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## Isotopic and hydrogeochemical characterization of groundwater and surface water from a mine site in Tanzania

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### ABSTRACT

This study used the hydrochemical properties of water to reveal the causes of water quality degradation. The results showed that most samples located downstream of the mine tailings dam were slightly acidic with pH as low as 4.6. Samples with high levels of Na<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> could not be isotopically linked to the local geochemistry, but the anthropogenic activities and evaporation were probably responsible for the observed water chemistry. The Piper diagram indicated cations were dominated by Ca and Mg, while anions were dominated by bicarbonates and sulphates. Pb and Hg levels (mean 70.29 and 17.95 µg/L, respectively) were all higher than the World Health Organization (WHO) and Tanzanian drinking water guidelines. Mining activities probably contributed to the observed low pH values and elevated concentration of cyanides, heavy metals, and metalloids. Stable isotope results indicated a vulnerability of the water to recent contamination that could be attributed to anthropogenic activities. Moreover, isotopic studies indicated a flow pattern from the eastern to the western side of the mine study site. Low-land samples were more <sup>3</sup>H-enriched than highland ones. The present study concludes that groundwater recharge from recent local precipitation may have an impact on the sources studied.

**Key words:** environmental stable isotopes, groundwater pollution, heavy metals and metalloids, Lake Victoria goldfields, North Mara gold mines, Tanzania mine pollution

### HIGHLIGHTS

- Slightly acidic groundwater in Tanzania.
- Levels of Pb and Hg higher than Tanzanian WHO standards.
- Vulnerability of groundwater to recent contamination.
- Contamination could be linked to local anthropogenic activities.
- Contamination increased from east to west, towards Lake Victoria.

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## GRAPHICAL ABSTRACT



## INTRODUCTION

Water is increasingly being demanded for human domestic consumption and economic development, albeit its quality and quantity have been deteriorating due to natural and anthropogenic environmental effects (Vaux 2011). In Tanzania, mining expansion is one of the recent human-related environmental impacts. Development of large-scale mines, especially in the Lake Victoria goldfields of Tanzania that began in the late 1990s, has brought about socio-economic changes in the country. The past two to three decades have seen village lands turn into suburban settlements, albeit with little settlement planning. These issues make water resources around large-scale mine operations in Tanzania to be put under pressure and make it challenging to ensure the availability of water in both good quality and quantity (Taylor *et al.* 2005). An important aspect in surface and groundwater monitoring studies is water quality analysis. Hydrochemistry studies can reveal suitable water quality aspects to increase the understanding of the changes due to natural or anthropogenic activities. Groundwater and surface water often consists of seven major ions:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{SO}_4^{2-}$ , which play a significant role in classifying and assessing water quality.

In the recent past, a new pollution concern has emerged resulting from domestic effluents due to increasing human settlement around the Tanzanian major mining operations. Few cases have been published in Tanzania on elevated levels of heavy metals and trace elements from water sources, soil, and plants near gold mining activities (Taylor *et al.* 2005; Dimitriou & Zacharias 2006; Bitala *et al.* 2009; Almás & Manoko 2012; Rwiza *et al.* 2016). Despite the environmental impacts caused by large-scale mining operations, studies that clearly characterize the hydrogeochemical properties of both ground and surface water around these mining operations are limited.

Most of the previous studies addressed only trace elements and heavy metals pollution and their spatial distribution in groundwater (Almás & Manoko 2012; Rwiza *et al.* 2016). However, assessing the vulnerability of water resources to contamination remains an important area of study for community livelihoods and environmental conservation. The vulnerability of water resources, especially groundwater, to contamination can be projected by estimating the residence time and the flow patterns of groundwater (Bowell *et al.* 1995; Dimitriou & Zacharias 2006). According to Hinkle (2009), estimating the rates of groundwater movement and contaminant transport can aid in assessing the groundwater system for potential contamination and contaminant distribution. This can also guide in determining the susceptibility of groundwater to near surface contamination. The study of contaminant transport is made possible by employing environmental isotopes that help in determining the relative groundwater age and flow pathways (Yeh *et al.* 2011; Hamutoko *et al.* 2017). Stable isotopes of  $^2\text{H}$  and  $^{18}\text{O}$  are usually employed in tracing the groundwater flow along its path for determination of the origin of groundwater and how the water mixes. On the other hand, radioactive isotopes can be employed to assess the dynamics of groundwater (Kendall & Doctor 2003). The radioactivity of tritium, measured in tritium units

(TU), whose half-life is approximately 12.43 years, can be applied in revealing the occurrence of recent groundwater recharge (Lucas & Unterweger 2000).

The present study aimed at determining the vulnerability of groundwater to contamination using hydrochemical characterization and isotopic signatures. The hydrochemical compositions of various water resources were analyzed for evaluation of the spatial distribution of pollutants. The spatial distribution of groundwater isotopes provided a basis for knowledge about the pathways and residence time. The results for stable and radioactive isotopes, in addition to the hydrochemical characteristics of water, also helped explain groundwater vulnerability to contamination.

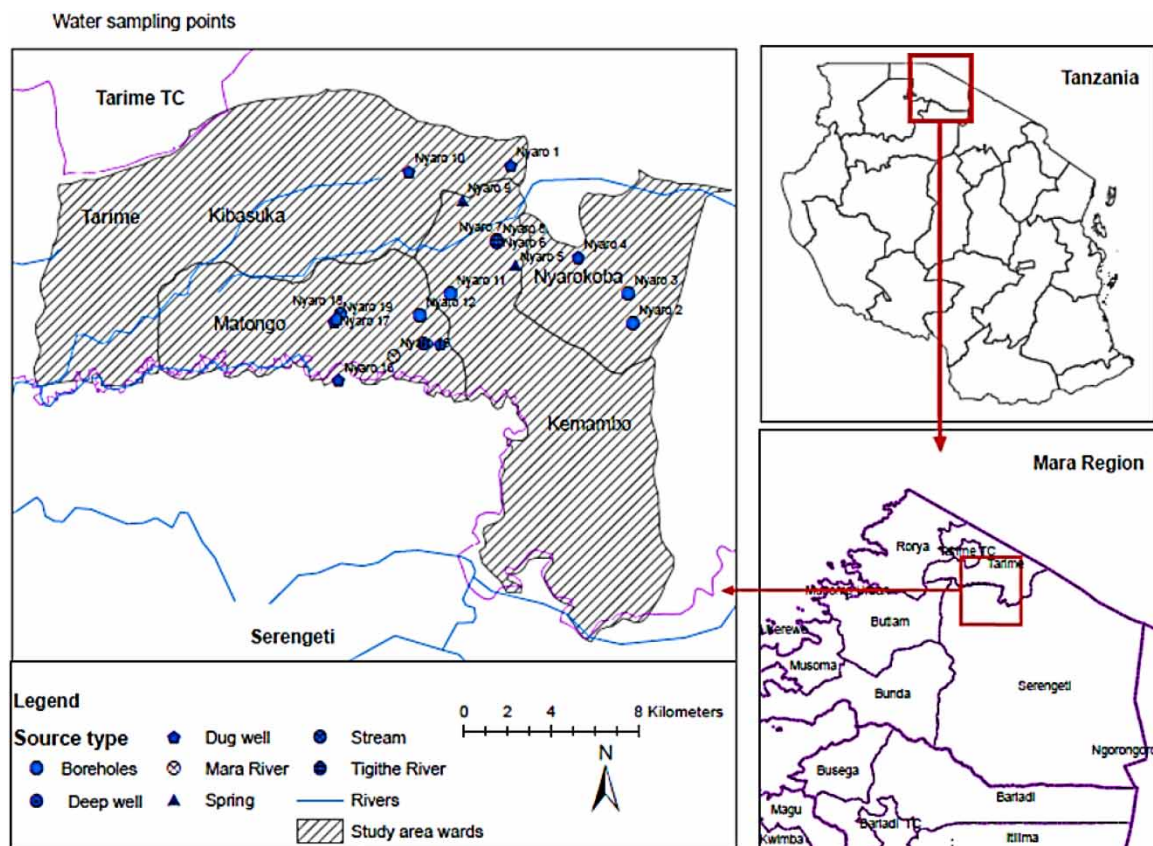
## MATERIALS AND METHODS

### Site description

The NMGM is located in Tarime district, Mara region, northwest Tanzania (1°25' 50'S, 34°33'51'E) and is within the Lake Victoria basin. To the north it borders Kenya and to the east it is bordered by Lake Victoria (Figure 1). The NMGM consists of the main open-pit mine and an underground mine named Nyabirama and Nyabigena, respectively; oriented to each other in the northeast to southwest direction. This gold-rich area is within the sulfide ore system, characterized by numerous deposits of base metals. The underlying rock is primarily pyrite (FeS<sub>2</sub>), while arsenopyrite (FeAsS), galena (PbS), and sphalerite ((Zn,Fe)S) form a small section (Bowell *et al.* 1995). Greenstone terranes, which are dominated by metavolcanic, metasedimentary rocks, and Archean granite, form the geology of the area and are part of the Tanzanian craton.

### Sample collection and analyses

A total of 19 water samples were taken from varying sources, including boreholes, shallow wells (dug wells), and springs. The sample points considered the distance from the active mine sites, within and between the two main aforementioned mines. Surface water samples were from the Mara River, the Tigithe River, and an unnamed



**Figure 1** | Tanzania map (top right corner) showing part of the Lake Victoria greenstone zone (bottom right) and locations of the sampling sites for the present study (left).

small stream in the Kwinyunyu subvillage whose flow passes from near the Nyabirama open pit mine tailings dam. Five subsamples were collected from each sampling point for statistical quality assurance, to make 95 samples in total. The field work for sample collection was conducted in April 2019 which marks the peak of the rainy season in this area of Tanzania. Before taking a well sample, the water was pumped out for 5 min to remove any stagnant contaminants. A handheld GPS unit was used for recording sampling point coordinates; observed site characteristics, i.e., latitude, longitude, altitude as well as nearby landmarks were also recorded. Water samples were collected in 3x rinsed bottles and the in-situ data, e.g., temperature, dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS) and pH, were collected immediately using a multi-parameter device (ScichemTech SCT-THER-PEN-6).

Furthermore, a 1,000 mL polypropylene bottle was used to collect samples for analysis of cations, anions, and nitrate. For stable isotopic analysis, 100–250 mL high density polypropylene (HDPE) bottles were used to collect samples for stable isotopes of hydrogen and oxygen, whereas 50 mL HDPE bottles were used for collecting samples for tritium isotope analysis. The HDPE bottles were sealed to prevent evaporation prior to laboratory analysis. Samples for cationic analysis were filtered *in situ* using 0.45 µm membrane filters and preserved by adding 2 mL of nitric acid to maintain pH 2.0. Samples for nitrate analysis were preserved by sulfuric acid. All samples were kept in ice cold chests before being transferred to a refrigerator. Upon arriving in the laboratory, the samples were kept at 4 °C until analysis.

Analyses for cations and anions were conducted in the laboratories of the Nelson Mandela African Institution of Science and Technology (NM-AIST) and the Ngurdoto Defluoridation Research Center, both located in Arusha, Tanzania. Common cations and anions measured included Na, K, Mg, Ca, NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and Cl<sup>-</sup>. The method used for the analyses of Ca and Mg was ISO 6059: 1984 – EDTA (0.05 N) titration. Na and K were analyzed using the Sodium Ion – Selective Electrode Method, while Cl<sup>-</sup> was analyzed using the AWWA/APHA: 4500-Cl-B Argentometric Method. CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> were analyzed using alkalinity in water by Titrimetric Method (titration with 0.01N H<sub>2</sub>SO<sub>4</sub>). SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were analyzed using spectrophotometric methods.

The analysis of stable isotopes was conducted at the University of Waterloo Isotope Laboratory (Ontario, Canada) using a ThermoScientific MAT 253 Stable Isotope Ratio Mass Spectrometer. The isotopic values were recorded in δ-values of per mil (‰) by comparing them with the international Vienna Standards Mean Ocean Water (V-SMOW), as defined by Equation (1):

$$\delta = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} \right) \times 1,000 \text{ (‰)} \quad (1)$$

where  $R_{\text{sample}}$  and  $R_{\text{standard}}$  represent <sup>2</sup>H/<sup>1</sup>H and <sup>18</sup>O/<sup>16</sup>O isotopic ratios of samples and standards, respectively (Craig 1961).

The analytical precision was measured within ±0.20‰ for δ<sup>18</sup>O and ±0.8‰ for δ<sup>2</sup>H according to the V-SMOW. Tritium quantification was performed using the liquid scintillation counting (LSC) technique. Quantification was direct (not enriched) with a detection limit of 6.0 ± 6.0 TU at 2 sigma and reported in tritium units (TU).

Heavy metals and metalloids were analyzed using WFX-210 (Beijing Rayleigh Analytical Instrument Corporation) atomic absorption spectroscopy (AAS) after wet acid digestion with a diacid mixture 9:4 (v/v) (nitric acid: hydrochloric acid). Cyanide analysis was performed using a revised Phenolphthalein Method. Analytical blanks were run in the same way as the samples and concentrations were determined using standard solutions prepared in the same acid matrix. All laboratory plastic and glassware was pre-cleaned by soaking overnight in a 10% HNO<sub>3</sub> solution and then rinsed with deionized water. All samples were collected and analyzed in triplicate, and the average results were used to represent the data. All calculations, including correlation analysis, were performed using Microsoft Excel Version 2015.

## RESULTS AND DISCUSSION

### General site characteristics and water quality

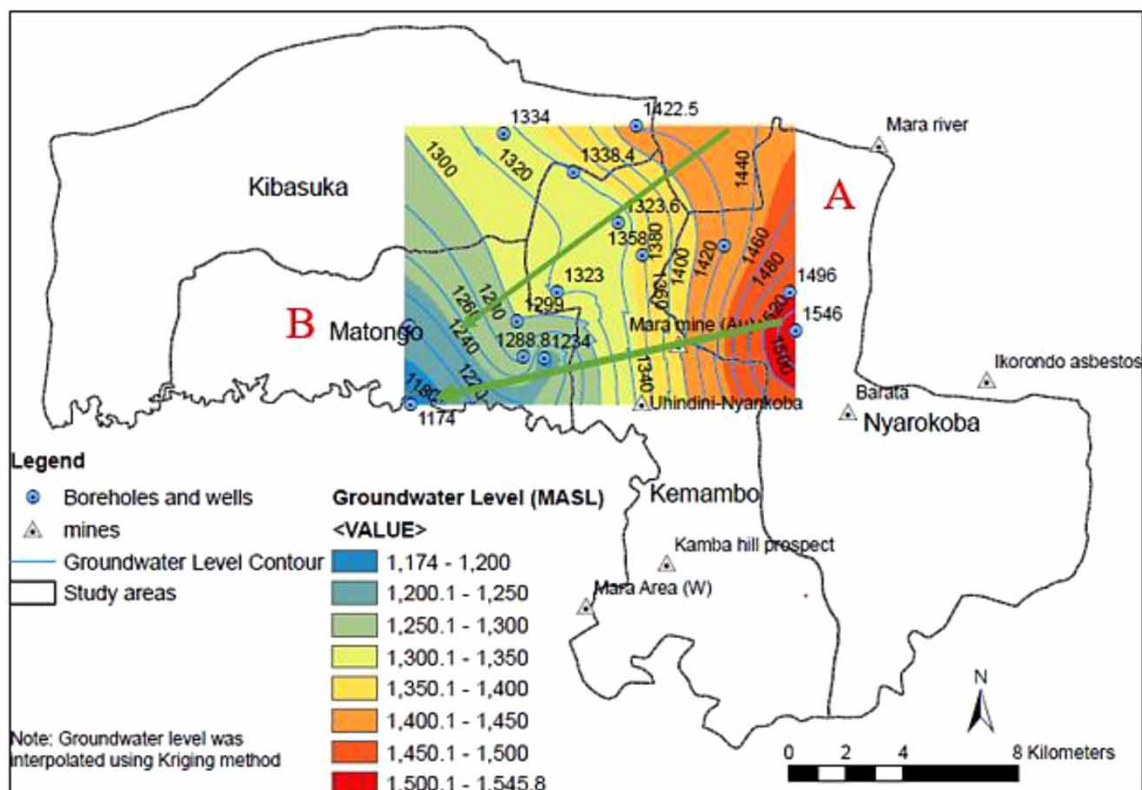
Water source depths varied from surface water to shallow wells and deep groundwater boreholes (Table S1, Supplementary Material). The water temperature ranged from 22.9 to 27.8 °C, a typical average annual temperature of a shallow water table aquifer. The water sources from which the samples were collected were located at

varying altitudes, expressed in meters above sea level (m.a.s.l.). Samples were collected from highland to lowland areas at the elevation ranging from 1,162 to 1,547 m above sea level. Other site-specific descriptions are as given in Table S1, Supplementary Material. The general groundwater flow pattern was in the east-to-west direction (Figure 2). As can be seen from Table S1, the present study collected data from varied groundwater and surface water sources at different distances from the mine tailings dam. These site characteristics could have an influence on the quality of surface and groundwater samples (Lerner & Harris 2009).

### Groundwater and surface water pH

The sample's pH, measured onsite, varied between 4.60 and 8.36, with a mean value of 6.99 (Table 1), which was close to neutral. The standard deviation of 0.9 showed that the data were highly spread out. Most of the collected samples had pH values above 6.3 but not more than 8.5 (Table 1). Samples from Nyaro3, Nyaro4, Nyaro5, Nyaro7, Nyaro8, Nyaro9, Nyaro10, Nyaro14, Nyaro17, and Nyaro19 points had pH values below 7.0. Except Nyaro14, 17, and 19, all of these samples were collected in areas close to the Nyabigena mine site, where most sampling sites were within 1 km of the mine tailings dam. Samples whose pH > 7.0 were randomly distributed around the Nyabigena and Nyabirama mine sites.

According to TBS (2005), the lower and upper limits of pH admissible for drinking water purposes are 6.5 and 8.5, respectively (Morgenstern *et al.* 2010). The international standards, for example, those by WHO for surface and groundwater systems, are also in a similar range of 6.0 to 8.5 pH values. Six water samples equivalent to 32% had pH values below the stipulated limit in the Tanzanian guidelines (Table 1). Most of these samples were collected from shallow wells and springs that were close to mining operations. These water sources were mostly used for domestic consumption. The low pH values found in some surface water and groundwater samples may be related to mining activities in these areas. Low pH values usually affect heavy metal's distribution and migration of making such water sources to be susceptible to pollution (Wang *et al.* 2016). The samples from the Mara River, the Tigithe River, an unknown stream, and the groundwater from the boreholes on the eastern side were mostly slightly alkaline (pH = 8.3–8.6), which is an indication of dominance of dissolved HCO<sub>3</sub><sup>-</sup> and that of CO<sub>3</sub><sup>-</sup> (Laar *et al.* 2011).



**Figure 2** | Groundwater contour lines showing the groundwater flow direction of the study area. Water flow is from A towards B as indicated by the green arrows.

**Table 1** | Isotope composition and hydrochemical composition of water samples collected from the NMGM operations

Sampling site code <sup>a,b</sup>	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$^3\text{H}$	pH	EC	$^{\circ}\text{TDS}$	$^{\circ}\text{Na}^+$	$^{\circ}\text{K}^+$	$^{\circ}\text{Ca}^{2+}$	$^{\circ}\text{Cl}^-$	$^{\circ}\text{CO}_3$	$^1\text{HCO}_3$	$^{\circ}\text{SO}_4^{2-}$	$^{\circ}\text{NO}_3$	$^{\circ}\text{Mg}^{2+}$
Nyaro1	-3.02	-10.22	N.M	7.26	712	356	73	4.4	43.4	7	0.55	324.4	11	11.4	16.6
Nyaro2	-3.37	-14.50	<5.0	8.18	676	338	120	5.2	10.3	21	4.53	318.4	6	2.7	5.1
Nyaro3	-2.69	-7.35	<5.0	6.68	164	82	19	7.9	10.1	18	0.02	45.0	1	24.1	6.6
Nyaro4	-2.76	-8.03	N.M	6.41	151	76	18	6.4	9.7	16	0.01	55.0	0	7.3	2.8
Nyaro5	-2.42	-7.33	N.M	6.33	142	71	20	6.7	15.6	8	0.01	57.0	1	14.7	4.9
Nyaro6	-0.96	-0.30	N.M	8.36	349	175	28	6.5	16.6	11	2.00	92.9	28	1.5	8.1
Nyaro7	-1.79	-2.96	9.0	4.60	1,388	698	210	19	94.5	190	0.00	0.0	136	10.6	47.7
Nyaro8	-1.14	-0.38	N.M	6.70	430	216	37	8.2	37.2	22	0.04	77.0	62	10.1	6.0
Nyaro9	-2.00	-3.27	11.5	6.20	226	114	19	5.5	10.8	9	0.01	52.0	15	19.1	5.4
Nyaro10	-2.60	-9.01	7.0	6.39	179	90	21	5.4	7.9	10	0.01	63.0	7	7	6.2
Nyaro11	-3.00	-11.55	<5.0	7.00	837	418	44	11	43.8	32	0.25	264.7	9	9.3	24.3
Nyaro12	-1.78	-1.57	<5.0	7.76	1,030	515	99	32	113.4	88	1.14	209.8	100	34.6	1.51
Nyaro13	-2.21	-4.22	<5.0	7.12	773	387	74	1.9	45.5	56	0.22	174.8	65	15.4	11.5
Nyaro14	-2.37	-5.55	<5.0	6.54	595	298	36	7.8	42.4	14	0.03	80.0	140	19.8	6.6
Nyaro15	-2.70	-11.74	N.M	7.31	992	496	71	1.8	55.97	22	0.55	286.4	12	214	4.33
Nyaro16	1.51	15.33	N.M	8.36	540	270	57	9.8	29.9	54	3.16	146.7	31	7.3	16.3
Nyaro17	0.98	9.94	N.M	6.81	3,456	1,736	310	54	558	53	0.11	174.9	103	8.9	160
Nyaro18	4.73	31.09	N.M	8.30	4,200	2,120	430	85	306.8	60	2.85	152.0	82	2	88.9
Nyaro19	1.25	14.24	8.3	6.48	3,988	1,996	6.3	1.6	10.7	7	0.00	5.0	1900	50.9	8.5
Mean	-1.39	-1.44	-	7.00	1,096.2	550.1	89.1	14.7	77.0	36.7	0.8	134.7	142.6	24.8	22.7
± SD	-	-	-	0.9	1,290.9	649.1	111.8	21.1	135.2	43.7	1.3	103.9	428.1	47.4	39.2
WHO standard limits				6-8.5		500-1,500	500-2,000	10-12	75-200	250-600		300-600	200-600	50	30-150

SD = standard deviation. N.M = not measured.

<sup>a</sup>The precision for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  were within  $\pm 0.8\%$ , and  $\pm 0.2\%$  respectively (VSMOW).

<sup>b</sup>The direct Tritium  $\pm 8$  TU.

<sup>c</sup>Chemical concentrations were measured in mg/L. EC was measured in  $\mu\text{S}/\text{cm}$ .

### TDS and EC levels

EC values varied between 142 and 3,988  $\mu\text{S}/\text{cm}$  (mean =  $1,096.2 \pm 1,290.9 \mu\text{S}/\text{cm}$ ), while TDS ranged between 71 to 1,996 mg/L (mean =  $550.1 \pm 649.1 \text{ mg}/\text{L}$ ) (Table 1). Both values indicated a very high dispersion from the mean. The general indication of the EC values showed that deeper wells were more mineralized compared to shallow wells and springs whose EC values ranged from 540 to 3,988  $\mu\text{S}/\text{cm}$  and 143 to 773  $\mu\text{S}/\text{cm}$ , respectively (Table 1). A similar trend was indicated by the TDS, which was higher in deeper wells than in shallow wells and springs. A trend in the variation of the EC and TDS with depth could be established such that as one moves from the north-east to south-west direction (from side A upstream to side B downstream, Figure 2) of the study site, the values of the EC and TDS increase. Thus, a general observation may be made that EC and TDS increased from upstream downward.

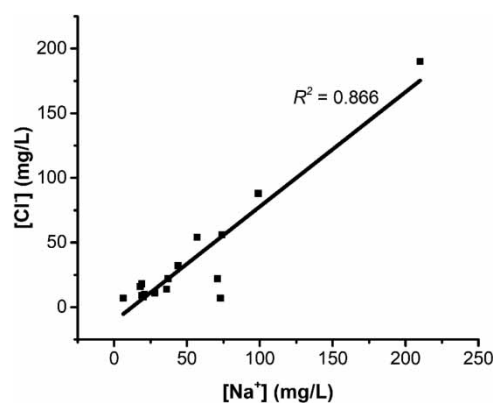
TDS of up to 500 mg/L is classified as desirable for drinking; while 500–1,000 mg/L TDS levels are classified as permissible for drinking; 3,000 mg/L TDS level acceptable for agricultural purposes, although not fit for drinking; while TDS levels greater than 3,000 mg/L in water may only be useful for irrigation (Singh *et al.* 2015). Of the 19 sampling sites (Table 1), samples collected from 15 sites fell in the ‘desirable for drinking’ category and only one was within the ‘permissible limit’ category. Analysis results also indicated that all water sources were suitable for irrigation purposes.

Raju *et al.* (2009) suggested that the variation in the concentrations of TDS, EC, and other ions could be partly attributed to variations in the geochemical processes of groundwater and mostly as a result of anthropogenic activities. Activities such as agriculture, industrial discharge, domestic waste discharge, and geological weathering may contribute to high levels of EC and TDS in natural waters (Dinka *et al.* 2015). Therefore, the high concentrations of TDS observed on the western side of the Nyabirama open pit mine can be directly related to the effluents from the mine tailings dam located within <200 m of the sampling area.

### Major ion geochemistry

For the measured cations, the dominant ion was  $\text{Na}^+$  with concentrations ranging from 16.3 to 430.0 mg/L (mean = 89.1 mg/L) (Table 1). Values for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  followed, respectively, with ranges of 7.9–306.8 mg/L (mean = 77.0 mg/L), 1.5–160 mg/L (mean = 22.7 mg/L), and 1.6–85 mg/L (mean = 14.7 mg/L) (Table 1).  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  had a much higher standard deviation of 135.2 and 39.2 compared to their means of 77.0 and 22.7, respectively. Cation chemistry was dominated by  $\text{Na}^+$  with about 44% followed by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with 38 and 11%, respectively, while  $\text{K}^+$  had a minor contribution of 7%. Thus, the chemistry of the cations, for 68% of the analyzed samples, followed the following trend:  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}/\text{K}^+$ , while 21% of the samples followed the order:  $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+}/\text{K}^+$ .

The cations such as  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  are usually associated with  $\text{Cl}^-$  and are usually found in natural waters in the range between 1 and 100 mg/L. The adjusted values of  $\text{Na}^+$  were well correlated with  $\text{Cl}^-$  (Figure 3). The measured values were generally higher than those found in natural waters. However, depending on the bedrock type, variations in the concentrations of Ca and Mg in natural waters ranging from 1 to 400 mg/L are not uncommon (Cotruvo & Bartram 2009). Because Ca and Mg are essential elements for human, soil, and plant health, the WHO does not impose strict regulations on the concentrations of these elements in drinking water. Numerical



**Figure 3** | A scatter plot of chloride concentrations vs. sodium concentrations from field data collected at the NMGM operations. 75% of the samples were used in plotting this graph as 5 sampling sites were found to be outliers.



limits for Ca and Mg in the WHO documents are given as a precaution related to the acceptability of water by consumers in terms of taste and scale deposition (WHO 1993, 2011). Furthermore, the total hardness of the water is mainly contributed by sedimentary rocks that contain Mg and Ca ions. Additionally, other elements such as Ba, Mn, Al, Sr, Zn, and Fe are usually found in surface and groundwater systems at varying concentrations (WHO 2011). Cation exchange could be the main process controlling the mobility and chemistry of these major cations in the groundwater and surface water systems in and around the NMGM (Hamutoko *et al.* 2017). Ca<sup>2+</sup> and Mg<sup>2+</sup> levels were higher than 100 mg/L in shallow water sources that were, therefore, subject to evaporation. This suggests that the effects of evaporation processes could have resulted in reduced dilution effects for shallow water sources.

For the anionic concentrations (Table 1), SO<sub>4</sub><sup>2-</sup> dominated the rest of the anions ranging from none to 1,900 mg/L (mean = 142.6 ± 428.1), followed by a HCO<sub>3</sub><sup>-</sup> range of none to 324.4 mg/L (mean = 134.7 mg/L), then Cl<sup>-</sup> that ranged from none to 190 mg/L (mean = 36.7 mg/L) and finally NO<sub>3</sub><sup>-</sup> with a range of 1.5–214 mg/L (mean = 24.8 mg/L) (Table 1). The salinity and hardness showed that about 42% of the samples equally belonged to HCO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> series. The Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> > HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> > HCO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> series represented a mere 5% of the total samples. Generally, the anionic chemistry of the total samples was dominated by SO<sub>4</sub><sup>2-</sup> (41%) and closely followed by HCO<sub>3</sub><sup>-</sup> dominance (39%), while a minor contribution of 10 and 7% was for Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions, respectively. Except Nyaro19, the other sampling points had SO<sub>4</sub><sup>2-</sup> concentrations below the WHO secondary maximum contaminant level (SMCL) for water quality (250 mg/L) designated for drinking (WHO 2011). In accordance to WHO (2011), naturally, SO<sub>4</sub><sup>2-</sup> occurs in groundwater at high levels due to the abundance of sulphate-containing materials in the natural environment. This might not be the case for sampling points that had a concentration of 1,900 mg/L downstream of the mine tailings dams. In this case SO<sub>4</sub><sup>2-</sup> levels could be an indication of the occurrence of recharge in groundwater with acidic water directly linked to the effluent discharged from the mine tailings dam, as well as associated atmospheric depositions.

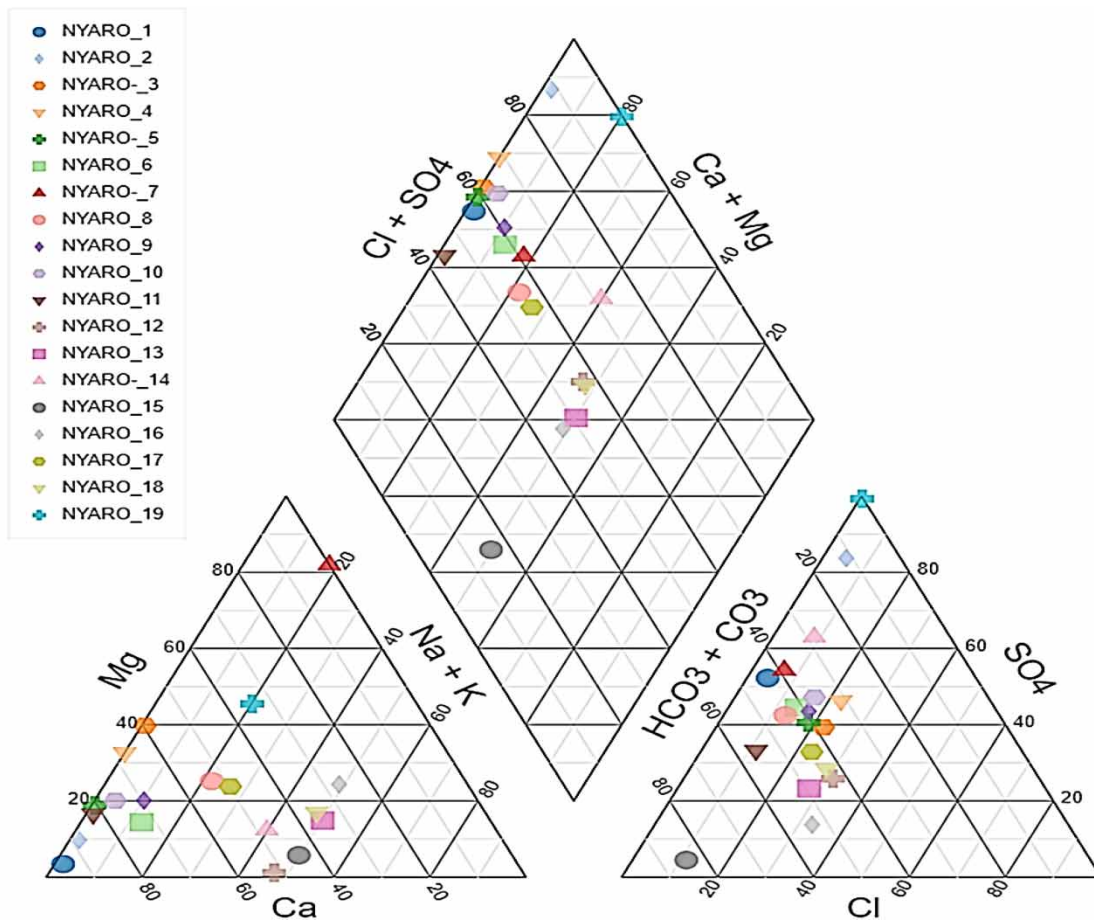
NO<sub>3</sub><sup>-</sup> concentrations ranged from 1.5 to 214 mg/L (mean = 24.8 mg/L) (Table 1), in which higher concentrations were measured from the surface waters of the Mara River (Nyaro15) and groundwater that was collected from some springs. The NO<sub>3</sub><sup>-</sup> concentration showed a spatial distribution with considerably high NO<sub>3</sub><sup>-</sup> in both the northern part (highland areas) and the western part (lowland areas of the studied area). The Tanzania Bureau of Standards (TBS) regulates NO<sub>3</sub><sup>-</sup> in drinking at a lower level of 10 mg/L and an upper level of 75 mg/L. Ten samples, equivalent to 52% of all samples, had nitrate concentrations within the Tanzanian permissible limits, while 48% of the samples had nitrate concentrations above the permissible upper limit. NO<sub>3</sub><sup>-</sup> contamination in water resources is usually linked to some activities like agriculture, human and animal waste, and lawns wastewater by 90, 9 and 1%, respectively (Bryan & Loscalzo 2011). Being highly soluble in water, NO<sub>3</sub><sup>-</sup> can easily seep unfiltered into the soil, especially during rainy periods, irrigation, and crop watering activities. These processes make its occurrence to be high in both surface water and groundwater. The samples with high concentrations of NO<sub>3</sub><sup>-</sup>, especially surface water from Mara and Tigithe rivers, was probably an indication of the impacts of anthropogenic activities.

### Hydrochemical classification

Some major ions analyzed in water samples were plotted on the Piper trilinear diagram (Figure 4). The results are hereby compared to those reported in the literature in order to classify water types (Ravikumar & Somashekar 2010). The results indicated that the water cations were dominated by Ca and Mg. The anions were dominated by SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>. This could mean that most of the water samples could be classified to contain the bicarbonates and sulphates of Ca and Mg.

### Correlation analysis

The coefficient of correlation (*r*) values are mostly used as a measure of dependence between two parameters of water and exhibit how well one variable predicts the other (Howladar *et al.* 2014). pH was negatively correlated with Cl<sup>-</sup>, Mg, SO<sub>4</sub><sup>2-</sup>, Hg, Pb, and Cd and it had a positive correlation with Na<sup>+</sup>, EC, K<sup>+</sup>, Ca<sup>2+</sup>, As, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, and CN<sup>-</sup> (Table 2). The relationship shown in Table 2 indicated how groundwater chemistry was influenced by CO<sub>3</sub><sup>2-</sup> and mineral dissolution of SO<sub>4</sub><sup>2-</sup> (Li & Jiang 2016). EC correlated positively with all other parameters except HCO<sub>3</sub><sup>-</sup> and Cd (Table 2). The EC is mostly used to indicate salinity in water and the highly significant correlation between it and major cations may be indicative of the contribution of major cations to the dissolved salts



**Figure 4** | Piper trilinear diagram illustrating the hydrochemical regimes of the studied waters (as modified by Ravikumar & Somashekar (2010)). The concentrations entered in the source data file were in units of milligrams per litre.

in the studied water. The correlation values also reflected well what was portrayed by the hydrochemical regimes in Figure 4. In the present study, cyanide correlated significantly only with EC, Na, and Pb. This could mean that sodium cyanide and cyanide complexed with Pb were the major cyanide species in the water analyzed (Hummel 2004; Nsimba 2009). Interestingly, there was no significant correlation between heavy metals and metalloids in the water samples studied.

### Concentration of cyanides, metals, and metalloids

A summary of the concentrations of heavy metals/metalloids and cyanide in groundwater and surface water samples collected from the NMGM has been given (Table 3). For free cyanide ( $\text{CN}^-$ ), high concentrations were found in samples collected from a stream in Kwinyunyu village near Nyabirama tailings dam (Nyaro18) with approximately  $20 \mu\text{g CN}^-/\text{L}$  and in samples collected from the Mara River (Nyaro15) with approximately  $15 \mu\text{g CN}^-/\text{L}$ . Cyanides usually occur in environmental waters in relatively low concentrations and mining operations are among the leading anthropogenic sources of  $\text{CN}^-$  (Mousavi *et al.* 2013). The WHO has set a health-based rounded value of  $500 \mu\text{g/L}$  as a limit on the level of cyanide in drinking water. In this study, the levels of  $\text{CN}^-$  were below the WHO threshold and were in agreement with cyanide levels found in the surface water of other countries such as Korea, Brazil, and Italy (Jaszczak *et al.* 2017). However, the fact that the highest concentrations of cyanide were found at a site close to the mine tailings dam (see Supplementary Material, Table S1 and Table 3) may raise some concerns about the influence of the tailings on the levels of cyanide in surface water.

The highest concentrations of Pb were found in samples collected from a community borehole (Nyaro7) near a mine tailings dam of Nyabigena mine site. Other high Pb values were also mostly from surface water and springs near the mine tailings dam. Nyaro4 and Nyaro17 were springs whose Pb concentrations were the highest with  $>130$  and  $>120 \mu\text{g Pb/L}$ , respectively. Surface water samples collected from the Tigithe river (Nyaro6), and

**Table 2** | Correlation coefficient matrix of groundwater and surface water quality parameters ( $n = 19$ )

	pH	EC	Na	K	Ca	Mg	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	CN <sup>-</sup>	Hg	As	Pb	Cd
pH	1														
EC	0.095	1													
Na	0.163	0.71*	1												
K	0.244	0.69*	0.92*	1											
Ca	0.092	0.68*	0.83*	0.82*	1										
Mg	-0.002	0.69*	0.83*	0.78*	0.97*	1									
Cl <sup>-</sup>	-0.32	0.22	0.51*	0.36	0.29	0.34	1								
HCO <sub>3</sub> <sup>-</sup>	0.58*	-0.01	0.19	0.07	0.15	0.08	-0.11	1							
SO <sub>4</sub> <sup>2-</sup>	-0.16	0.59*	-0.12	-0.09	-0.06	-0.04	-0.09	-0.32	1						
NO <sub>3</sub> <sup>-</sup>	0.017	0.047	-0.12	-0.19	-0.08	-0.17	-0.09	0.27	0.12	1					
CN <sup>-</sup>	0.058	0.54*	0.49*	0.35	0.26	0.32	0.12	-0.01	0.22	0.27	1				
Hg	-0.061	0.016	-0.12	-0.12	-0.26	-0.16	0.02	-0.07	0.14	0.09	0.23	1			
As	0.164	0.072	0.02	0.13	-0.17	-0.14	-0.04	0.08	0.09	-0.34	-0.19	0.41	1		
Pb	-0.26	0.53*	0.35	0.3	0.31	0.43	0.29	-0.49*	0.41	-0.17	0.59*	0.31	-0.06	1	
Cd	-0.15	-0.08	-0.22	-0.21	-0.04	-0.01	-0.12	-0.17	0.09	0.26	-0.09	-0.19	-0.1	0.2	1

\*Indicates significant correlation at  $p$ -value = 0.05.

**Table 3** | Levels of cyanide and selected heavy metal/metalloid ions in water samples collected from the NMGM of Tanzania

Sample name	CN <sup>-</sup> µg/L	Hg	As	Pb	Cd
Nyaro1	12.48	16.64	0.03	43.50	0.72
Nyaro2	7.49	11.46	0.09	3.79	0.21
Nyaro3	12.48	27.23	0.08	65.03	0.55
Nyaro4	12.48	17.82	0.02	131.48	0.80
Nyaro5	4.99	8.79	0.06	50.14	2.71
Nyaro6	9.98	18.68	0.06	134.40	1.95
Nyaro7	12.48	20.77	0.04	153.75	1.04
Nyaro8	7.49	9.21	0.02	0.30	0.03
Nyaro9	7.49	7.56	0.06	28.24	1.36
Nyaro10	4.99	33.59	0.08	72.30	0.54
Nyaro11	4.99	29.44	0.13	37.64	0.92
Nyaro12	2.50	11.69	0.08	3.97	0.61
Nyaro13	12.48	21.71	0.05	86.14	0.44
Nyaro14	5.99	15.64	0.02	49.43	0.12
Nyaro15	14.98	20.56	BDL <sup>a</sup>	31.29	1.61
Nyaro16	7.49	17.96	0.02	40.32	0.90
Nyaro17	9.98	7.86	0.01	120.36	1.29
Nyaro18	19.97	21.49	0.09	130.60	0.10
Nyaro19	13.62	22.88	0.07	152.75	1.25
Overall mean	9.70	17.95	0.05	70.29	0.90

<sup>a</sup>BDL = below detection limit.

samples collected from a stream in the Kwinyunyu subvillage (Nyaro18) had Pb levels >134 and 130 µg Pb/L, respectively. A total of 16 samples equivalent to 84% were found to contain Pb levels above the WHO recommended value of 10 µg/L, while six samples contained Pb levels above the 100 µg/L value recommended by TBS (TBS 2005; WHO 2011). Pb is defined by the United States Environmental Protection Agency (USEPA) as a hazardous substance to most forms of life and is considered toxic and relatively accessible to aquatic organisms even at low concentrations (USEPA 1986 in Adesiyan *et al.* (2018)). Pb is a known neurotoxin that negatively affects the cognitive abilities of under-five children (Rwiza *et al.* 2018). Therefore, the levels of Pb found in surface and groundwater sources in the present study are quite alarming.

For As, the concentrations ranged from 'no detection' at Nyaro15 to 0.13 µg As/L at Nyaro11. Generally, for As, the concentrations for all 19 sampling sites were negligible and fell within both the WHO and the TBS standards. According to (Ritter *et al.* 2002), As has the average concentration of 2 µg/L in the earth's crust. It may normally be available in enriched quantity in areas such as the NMGM sites that have small sections of As-containing ores, e.g., arsenopyrite (FeAsS) and pyrite (FeS<sub>2</sub>). Arsenic sources include natural weathering of geological material mostly found near such gold-rich areas.

For Cd, the highest level of 2.71 µg/L was detected in samples collected from Nyaro5, a shallow natural spring water source close to the Nyabigena mine tailings dam. However, the recorded Cd concentrations were all below both the WHO maximum allowed limits for drinking water of 3 µg Cd/L (WHO 2011) and 100 µg Cd/L recommended by TBS (TBS 2005). Usually, unpolluted water contains less than 1 µg Cd/L. Cd is a highly toxic metal and can dissolve in water easily. Despite being a chief pollutant in aquatic environments, Cd is a nonessential metal with adverse effects on living organisms (Adesiyan *et al.* 2018). The two sampling sites (Nyaro5 and Nyaro6) that had the highest Cd levels were surface water sources, an indication that the concentration of Cd in those samples were probably attributable to atmospheric deposition. However, Nyaro5, a spring water source, posed some concern because the Cd level of 2.71 µg/L was close to the limit set by WHO.

For Hg, the samples collected at Nyaro9 had the lowest concentration of 7.56 µg/L and the samples collected at Nyaro10 had the highest concentration of 33.6 µg/L. The WHO drinking water quality guideline for Hg is 6 µg/L.

As a pollutant, Hg is known for its toxicity and tendency to bioaccumulate and persist in the environment. Metal (e.g., gold–Au) refinery is a major source of Hg in most mining areas of sub-Saharan Africa. All samples in the present study had Hg levels well above the recommended WHO guideline (Table 3). In most raw and treated water, the Hg concentrations are expected to be low except for areas that are severely contaminated (Ritter *et al.* 2014). The observed values in the present study give an indication that Hg was probably being intensively used for Au extraction in the study area and is leached into the aquatic environment in appreciable quantities.

**Hydrogen ( $\delta^2\text{H}$ ) and oxygen ( $\delta^{18}\text{O}$ ) isotope composition**

The analytical results for the isotopic signatures of  $^2\text{H}$  and  $^{18}\text{O}$  compared to the standards (Table 1) showed that the water samples had means of  $-1.39$   $^{18}\text{O}$  and  $-1.44$   $^2\text{H}$ , while the ranges were  $-3.37$  to  $4.73$   $^{18}\text{O}$  and  $-14.5$  to  $31.09$   $^2\text{H}$ . Stable isotopic compositions of surface and groundwater were plotted together with a Global Meteoric Water Line (GMWL) (Figure 5). For the plotted isotopic values in water samples, regression analysis was applied accordingly followed by insertion of the GMWL. The GMWL relationship is given by Equation (2):

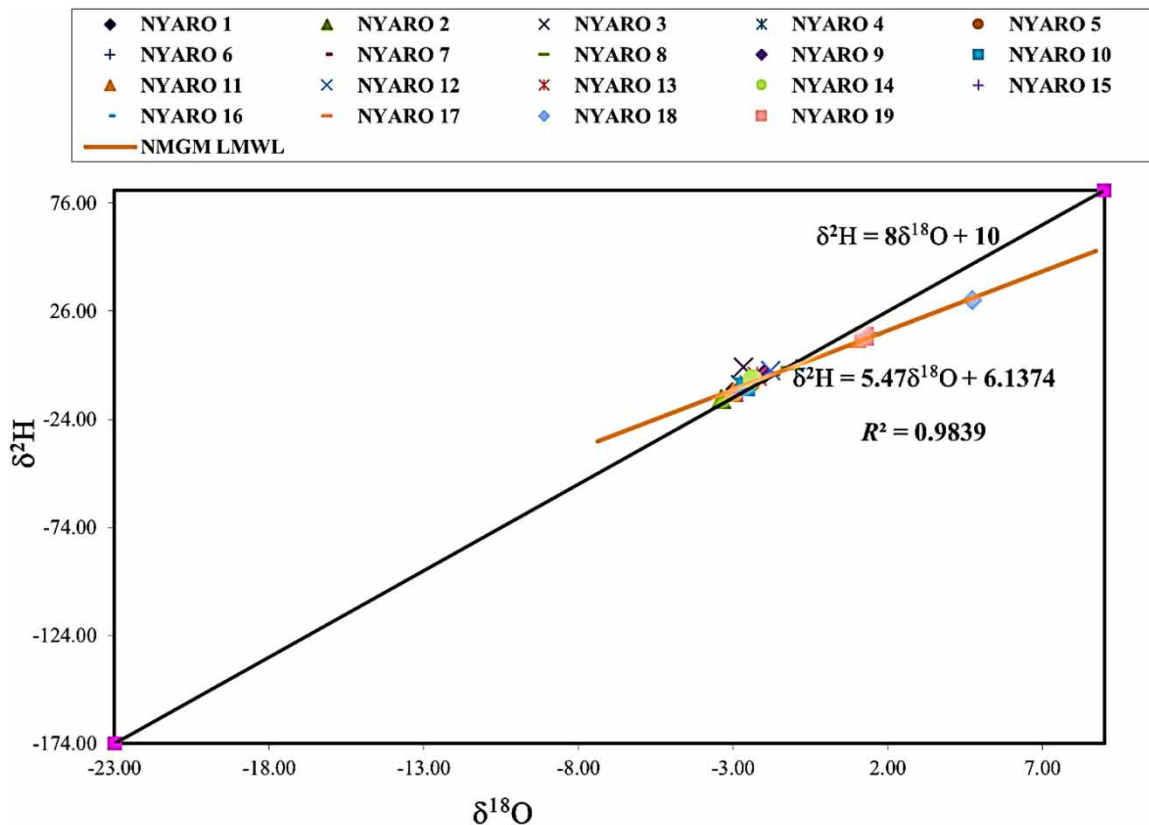
$$\delta^2\text{H} = 8 \cdot \delta^{18}\text{O} + 10 \tag{2}$$

where  $\delta$  is the parameter for isotopic enrichment,  $^{18}\text{O}$  and  $^2\text{H}$  are heavy oxygen and hydrogen isotopes, respectively (Craig 1961). The obtained regression equation and the Local Meteoric Water Line (LMWL) are indicated by Equation (3), representing both surface water and groundwater samples.

$$\delta^2\text{H} = 5.47 \cdot \delta^{18}\text{O} + 6.137, R^2 = 0.984 \tag{3}$$

where  $R^2$  is the coefficient of determination.

Most of the samples when plotted on a  $\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$  plane clustered around the GMWL with a gradient of 5.5, indicating the influence of precipitation. Analysis of  $^2\text{H}$  and  $^{18}\text{O}$  isotopic signatures relative to standards found



**Figure 5** | A plot of stable isotopes of oxygen and hydrogen for some groundwater samples. The regression line is in peach/coral color.

that water resources located on the eastern part of the NMGM (side A – highland) were much isotopically depleted than samples from the western part (side B – lowland) of Figure 2. This is an indication that the flow of groundwater in the study area was from the east to the west side of the study area, making the generalization that pollutants flow following the east-west direction. Therefore, the groundwater  $\delta^{18}\text{O}$  values indicated a preferential trend in their spatial distribution. Lighter  $\delta^{18}\text{O}$ -bearing water was located mainly at higher elevations and the heavier  $\delta^{18}\text{O}$ -bearing water was located mainly at lower elevations. The  $\delta^{18}\text{O}$  enrichment could also be representative of the effects of evaporation from mixed groundwater and surface water. Therefore, evaporation was probably among the main processes influencing groundwater chemistry in the study area.

### Tritium activity

Ten samples were analyzed for  $^3\text{H}$  activity. The minimum value had direct tritium less than 5.0 while the maximum value was 11.5 TU based on  $\pm 8.0$  TU. Looking at tritium activity solely may not give conclusive data on the groundwater relative age. However, it can provide a general overview on whether the water is young (<50 years) or premodern (>50 years) (Clarke *et al.* 1976; Zouari *et al.* 2002). The relative age indicated by the decay of tritium radioisotopes in the present study helps to conclude the time dependence of the vulnerability of water resources to recent water contamination. In the present study, 40% (equivalent to 4 out of 10) of groundwater samples represented recent water – with 5 to 15 TU, while 60% represented a mixture of modern and old water – with <5 TU (Ako *et al.* 2012; Abiye & Shaduka 2017). Modern groundwater is generally more susceptible to contamination than old groundwater. This is due to the introduction of many anthropogenic contaminants. Therefore, the sites with depleted  $^3\text{H}$  values belong to old groundwater, and those with high  $^3\text{H}$  values represent recharge from recent precipitation events. The spatial distribution of tritium in the present study indicated that lower tritium activity was generally found at higher elevations. Likewise, in the present study, tritium activity increased along the direction of groundwater flow characterized by upstream depletion and downstream enrichment.

## CONCLUSION

The present study examined the hydrochemical and isotopic composition of groundwater and surface water near the NMGM in Tanzania. The combination of major elements, geochemistry, and stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) have provided some understanding of the flow pattern and the processes leading to the deterioration of water quality. The isotopic analysis showed that the water chemistry was, to some extent, controlled by evaporation and altitudinal effects. Tritium ( $^3\text{H}$ ) radioactivity indicated that groundwater was vulnerable to recent near-surface contamination as it received recharge from a modern local precipitation rather than recharge from a paleoclimatic age.

It is worth mentioning that most of the major ions were high in the shallow depths of the groundwater. Spatially, as one moves along the water flow pattern, the water quality deteriorated. The sources of the major ions in surface and shallow groundwater may be partly attributed to lithogenic and mostly to anthropogenic activities such as domestic effluents, agriculture, and mining activities. Most samples had low pH values (mini. = 4.6) and were enriched with heavy metals, e.g., Hg (max. = 33.6  $\mu\text{g/L}$ ), Pb (max. = 153.8  $\mu\text{g/L}$ ), and Cd (max. = 2.7  $\mu\text{g/L}$ ) as well as cyanide (max. = 20  $\mu\text{g/L}$ ) that could be linked to anthropogenic activities. 84% of water samples contained Pb levels above the levels recommended in the Tanzanian standards. At two sites, Cd levels (2.7 and 2  $\mu\text{g/L}$ ) were close to the limit set by WHO. The general flow pattern of pollutant-carrying water was on the west side, where the Mara River and Lake Victoria are located. This may have some implications for the loading of pollutants into the two aquatic ecosystems of high economic importance in the East African region.

A recommendation is thus made that the uses of shallow boreholes and dug wells in the study area need to be avoided to minimize exposure risk to pollutants. Furthermore, community boreholes should be located in the highland areas where the levels of pollutants were found to be relatively low. More studies that utilize stable and radioactive isotopes in this region of East Africa are needed. The region is one of the fastest growing regions in sub-Saharan Africa in terms of human population, industrial activities, mining activities, and agricultural activities. Therefore, more studies to examine the impacts of human pressure on water resources are of paramount importance.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## REFERENCES

- Abiye, T. & Shaduka, I. 2017 Radioactive seepage through groundwater flow from the uranium mines, Namibia. *Hydrology* **4** (1), 11, 1–14.
- Adesiyan, I. M., Bisi-Johnson, M., Aladesanmi, O. T., Okoh, A. I. & Ogunfowokan, A. O. 2018 Concentrations and human health risk of heavy metals in rivers in southwest Nigeria. *Journal of Health and Pollution* **8** (19).
- Ako, A. A., Shimada, J., Hosono, T., Ichianagi, K., Nkeng, G. E., Eyong, G. E. T. & Roger, N. N. 2012 Hydrogeochemical and isotopic characteristics of groundwater in Mbanga, Njombe and Penja (Banana Plain) – Cameroon. *Journal of African Earth Sciences* **75**, 25–36. <https://doi.org/10.1016/j.jafrearsci.2012.06.003>.
- Almás, Á. R. & Manoko, M. L. 2012 Trace element concentrations in soil, sediments, and waters in the vicinity of Geita Gold Mines and North Mara Gold Mines in Northwest Tanzania. *Soil and Sediment Contamination: An International Journal* **21** (2), 135–159.
- Bitala, M., Kweyunga, C. & Manoko, M. 2009 Levels of Heavy Metals and Cyanide in Soil, Sediment and Water from the Vicinity of North Mara Gold Mine in Tarime District, Tanzania. unpublished.
- Bowell, R., Warren, A., Minjera, H. & Kimaro, N. 1995 Environmental impact of former gold mining on the Orangi River, Serengeti NP, Tanzania. *Biogeochemistry* **28** (3), 131–160.
- Bryan, N. S. & Loscalzo, J. 2011 *Nitrite and Nitrate in Human Health and Disease*. Springer, New York.
- Clarke, W. B., Jenkins, W. & Top, Z. 1976 Determination of tritium by mass spectrometric measurement of <sup>3</sup>He. *The International Journal of Applied Radiation and Isotopes* **27** (9), 515–522.
- Cotruvo, J. A. & Bartram, J. 2009 *Calcium and Magnesium in Drinking-Water: Public Health Significance*. World Health Organization, Geneva, Switzerland.
- Craig, H. 1961 Isotopic variations in meteoric waters. *Science* **133** (3465), 1702–1703.
- Dimitriou, E. & Zacharias, I. 2006 Groundwater vulnerability and risk mapping in a geologically complex area by using stable isotopes, remote sensing and GIS techniques. *Environmental Geology* **51** (2), 309–323.
- Dinka, M. O., Loiskandl, W. & Ndambuki, J. M. 2015 Hydrochemical characterization of various surface water and groundwater resources available in Matahara areas, Fantalle Woreda of Oromiya region. *Journal of Hydrology: Regional Studies* **3**, 444–456.
- Hamutoko, J. T., Wanke, H., Koeniger, P., Beyer, M. & Gaj, M. 2017 Hydrogeochemical and isotope study of perched aquifers in the Cuvelai-Etoshia Basin, Namibia. *Isotopes in Environmental and Health Studies* **53** (4), 382–399.
- Hinkle, S. R. 2009 *Tritium/Helium-3 Apparent Ages of Shallow Ground Water, Portland Basin, Oregon, 1997–98*. U. S. Geological Survey, Reston, VA.
- Howladar, M. F., Deb, P. K., Muzemder, A. S. H. & Ahmed, M. 2014 Evaluation of water resources around barapukuria coal mine industrial area, Dinajpur, Bangladesh. *Applied Water Science* **4** (3), 203–222.
- Hummel, W. 2004 The influence of cyanide complexation on the speciation and solubility of radionuclides in a geological repository. *Environmental Geology* **45** (5), 633–646. doi:10.1007/s00254-003-0928-5.
- Jaszczak, E., Polkowska, Ż., Narkowicz, S. & Namieśnik, J. 2017 Cyanides in the environment – analysis – problems and challenges. *Environmental Science and Pollution Research* **24** (19), 15929–15948.
- Kendall, C. & Doctor, D. 2003 Stable isotope applications in hydrologic studies. *Treatise on Geochemistry* **5**, 605.
- Laar, C., Akiti, T., Brimah, A., Fianko, J., Osae, S. & Osei, J. 2011 Hydrochemistry and isotopic composition of the Sakumo Ramsar site. *Research Journal of Environmental and Earth Sciences* **3** (2), 146–152.
- Lerner, D. N. & Harris, B. 2009 The relationship between land use and groundwater resources and quality. *Land use Policy* **26**, S265–S273.
- Li, Q. & Jiang, S. 2016 Trace and rare earth element characteristics in Fe-Mn carbonates associated with stratiform Ag-Pb-Zn mineralization from the Lengshuikeng ore district, Jiangxi Province: Implications for their genesis and depositional environment. *Journal of Earth Science* **27** (4), 571–583.
- Lucas, L. L. & Unterweger, M. P. 2000 Comprehensive review and critical evaluation of the half-life of Tritium. *Journal of Research of the National Institute of Standards and Technology* **105** (4), 541.
- Morgenstern, U., Stewart, M. K. & Stenger, R. 2010 Dating of streamwater using tritium in a post nuclear bomb pulse world: continuous variation of mean transit time with streamflow. *Hydrology and Earth System Sciences* **14** (11), 2289–2301.

- Mousavi, S. R., Balali-Mood, M., Riahi-Zanjani, B. & Sadeghi, M. 2013 Determination of cyanide and nitrate concentrations in drinking, irrigation, and wastewaters. *Journal of Research in Medical Sciences: the Official Journal of Isfahan University of Medical Sciences* **18** (1), 65.
- Nsimba, E. B. 2009 *Cyanide and cyanide complexes in the goldmine polluted land in the east and central rand goldfields, South Africa*.
- Raju, N. J., Ram, P. & Dey, S. 2009 Groundwater quality in the lower Varuna river basin, Varanasi district, Uttar Pradesh. *Journal of the Geological Society of India* **73** (2), 178.
- Ravikumar, P. & Somashekar, R. 2010 Multivariate analysis to evaluate geochemistry of groundwater in Varahi river basin of Udupi in Karnataka (India). *Ecoscan* **4** (2–3), 153–162.
- Ritter, C., Cottingham, M., Leventhal, J. & Mickelson, A. 2014 Remote delay tolerant water quality monitoring. *IEEE Global Humanitarian Technology Conference (GHTC 2014)*, 462–468.
- Ritter, L., Solomon, K., Sibley, P., Hall, K., Keen, P., Mattu, G. & Linton, B. 2002 Sources, pathways, and relative risks of contaminants in surface water and groundwater: a perspective prepared for the Walkerton inquiry. *Journal of Toxicology and Environmental Health Part A* **65** (1), 1–142.
- Rwiza, M. J., Kim, K. W. & Kim, S. D. 2016 Geochemical distribution of trace elements in groundwater from the North Mara Large-Scale Gold Mining Area of Tanzania. *Groundwater Monitoring & Remediation* **36** (2), 83–93.
- Rwiza, M. J., Oh, S.-Y., Kim, K.-W. & Kim, S. D. 2018 Comparative sorption isotherms and removal studies for Pb (II) by physical and thermochemical modification of low-cost agro-wastes from Tanzania. *Chemosphere* **195**, 135–145.
- Singh, S., Raju, N. J. & Ramakrishna, C. 2015 Evaluation of groundwater quality and its suitability for domestic and irrigation use in parts of the chandauli-Varanasi region, uttar pradesh. *India. Journal of Water Resource and Protection* **7** (07), 572.
- Taylor, H., Appleton, J., Lister, R., Smith, B., Chitamweba, D., Mkumbo, O., Machiwa, J., Tesha, A. & Beinhoff, C. 2005 Environmental assessment of mercury contamination from the Rwamagasa artisanal gold mining centre, Geita District, Tanzania. *Science of the Total Environment* **343** (1–3), 111–133.
- TBS. 2005 *Municipal and Industrial Wastewaters-General Tolerance Limits for Municipal and Industrial Wastewaters (TZS860:2005)*. Tanzania Bureau of Standards, Dar Es Salaam, Tanzania.
- USEPA. 1986 *Test methods for evaluating solid waste. Office of Solid Waste and Emergency Response*, Washington DC, USA.
- Wang, C., Yang, Z., Zhong, C. & Ji, J. 2016 Temporal-spatial variation and source apportionment of soil heavy metals in the representative river-alluviation depositional system. *Environmental Pollution* **216**, 18–26.
- Vaux, H. 2011 Groundwater under stress: the importance of management. *Environmental Earth Sciences* **62** (1), 19–23.
- WHO. 1993 *Guidelines for Drinking-Water Quality*. World Health Organization, Geneva, Switzerland.
- WHO. 2011 *Guidelines for Drinking-Water Quality: World Health Organization*. World Health Organization, Geneva. [27].
- Yeh, H.-F., Lee, C.-H. & Hsu, K.-C. 2011 Oxygen and hydrogen isotopes for the characteristics of groundwater recharge: a case study from the Chih-Pen Creek basin. *Taiwan. Environmental Earth Sciences* **62** (2), 393–402.
- Zouari, K., Chkir, N. & Ouda, B. 2002 *Paleoclimatic Variations in Maknassy Basin (Central Tunisia) During the Holocene Period Using Multidisciplinary Approaches*. Laboratory of Radio-Analysis and Environment, Tunis, Tunisia. [IAEA-CN-80/28].

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