/l), selenium (WHO standard 40 μ g/l), uranium (WHO standard 30 μ g/l).

The arsenic drinking water quality guideline (WHO 10 μ g/l) is exceeded in 5 of 21 groundwaters (values from 13.7 μ g/l to 129 μ g/l).

The fluoride drinking water quality guideline (WHO 1.5 mg/l) is exceeded in two boreholes and one spring (values of 1.7–2.02 mg/l).

The inorganic mercury WHO standard for drinking water is 6 μ g/l. Mercury was above the detection limit of 0.007 μ g/l in 11 water samples (median value of 0.016 μ g/l), but never greater than 0.164 μ g/l. This highest value was from a dug well in the proximity of an ASGM site that was using vat leaching with cyanide solution to extract gold, and had accumulated spent tailings heaps. As discussed above, because the samples weren't preserved by acidifying immediately in the field, but only after returning to UK, the analysed values may not be representative of field samples and need to be confirmed by further sampling.



Figure 6 Piper plot of all water samples.

Variable	SOURCE	Total Count	Mean	StDev	Min	Median	Max	WHO
Ca mg/l	BH	8	81.3	16.8	52.0	83.6	101	
	BH/HP	4	56.7	42.5	17.8	57.0	95.0	
	DW	6	23.3	22.8	2.70	14.2	64.0	
	SP	3	31.9	22.2	10.2	30.9	54.6	
Mg mg/l	BH	8	32.2	10.1	21.9	30.7	47.9	
	BH/HP	4	14.7	13.3	2.46	12.1	32.2	
	DW	6	6.75	6.20	0.93	4.31	17.6	
	SP	3	11.8	9.87	2.81	10.2	22.4	
Na mo/l	ВН	8	68.6	33.5	21.3	63.3	120	
0	BH/HP	4	36.6	36.8	6.7	25.9	88.1	
	DW	6	20.1	15.7	11.1	14.5	52.1	
	SP	3	41.2	43.0	7.8	26.0	89.7	
K ma/l	BH	8	83	6 94	1 49	5 93	20.8	
ix ing/i	BH/HP	4	6.63	4 22	3 18	5 44	12.4	
			6.43	4 54	1.34	4 70	12.4	
	SP	3	5.5	2 28	2.88	6.54	7 08	
	01		0.0	2.20	2.00	0.01	1.00	
CI mg/l	BH	8	14	11.7	1.24	11.3	32.8	
	BH/HP	4	5.03	2.14	2.58	5.33	6.90	
	DW	6	26.2	26.7	4.6	18.3	75.8	
	SP	3	21.4	14.0	11.1	15.8	37.3	
SO ₄ mg/l	BH	8	24.7	27.4	0.50	14.4	80.1	
0	BH/HP	4	6.52	4.83	1.96	5.42	13.3	
	DW	6	11.9	18.0	2.01	3.56	47.8	
	SP	3	9.15	4.91	3.50	11.6	12.3	
HCO ₃ mg/l	BH	8	593	97.3	432	589	727	
	BH/HP	4	378	328	73	327	787	
	DW	6	102	49.0	36.6	93.9	171	
	SP	3	247	227	93	141	507	
NO₃ mg/l	BH	8	10.7	9.33	0.30	9.05	24.6	50
	BH/HP	4	4.76	7.28	0.30	1.57	15.6	
	DW	6	34.7	36.0	10.2	20.8	105	
	SP	3	27.5	32.2	3.4	15.0	64.0	
Si ma/l	BH	8	21.1	3 99	15.6	20.9	27.7	
Si ilig/i	BH/HP	<u> </u>	27.6	10.6	19.0	20.9	42.8	
	DW		26.6	8 69	12.7	27.2	36.6	
	SP	3	23.8	3.07	20.2	25.4	25.7	

Table 1 Descriptive statistics of major and minor cations and anions by water source type. See Figure 5 for type descriptions.

Table 1 (cont.) Summary statistics of major and minor cations and anions by water source type. See Figure 5 for type descriptions.

Variable	SOURCE	Total Count	Nol Cens	Mean	StDev	Min	Median	Max	WHO
Br mg/l	BH	8	8			< 0.2			
	BH/HP	4	4			<0.2			
	DW	6	6			<0.2			
	SP	3	3			<0.2			
HPO₄mg/l	BH	8	8			<0.2			
	BH/HP	4	4			<0.2			
	DW	6	6			<0.2			
	SP	3	3			<0.2			
F mg/l	BH	8	0	1.15	0.547	0.308	1.08	2.02	1.5
	BH/HP	4	0	0.634	0.489	0.196	0.62	1.1	
	DW	6	1	0.351	0.254	<0.1	0.335	0.773	
	SP	3	1	0.639	0.907	<0.1	0.184	1.688	
NPOC mg/l	BH	8	2	0.62	0.26	<0.5	0.70	0.97	
	BH/HP	4	1	3.41	3.70	<0.5	2.58	8.23	
	DW	6	0	2.46	1.69	<0.5	1.80	5.41	
	SP	3	1	1.36	1.05	<0.5	1.48	2.34	

Table	2 Descriptive	statistics	of trace	elements	by water	source	type.	See	Figure	5 for	type
descri	ptions.										

Variable	SOURCE	Total Count	No Cens.	Unit	Mean	StDev	Minimum	Median	Maximum	WHO
Ag	BH	8	8	µg/l			<0.04			
	BH/HP	4	4	µg/l			<0.04			
	DW	6	5	µg/l			<0.04		0.05	
	SP	3	3	µg/l			<0.04			
Al	BH	8	1	µq/l	2.84	3.39	<0.6	1.1	10.3	
	BH/HP	4	0	µg/l	95.3	146	0.9	36	308	
	DW	6	0	µg/l	308	339	2	198	784	
	SP	3	0	µg/l	83.1	130	0.9	16.1	232	
As	BH	8	0	ua/l	32	5	0.32	1 52	15 38	10
	BH/HP	4	0	ua/l	52.7	54.7	1.1	40.6	128.6	10
	DW	6	0	µg/l	3.75	4.93	0.21	2.29	13.66	
	SP	3	0	µg/l	3.04	3.47	0.78	1.31	7.04	
B	BH	8	7	ua/l			<53		161	2400
	BH/HP	4	4	ua/l			<53			
	DW	6	6	µg/l			<53			
	SP	3	3	µg/l			<53			
Ba	RH	8	0	ua/l	69.8	70.5	3 1	57.8	197 5	1300
	BH/HP	4	0	<u>ua/l</u>	10.9	11.5	0.77	7 63	27.5	1000
	DW	6	0	ua/l	75.1	87.8	3.3	58.4	239	
	SP	3	0	µg/l	80.5	58.1	20.9	83.8	137	
Po	DU	0	7	10			<0.00		0.12	
ре		0	1				<0.00		0.12	
			0	μ <u>μ</u> γ/Ι	0.21	0.07	<u> </u>	0.24	0.23	
	SP	3	1	ua/l	0.21	0.07	<0.08	0.24	0.27	
D:	DU			//			-0.00			
Ы		8	<u>8</u>	µg/i			<0.08			
		6	6	μ <u>μ</u> γ/ι μα/Ι			<0.08			
	SP	3	3	ua/l			<0.08			
				"."			10.005		0.000	0
Ca	BH/UD	8	5	µg/I	0.017	0.012	<0.005	0.017	0.028	3
		4	0	<u>µg/i</u>	0.017	0.013	0.005	0.017	0.03	
	SP	3	1	<u>µg/i</u> ua/l	0.013	0.003	<0.000	0.014	0.02	
	01	0		μ9/1	0.000	0.007	40.000	0.000	0.010	
Се	BH	8	1	µg/l	0.041	0.037	< 0.004	0.031	0.122	
	BH/HP	4	0	µg/I	0.318	0.474	0.013	0.12	1.02	
		6	0	µg/I	1.79	2.30	0.052	0.789	5.98	
	35	3	0	μy/i	0.040	0.759	0.012	1.04	1.49	
Со	BH	8	0	µg/l	0.138	0.119	0.008	0.131	0.346	
	BH/HP	4	0	µg/l	0.085	0.035	0.039	0.090	0.120	
	DW	6	0	µg/l	0.863	1.09	0.045	0.272	2.28	
	5P	3	0	µg/i	0.279	0.337	0.019	0.158	0.659	
Cr	BH	8	6	µg/l			<0.04		0.12	50
	BH/HP	4	1	µg/l	0.17	0.18	< 0.04	0.12	0.42	
	DW	6	1	µg/l	0.37	0.43	< 0.04	0.22	1.16	
	SP	3	1	µg/I	0.14	0.17	<0.04	0.07	0.34	
Cs	BH	8	1	µg/l	2.92	5.85	<0.04	0.29	16.82	
	BH/HP	4	2	µg/l			<0.04		0.4	
	DW	6	6	µg/l			< 0.04			
	SP	3	2	µg/l			<0.04		0.15	
Cu	BH	8	0	µg/l	1.93	2.62	0.06	1.08	7.75	
	BH/HP	4	0	µg/l	8.34	14.6	0.37	1.41	30.2	
	DW	6	0	µg/l	1.94	1.50	0.41	1.65	3.83	
	SP	3	0	µg/l	0.88	0.93	0.13	0.60	1.92	

Table 2 (cont.) Descriptive statistics of trace elements by water source type.	See Figure 5 for
type descriptions.	-

Variable	SOURCE	Total Count	No Cens.	Unit	Mean	StDev	Minimum	Median	Maximum	WHO
Dy	BH	8	1	µg/l	0.009	0.005	<0.003	0.009	0.018	
	BH/HP	4	1	µg/l	0.145	0.262	<0.003	0.021	0.537	
	DW	6	0	µg/l	0.338	0.305	0.003	0.331	0.766	
	SP	3	1	µg/l	0.203	0.301	<0.003	0.057	0.549	
Er	BH	8	2	µg/l	0.007	0.005	<0.003	0.006	0.015	
	BH/HP	4	1	µg/l	0.094	0.164	<0.003	0.018	0.340	
	DW	6	0	µg/l	0.209	0.183	0.011	0.202	0.459	
	SP	3	1	µg/l	0.128	0.175	<0.003	0.054	0.327	
Eu	BH	8	6	µg/l			<0.003		0.004	
	BH/HP	4	2	µg/l			<0.003		0.096	
	DW	6	0	µg/l	0.062	0.054	0.004	0.063	0.130	
	SP	3	1	µg/l	0.031	0.044	<0.003	0.010	0.082	
Fe	BH	8	0	µg/l	28.5	52.4	1.4	8.1	156	
	BH/HP	4	0	µg/l	330	475	1	142	1034	
	DW	6	0	µg/l	152	197	1.2	59.3	474	
	SP	3	0	µg/l	46.5	62.5	0.5	21.4	118	
Ga	BH	8	8	µg/l			<0.04			
	BH/HP	4	3	µg/l			<0.04		0.08	
	DW	6	3	µg/l			<0.04		0.19	
	SP	3	2	µg/l			<0.04		0.05	
Gd	BH	8	2	µq/l	0.008	0.005	<0.005	0.008	0.014	
	BH/HP	4	1	µq/l	0.150	0.272	<0.005	0.019	0.557	
	DW	6	0	µg/l	0.370	0.332	0.015	0.379	0.807	
	SP	3	1	µg/l	0.201	0.291	<0.005	0.064	0.535	
Hg	BH	6	2	µg/l	0.011	0.006	<0.007	0.013	0.019	6
U	BH/HP	4	2	µg/l			<0.007		0.026	
	DW	6	3	µg/l			<0.007		0.164	
	SP	2	1	µg/l			<0.007		0.007	
Hf	BH	8	8	µg/l			<0.006			
	BH/HP	4	2	µg/l	0.016	0.019	<0.006	0.008	0.043	
	DW	6	3	µg/l	0.033	0.035	<0.006	0.025	0.083	
	SP	3	1	µg/l	0.016	0.018	<0.006	0.009	0.036	
Ho	BH	8	5	µg/l			<0.003		0.006	
	BH/HP	4	1	µg/l	0.032	0.055	<0.003	0.006	0.115	
	DW	6	1	µg/l	0.069	0.062	<0.003	0.069	0.155	
	SP	3	1	µg/l	0.041	0.059	<0.003	0.013	0.109	
La	BH	8	0	µg/l	0.0564	0.0404	0.005	0.048	0.116	
	BH/HP	4	0	µg/l	1.33	2.41	0.02	0.18	4.93	
	DW	6	0	µg/l	2.717	2.404	0.124	2.893	5.329	
	SP	3	0	µg/l	1.46	2.14	0.01	0.44	3.92	
Li	BH	8	0	µg/l	21	7.15	13	20.5	34	
	BH/HP	4	1	µg/l	17.88	17.32	<7	12.5	43	
	DW	6	6	µg/l			<7			
	SP	3	2	µg/l			<7		20	
Lu	BH	8	8	µg/l			<0.003			
	BH/HP	4	2	µg/l			<0.003		0.045	
	DW	6	0	µg/l	0.030	0.025	0.004	0.028	0.065	
	SP	3	1	µg/l	0.018	0.020	< 0.003	0.012	0.04	

Table 2 (cont.) Descriptive statistics of trace elements by water source type.	See Figure 5 for
type descriptions.	

Variable	SOURCE	Total Count	No Cens.	Unit	Mean	StDev	Minimum	Median	Maximum	WHO
Mn	BH	8	0	µg/l	33.9	42.5	0.4	12.1	99.8	400
	BH/HP	4	0	μg/l	19.2	16.59	3.6	16.75	39.7	
	DW	6	0	μg/l	154	305	6	35	774	
	SP	3	0	µg/l	44.8	63.7	1.3	15.2	117.9	
Mo	BH	8	0	ua/l	21	3.08	0.2	1 3	9.5	
IVIO	BH/HP	4	0	<u>μα/Ι</u>	11	0.00	0.2	1.5	22	
	DW	6	2	<u>ua/l</u>	0.5	0.0	<0.2	0.4	11	
	SP	3	1	µg/i	1.0	1 25	<0.2	0.1	2.4	
							0.2	••••		
Nb	BH	8	8	µg/l			<0.01		0.4	
	BH/HP	4	2	µg/I	0.07	0.07	<0.01	0.00	0.1	
		0		µg/i	0.07	0.07	<0.01	0.06	0.18	
	5P	3	1	µg/I	0.03	0.04	<0.01	0.01	0.08	
Nd	BH	8	0	µg/l	0.048	0.034	0.012	0.036	0.101	
	BH/HP	4	0	µg/l	1.046	1.893	0.006	0.149	3.881	
	DW	6	0	µg/l	2.283	2.01	0.106	2.358	4.346	
	SP	3	0	µg/l	1.22	1.8	0.01	0.37	3.29	
Ni	BH	8	1	ua/l	0.364	0.305	<0.01	0 295	1	70
	BH/HP	4	0	µg/i	3 51	4.6	0.31	1.8	10 14	10
	DW	6	0	ua/l	1.655	0.958	0.8	1.365	3.29	
	SP	3	1	ua/l	1.552	1.339	<0.01	2.32	2.33	
	5.				0.50	0.40	0.00	0.00	4.00	10
Pb	BH	8	0	µg/l	0.50	0.48	0.09	0.23	1.33	10
	BH/HP	4	0	µg/I	0.27	0.24	0.07	0.22	0.56	
		6	1	µg/l	0.57	0.78	0.01	0.25	2.03	
	SP	3	1	µg/I	0.11	0.1	0.01	0.11	0.21	
Pr	BH	8	1	µg/l	0.0122	0.0076	<0.003	0.011	0.024	
	BH/HP	4	0	µg/l	0.274	0.497	0.003	0.037	1.018	
	DW	6	0	µg/l	0.593	0.529	0.023	0.607	1.128	
	SP	3	1	µg/l	0.318	0.467	<0.003	0.098	0.854	
Rh	BH	8	0	ua/l	2.68	3 09	0.31	1 18	8.81	
	BH/HP	4	0	<u>ua/l</u>	2.00	3 75	0.01	0.95	8 11	
		6	0	<u>µg/i</u> ua/l	7 59	9.52	0.00	4 72	26.51	
	SP	3	0	ua/l	3 48	0.02	2 78	3.33	4 32	
			0	M9/1	0.10	0.10	2.76	0.00	1.02	
Sb	BH	8	2	µg/l	0.29	0.42	<0.04	0.08	1.1	20
	BH/HP	4		µg/l	0.13	0.10	<0.04	0.13	0.22	
	DW	6	2	µg/l	0.07	0.06	< 0.04	0.06	0.17	
	SP	3	3	µg/I			<0.04			
Se	BH	8	1	µg/l	0.27	0.29	<0.07	0.15	0.92	40P
	BH/HP	4	3	μg/l			< 0.07		0.15	
	DW	6	2	µg/l	0.08	0.04	<0.07	0.08	0.14	
	SP	3	2	µg/l			<0.07		0.1	
Sm	BH	8	2	ua/l	0.008	0.005	<0.005	0.008	0.018	
0111	BH/HP	4	1	<u>µg/i</u> ua/l	0.000	0.000	<0.005	0.000	0.010	
	DW	6	0	<u>ua/l</u>	0.101	0.377	0.000	0.025	0.866	
	SP	3	1	ua/l	0.236	0.335	<0.005	0.084	0.62	
				י ׳פייז	0.200	0.000	5.000	0.001	0.02	
Sn	BH	8	8	µg/l			<0.08			
	BH/HP	4	4	µg/l			<0.08			
		6	6	µg/l			<0.08			
	SP	3	3	µg/l			<0.08			
Sr	BH	8	0	µg/l	939	655	253	835	2311	
	BH/HP	4	0	µg/l	301	197	115	296	497	
	DW	6	0	µg/l	383	478	22	159	1287	
	SP	3	0	ua/l	596	603	119	394	1274	

Table 2 (cont.) Descriptive statistics of trace elements by water source type.	See Figure 5 for
type descriptions.	-

Variable	SOURCE	Total Count	No Cens.	Unit	Mean	StDev	Minimum	Median	Maximum	WHO
Та	BH	8	8	µg/l			<0.006			
	BH/HP	4	4	µg/l			<0.006			
	DW	6	5	µg/l			<0.006		0.008	
	SP	3	3	µg/l			<0.006			
Tb	BH	8	8	ua/l			<0.004			
	BH/HP	4	2	ua/l			<0.004		0.092	
	DW	6	1	ua/l	0.058	0.054	<0.004	0.057	0.13	
	SP	3	1	µg/l	0.032	0.047	< 0.004	0.008	0.086	
T L	DU	0	0	10	0.00	0.00	10.00	0.045	0.00	
In	BH	8	8	µg/I	0.02	0.00	< 0.03	0.015	0.02	
	BH/HP	4	3	µg/i	0.03	0.03	<0.03	0.015	0.07	
		0	4		0.04	0.03	<0.03	0.015	0.1	
	36	3	2	µg/i	0.03	0.03	<0.03	0.015	0.06	
Ti	BH	8	4	µg/l	0.08	0.07	<0.06	0.06	0.22	
	BH/HP	4	1	µg/l	1.08	1.26	<0.06	0.81	2.65	
	DW	6	0	µg/l	2.52	2.54	<0.06	2.1	5.99	
	SP	3	1	µg/l	0.92	1.41	<0.06	0.19	2.54	
TI	BH	8	7	ua/l	0.01	0.01	< 0.02	0.01	0.04	
	BH/HP	4	4	ua/l	0.01	0	< 0.02	0.01	0.01	
	DW	6	4	µg/l	0.02	0.01	< 0.02	0.01	0.03	
	SP	3	3	µg/l	0.01	0	<0.02	0.01	0.01	
Tm	вц	0	0		0.000	0	<0.002	0.000	0.002	
Im		8	8	µg/i	0.002	0 0 0 2 2	<0.003	0.002	0.002	
		4	1	μ <u>μ</u> γ/Ι	0.013	0.022	<0.003	0.002	0.040	
	SP	<u> </u>	1		0.031	0.020	<0.003	0.029	0.007	
	01	5		μg/i	0.013	0.024	-0.000	0.003	0.047	
U	BH	8	0	µg/l	4.44	2.87	0.30	4.24	8.44	30P
	BH/HP	4	0	µg/l	1.47	1.62	0.07	1.25	3.30	
	DW	6	0	µg/l	0.09	0.05	0.03	0.09	0.16	
	SP	3	0	µg/l	2.89	4.88	0.03	0.10	8.52	
V	BH	8	0	µg/l	1.34	1.24	0.23	0.93	3.83	
	BH/HP	4	0	µg/l	5.76	7.32	1.55	2.41	16.69	
	DW	6	0	µg/l	1.77	0.89	0.37	1.85	2.71	
	SP	3	0	µg/l	2.16	2.03	0.69	1.31	4.48	
\M/	BH	8	1	ua/l			<0.06		0.28	
••	BH/HP	4	2	ua/l			<0.00		0.20	
	DW	6	6	ua/l			<0.06		0.02	
	SP	3	3	ua/l			< 0.06			
					0.000	0.000	0.000	0.070	0.040	
Y	BH/UD	8	0	µg/I	0.099	0.066	0.032	0.072	0.212	
		4	0	µg/I	1.923	1.539	0.017	0.225	3.227	
		0 2	0	µg/I	1.972	1.74	0.097	1./0Z	4.1/9	
	о г	3	U	µy/I	1.072	1.34	0.022	0.303	2.04	
Yb	BH	8	2	µg/l	0.006	0.004	<0.004	0.006	0.013	
	BH/HP	4	1	µg/l	0.080	0.135	<0.004	0.018	0.283	
	DW	6	0	µg/l	0.188	0.158	0.017	0.176	0.409	
	SP	3	1	µg/l	0.122	0.152	<0.004	0.071	0.293	
Zn	BH	8	0	µg/l	39.2	35.8	8.3	19.1	92.1	3000a
	BH/HP	4	0	µg/l	337	621	15	33	1268	
	DW	6	0	µg/l	3.85	1.98	2	3.2	6.5	
	SP	3	1	µg/l	6.7	10.75	<0.2	0.9	19.1	
- 7r	RH	Q	1		0.036	0 022	<0.000	0 030	0.073	
<u></u> I	BH/HP	о /	1	µy/I	0.030	1 106	<0.009	0.039	2 266	
	DW	+ 6	<u>،</u>	<u>P9/1</u>	1 888	1 80/	-0.009 0.009	1 881	2.000	
	SP		1	<u>na/l</u>	0.748	0.965	<0.022	0 403	1 839	



Figure 7 Distribution of major cations and anions. See Figure 5 for type descriptions.



Figure 8 Distribution of nitrate (NO₃), non-purgeable organic carbon (NPOC), iron (Fe) and manganese (Mn). See Figure 5 for type descriptions.



Figure 9 Distribution of aluminium (AI), fluoride (F), barium (Ba), strontium (Sr), rubidium (Rb) lithium (Li), cesium (Cs), and uranium (U). For all DW samples, Li is below the detection limit of 7 μ g/l and Cs below the detection limit of 0.04 μ g/l. See Figure 5 for type descriptions.



Figure 10 Distribution of trace elements potentially related to the gold ore present in the study area, grouped by water source: arsenic (As), selenium (Se), antimony (Sb) and molybdenum (Mo). See Figure 5 for type descriptions.



Figure 11 Distribution of trace elements potentially related to the gold ore present in the study area, grouped by water source: cadmium (Cd), chromium (Cr), cobalt (Co) and copper (Cu). See Figure 5 for type descriptions.



Figure 12 Distribution of trace elements potentially related to the gold ore present in the study area, grouped by water source: nickel (Ni), lead (Pb), vanadium (Va) and zinc (Zn). See Figure 5 for type descriptions.

3.2 MINE WATERS

Four mine shafts were sampled, from west to east along the greenstone belt at Osiri Matanda mine, Kakula mine, Masara Kolongo and Kakasera. At Osiri Matanda mine, water is continuously pumped from a ~ 180 m deep mine shaft into an open pipe that runs to the mine village. At Kakula mine, water is pumped out of a relatively shallow (~ 18 m) mine shaft and used for domestic purposes. At Masara Kolongo water is pumped by a petrol pump from a 60 m deep mine shaft to pipes and tanks. At Kakasera mine, water from an uncovered mine shaft is collected with buckets by the local community.

The physico-chemical parameters and major, minor and trace element analysis results for the samples are reported in Table 3.

All the mine water samples are oxidising (Eh >400 mV). The dissolved oxygen (DO) content is low (0.7–2.3 mg/l) in three of the mine waters and slightly higher (4.7 mg/l) at the fourth site (Table 3). SEC varies greatly from 164 to 1733 μ S/cm. An increasing SEC pattern with shaft depth is noted, with the deepest mine shaft (OSIRI mine) showing distinctively higher SEC. The pH varies from alkaline pH 7.75 and 7.35 at Osiri mine and Kakula mine to a slightly acidic pH 6.83 and pH 6.19 at Masara Kolongo and Kakasera mine shafts.

The chemical composition of the four mine waters is variable (Figure 13 to Figure 15). Three of the mine waters are Na-HCO₃ water type and one is Ca-HCO₃ water type (Masara Kolongo) (Figure 6). Osiri mine water is also relatively higher in sulphate (381 mg/l), while all the other mine waters have low SO₄ (<30 mg/l).

Many measured parameters in the mine waters are no higher than the upper interquartile value (75th percentile) of the distribution of the same parameter in the baseline groundwaters (Figure 13 to Figure 15). The most significant exception is the Osiri mine water, which is greatly above the 75th percentile of the baseline groundwaters for most parameters, except for alkalinity nitrate, and chromium. Additionally, concentrations of iron (range 86–306 μ g/l), manganese (range 65–297 μ g/l), and arsenic (range 15–190 μ g/l) in all the mine waters are also higher than the baseline interquartile top range.

The measured mine water quality has been assessed against the WHO drinking water quality standards which, although they apply to public drinking water supplies, can be used as a reference for evaluating the quality of any water used for drinking. As noted above, water pumped from the mines is used by local communities for domestic purposes. Fluoride is above the WHO standard of 1.5 mg/l at the deep mine shaft Osiri mine (2 mg/l), but around 1 mg/l in Masara Kolongo and Kakula mines, similar to the baseline deep borehole median values (1.08 mg/l); it is much lower (0.2 mg/l) at Kakasera mine.

Arsenic concentrations are all above the WHO drinking water standard of 10 μ g/l, but vary greatly in the four mine waters: Masara Kolongo (178 μ g/l) and Kakula (190 μ g/l) mine waters greatly exceed the WHO standard, while Kakasera (15.1 μ g/l) and Osiri (15.6 μ g/l) mine waters are only slightly above the WHO standard. There are no significant correlations of arsenic concentrations with iron, sulphate, organic matter, Eh, pH or other trace metals associated with the local ore, although the small sample number limits any robust interpretation.

Mercury concentrations in three of the mine waters $(0.01-0.02 \ \mu g/l)$ are similar to the maximum values measured in the baseline hand-pumped and deep boreholes (cf. Table 2). The concentration in the fourth mine water is slightly higher $(0.06 \ \mu g/l)$.

As with the baseline groundwater samples, none of the other trace elements in the mine waters exceeds the WHO drinking water quality standards.

The waters from the two panning ponds at Macalder and Osiri mine sites are both highly mineralised (SEC 1428–2230 µS/cm) and are sulphate water type ("mine processing water" group in Figure 6). However substantial differences are associated to the two sites. The panning pond water with the spoil leachate at Macalder mine are both acidic waters (pH 3.73 and 2.87), with sulphate concentrations of 2387 and 2036 mg/l, respectively, which is consistent with past observations (Odumo et al, 2014) and the expected acid mine drainage associated with massive sulphide ore deposit types (Section 1.7.1). Dissolved iron (up to 61 mg/l) and aluminium (up to 67 mg/I) in both samples are very high. Linked to the very low pH, many metals are present at high concentrations, in particular copper (up to 151 mg/l), zinc (up to 236 mg/l), cobalt (5.3 mg/l), lead (2.49 mg/l), cadmium (0.9 mg/l) and arsenic (0.2 mg/l). Mercury concentrations were all below the sample analytical detection limit of 0.2 µg/l. By contrast to these samples, water sampled from a panning pond at Osiri Matanda is alkaline (pH 7.85) with a sulphate of 641 mg/l, with low dissolved cadmium (0.02 µg/l), arsenic, zinc, and cobalt, (<5 µg/l), and copper and nickel (<10 µg/l), similar to the mine water from the local shaft. This panning pond also showed a concentration of 1 μ g/l mercury, the highest recorded in the dataset, likely related to the local practice of amalgamation using mercury.

Parameter	Unit	Detection Limit	Masara Kolongo	Kakula	Kakasera	Osiri Matanda	WHO (2017)
Т	°C	-	27.3	24.0	24.5	26.9	
pН		-	6.83	7.35	6.19	7.75	6.5-8.5
Eh	mV	-	441	457	412	470	
DO	mg/l	-	0.7	2.3	1.5	4.7	
SEC	µS/cm	-	805	348	164	1733	
Ca	mg/l	0.3	87.7	11.1	8.5	125	
Mg	mg/l	0.003	23.5	3.19	2.80	53.3	
Na	mg/l	0.4	47.8	49.1	16.4	174	
К	mg/l	0.04	10.0	7.19	3.07	6.06	
HCO3 ⁻	mg/l	-	539	118	132	517	
Cl-	mg/l	-	10.8	15.9	11.8	93.3	
SO4 ²⁻	mg/l	-	12.4	32.3	<1	381	
NO3 ⁻	mg/l	-	0.664	6.14	16.2	6.38	50
Br	mg/l	-	<0.2	<0.2	<0.2	0.438	
NO ₂ -	mg/l	-	<0.1	<0.1	<0.1	0.682	
HPO ₄ ²⁻	mg/l	-	<0.2	<0.2	<0.2	<0.2	
F-	mg/l	-	1.11	1.08	0.207	2.00	1.5
NPOC	mg/l	-	1.18	7.33	5.14	1.72	
Р	mg/l	0.005	<0.005	<0.005	<0.005	<0.005	
Si	mg/l	0.042	20.3	6.92	27.9	23.1	
Ag	µg/l	0.04	<0.04	<0.04	<0.04	<0.04	
AI	µg/l	0.6	6.4	529	337	68.4	
As	µg/l	0.04	178	190	15.1	15.6	10
В	µg/l	53	<53	<53	<53	<53	2400
Ba	µg/l	0.05	40.3	73.7	28.1	59.2	1300
Be	µg/l	0.08	<0.08	0.13	0.40	<0.08	
Bi	µg/l	0.08	<0.08	<0.08	<0.08	0.28	
Cd	µg/l	0.005	0.006	0.021	0.024	0.075	3
Ce	µg/l	0.004	0.085	3.24	6.45	0.195	
Co	µg/l	0.006	4.43	0.285	1.50	4.79	
Cr	µg/l	0.04	0.11	0.35	0.27	0.17	50
Cs	µg/l	0.04	<0.04	<0.04	<0.04	3.27	
Cu	µg/l	0.05	1.24	2.46	5.44	4.76	2000
Dy	µg/l	0.003	0.018	0.167	0.859	0.018	
Er	µg/l	0.003	0.011	0.095	0.547	0.009	

Table 3 Chemical analysis of the four mine shaft water samples

< values denote concentrations below detection limit reported by the laboratory.

WHO health-based guideline value, "a": these values are recommendations based on aesthetic considerations such as taste and colour; "P": provisional guideline value because of uncertainties in the health database.

Guidelines for drinking-water quality: fourth edition incorporating the first addendum. Geneva: World Health Organization; 2017.

Parameter	Unit	Detection Limit	Masara Kolongo	Kakula	Kakasera	Osiri Matanda	WHO (2017)
Eu	µg/l	0.003	0.003	0.053	0.169	0.007	
Fe	µg/l	0.4	86.0	172	273	306	
Ga	µg/l	0.04	<0.04	0.12	0.10	<0.04	
Gd	µg/l	0.005	0.017	0.215	0.997	0.026	
Hg	µg/l	0.007	0.010	0.059	0.019	0.012	6
Hf	µg/l	0.006	<0.006	0.069	0.067	<0.006	
Но	µg/l	0.003	0.005	0.034	0.175	0.005	
La	µg/l	0.003	0.115	1.73	8.49	0.108	
Li	µg/l	7	18	<7	<7	19	
Lu	µg/l	0.003	<0.003	0.013	0.080	<0.003	
Mn	µg/l	0.2	297	65.3	206	140	400
Мо	µg/l	0.2	1.7	1.8	0.2	4.1	
Nb	µg/l	0.01	<0.01	0.04	0.12	<0.01	
Nd	µg/l	0.005	0.094	1.55	6.92	0.128	
Ni	µg/l	0.01	1.31	0.92	5.28	8.94	70
Pb	µg/l	0.02	0.21	1.91	0.83	4.97	10
Pr	µg/l	0.003	0.028	0.391	1.85	0.025	
Rb	µg/l	0.05	0.59	5.22	3.12	7.29	
Sb	µg/l	0.04	0.29	1.73	0.09	1.09	20
Se	µg/l	0.07	0.19	0.15	<0.07	3.51	40P
Sm	µg/l	0.005	0.015	0.266	1.22	0.032	
Sn	µg/l	0.08	<0.08	0.10	<0.08	0.23	
Sr	µg/l	0.2	823	137	102	1471	
Та	µg/l	0.006	<0.006	<0.006	<0.006	<0.006	
Tb	µg/l	0.004	<0.004	0.030	0.147	0.004	
Th	µg/l	0.03	<0.03	0.08	<0.03	<0.03	
Ti	µg/l	0.06	0.06	1.77	3.39	0.43	
ТІ	µg/l	0.02	<0.02	0.04	<0.02	<0.02	
Tm	µg/l	0.003	<0.003	0.013	0.077	<0.003	
U	µg/l	0.009	3.38	0.525	0.143	6.33	30P
V	µg/l	0.02	0.97	0.62	0.92	1.01	
W	µg/l	0.06	0.13	4.81	<0.06	1.85	
Y	µg/l	0.006	0.140	0.902	5.34	0.140	
Yb	µg/l	0.004	0.013	0.088	0.494	0.007	
Zn	µg/l	0.2	3.5	7.5	14.1	9.3	3000a
Zr	µg/l	0.009	0.050	2.92	3.04	0.041	

Table 3 (cont.) Chemical analysis of the four mine shaft water samples

< values denote concentrations below detection limit reported by the laboratory.

WHO health-based guideline value, "a": these values are recommendations based on aesthetic considerations such as taste and colour; "P": provisional guideline value because of uncertainties in the health database.

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Figure 13 Comparison between mine water and baseline groundwater samples: physicochemical parameters and major anions and cations.



Figure 14 Comparison between mine water and baseline groundwater samples: fluoride (F), nitrate (NO_3), strontium (Sr), iron (Fe), manganese (Mn), lithium (Li), uranium (U), chomium (Cr), nickel (Ni).



Figure 15 Comparison between mine water and baseline groundwater samples: arsenic (As), selenium (Se), copper (Cu), antimony (Sb), cadmium (Cd), zinc (Zn), molybdenum (Mo), cobalt (Co), lead (Pb).

4 Discussion and conclusive remarks

We have shown the concentration ranges for selected physico-chemical properties and dissolved inorganic chemicals in water samples collected from primary drinking water supplies obtained from different groundwater source types: boreholes, dug wells, and springs. The different source types were categorised into four groups: deep (> 50m) boreholes, shallow (<30 m) hand-pumped boreholes, dug wells (< 10 m deep), and springs. These groups may represent different aguifer settings. Groundwater from the dug wells, and, to a lesser extent, hand-pumped boreholes, had some of the lowest pH values, conductivity and alkalinity. This is typical of recent rainfall recharge to aquifers that experiences limited water-rock interaction, and consistent with observed patterns in crystalline Basement aquifers; here recharge rates are high and flow paths are shallow and short-term, resulting in predominantly low concentrations of total dissolved solids (Lapworth et al., 2017). Groundwater from the eight deep boreholes had, instead, much higher conductivity, neutral to alkaline pH, and higher alkalinity. This may reflect deeper groundwater that has travelled a greater distance from its recharge zone, thereby increasing the potential for water-rock interaction. The spring samples have a large conductivity range (144-830 µS/cm), possibly representing discharge of groundwater of different ages / from different aguifer depths. The highest salinity is in the NDIWA spring, similar to the adjacent deep borehole, and therefore possibly reflecting upflow of deep groundwater at this location.

A summary of the presence or absence of selected health-based inorganic quality concerns, and the apparent suitability of the inorganic chemistry of the sampled groundwaters for drinking purposes, is summarised below. This was a small study with a small number of samples, and our conclusions on the baseline quality of groundwaters are correspondingly limited. Further work is needed to extend this baseline assessment, with larger numbers of samples over a wider area. Within the limits of this study, most of the major inorganic ionic parameters analysed in the sampled waters are within the acceptable limits of the World Health Organization (WHO, 2017). Most groundwaters are in the optimum pH range 6.5–8.5 for drinking water (WHO, 2017), with only two dug wells (pH 5.60 and 6.20) and one spring (pH 5.71) showing more acidic water. Nevertheless, there are a number of exceedances of the WHO permissible drinking water limits. The proportion of these exceedances is similar to that reported by Lapworth et al. (2020) in a study across the Ethiopian Highlands, Malawi and Uganda, where WHO health-based chemical drinking water quality values for manganese, fluoride, and nitrate were exceeded in 9% of rural hand-pumped boreholes sampled. The exceedances of WHO (2017) permissible limits in groundwater samples from the current study are as follows:

- Nitrate (NO₃) exceedance of the WHO limit of 50 mg/l was observed in one dug well and one spring. These waters also had relatively high SEC values and may reflect local recharge contaminated by nutrients from domestic wastewaters or leakage from household septic tanks and pit latrines. A dug well of only a few metres depth may receive groundwater recharging from a very small surrounding area, so that its groundwater may reflect localised rather than wider effects of land use on groundwater chemistry.
- The fluoride (F) drinking water quality guideline (WHO 1.5 mg/l) is exceeded (<2 mg/l) in two deep boreholes and the NDWIA spring, which is likely to represent the discharge of deep groundwater. The positive correlation (p-value=0.000) of F with SEC, alkalinity, calcium, magnesium, as well as uranium and strontium (trace elements known to increase with residence time in most aquifers (Edmunds, 1994)), may suggest a residence time control on F concentrations.
- Manganese (Mn) is well below both the health-based value of 0.4 mg/l (400 μg/l) and the taste-based guideline of 0.1 mg/l (100 μg/l) in all samples, except for one much higher concentration of 774 μg/l measured in one of the dug wells, which also had a high iron concentration.
- The WHO drinking water quality guideline (10 µg/l) for arsenic (As), was exceeded in five
 of the twenty-one sampled groundwaters. These were spatially scattered and found in dug
 wells and both shallow and deep boreholes. The lack of any significant correlation
 between arsenic and any of iron, sulphate, redox, alkalinity, dissolved oxygen or pH,
 makes it impossible to identify the sources and mechanism of release of these instances

of high arsenic without further investigation. It is noticeable, however, that the highest two concentrations of 52 μ g/l and 129 μ g/l were found in two hand-pumped boreholes with moderately reducing waters (Eh values of ~ 250 mV), one of which also had high levels of dissolved iron (~ 1 mg/l). It is possible that some of the arsenic derives from reductive dissolution of iron oxyhydroxides with subsequent release of the arsenic adsorbed on the oxide mineral surface.

Other trace metals potentially linked to the quartz-gold vein ore mineralogy in the study area (e.g. Cd, Co, Cu, Ni, Pb, Sb, Zn) were found to be below WHO guideline values in all the groundwater samples. Although, as discussed in detail above, the preservation methodology for the mercury samples means the mercury data should be treated with caution, mercury was below the WHO drinking water standard (for inorganic mercury) of 6 μ g/l in all samples. The highest mercury value analysed in groundwater in this study (0.16 μ g/l) was from a dug well in the proximity of an ASGM site where vat leaching with cyanide solution is used to extract gold, and spent tailings heaps accumulate. This highlights the potential environmental threat that mercury-laden tailings from ASGM can pose to groundwater, especially when the cyanide gold leaching practice enhances mercury release into the aquatic environment because of the formation of water-soluble cyanide-mercury complexes.

Additional sampling and analysis were done of mine waters, not only because they represent a potential source of contamination to natural groundwater, but are also, in some cases, a household water supply. The mine water sampled from shafts mining the gold-quartz veins at four different sites shows wide variation in the concentrations of total dissolved elements, but none were acid mine waters, as predicted based on the relevant geoenvironmental model of the ore deposit type described before. They are all bicarbonate waters, and their conductivity (SEC 164 to 1733 μ S/cm) increases with shaft depth. Apart for the Osiri mine water, which is the only mine water enriched in sulphate (381 mg/l), most parameters in the other mine waters are no higher than the upper interquartile value of the baseline groundwater distribution. Noticeable exceptions are iron, manganese, and arsenic concentrations in mine waters, which are frequently higher than the baseline upper interquartile value.

In the mine waters as for some of the baseline groundwaters, fluoride and arsenic exceed the WHO drinking water standards: fluoride is above the WHO of 1.5 mg/l at the deep mine shaft Osiri mine; arsenic is above the WHO standard of 10 μ g/l in all of the four mine shaft waters, and greatly exceeds it (178 and 190 μ g/l) in two of them.

Although to the best of our knowledge, high arsenic in groundwater has not previously been recorded in this area, these findings are comparable to groundwater arsenic concentrations in the Lake Victoria Basin mining areas in Tanzania (Kassenga and Mato, 2008; Ligate et al., 2016). They are further evidence to support the "gold-quartz vein" ore deposit geoenvironmental model by Plumlee et al., 1999, which describes near-neutral mine waters with high arsenic concentrations, but otherwise a general low base metal content. The relative importance of anthropogenic and geogenic sources, and the processes affecting high concentrations of arsenic in waters, require further research.

Confirming previous work, the two panning ponds contain highly mineralised water, with sulphate as the major ion. The different composition of potential hazardous elements in each pond is likely to reflect the different ore type processed at each mine, with acid, metal-rich waters at Macalder and neutral waters with low hazardous element content at Osiri mine. Mercury, was detected at a concentration of 1 μ g/l in the Osiri pond, which is below the WHO standard for drinking water of 6 μ g/l.

The results for mercury, although they should be confirmed by further testing, seem to confirm that groundwater is not a good indicator of mercury pollution given the inherent insolubility of most inorganic mercury compounds in natural waters, and suggest mercury occurrence in groundwater is a lower risk than its enrichment in soils and sediments.

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