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Geochemical Distribution of Trace Elements in Groundwater from the North Mara Large-Scale Gold Mining Area of Tanzania

by Mwemezi Johaiven Rwiza, Kyoung-Woong Kim, and Sang-don Kim

Abstract

The influence of large-scale mining operations on groundwater quality was investigated in this study. Trace element concentrations in groundwater samples from the North Mara mining area of northern Tanzania were analyzed. Statistical analyses for relationships between elemental concentrations in the samples and distance of a sampling site from the mine tailings dam were also conducted. Eleven trace elements (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were determined, and averages of Fe and Al concentrations were higher than levels accepted by the Tanzanian drinking water guideline. Levels of Pb in three samples were higher than the World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) drinking water guidelines of 10 and 15 μg/L, respectively. One sample contained a higher As level than the WHO and USEPA guideline of 10 μg/L. The correlation between element concentrations and distance from the mine tailings dam was examined using the hierarchical agglomeration cluster analysis method. A significant difference in the elemental concentration existed depending on the distance from the mine tailings dam. Mann–Whitney U-test post hoc analysis confirmed a relationship between element concentration and distance of a sampling site from the mine tailings dam. This relationship raises concerns about the increased risks of trace elements to people and ecosystem health. A metal pollution index also suggested a relationship between elemental concentrations in the groundwater and the sampling sites' proximity from the mine tailings dam.

Introduction

Trace elements are elements that are either essential or toxic in small quantities to microorganisms, plant, and animals, including humans. This definition also encompasses elements with no known physiological functions and that are present in a system, for example, groundwater, at levels less than 0.1% of the total elemental load in that system (Senesi et al. 1999). In the environment, these elements are of concern because they are not biodegradable. At high concentrations, trace elements may also adversely affect both human and ecosystem health.

Both natural and anthropogenic sources of trace elements may result in excessive pollutant levels in groundwater systems. For example, groundwater sources in countries such as Cambodia, Bangladesh, and Vietnam may become contaminated due to the high natural geological content of the elements (Gault et al. 2008; Hug et al. 2008; Bera et al. 2010; Phan et al. 2010). However, in other countries, groundwater contamination may be attributed to anthropogenic activities such as gold mining (Inam et al. 2011). Trace elements in groundwater supplies are a major concern in developing countries (e.g., Tanzania) due to the high proportion (>50%) of the population that use groundwater as their sole source of potable water (Taylor et al. 2013).

Little published research exists that has investigated trace element enrichment of groundwater resulting from large-scale mining operations in Tanzania. For many years, gold mining in Tanzania was done at a small-scale. Because of this history, the focus of trace element research in Tanzania was also patchy and artisanal-oriented (Mohammed 2002; Bose-O'Reilly et al. 2010). Specifically, most trace element research in Tanzania has focused on pollution associated with mercury (Hg) at the expense of a broader spectrum of metallic pollutants (Semu et al. 1986; Ikingura and Akagi 2003; Ikingura et al. 2006; Chibunda and Janssen 2009). Recently, large-scale gold mining in Tanzania by large multinational corporations has begun. This intensification of gold mining operations across Tanzania increases the risk of groundwater pollution with trace elements.

Mwegoha (2008), for example, addresses environmental loadings of heavy metals such as As, Cd, Co, Pb, and Zn resulting from large-scale mining operations in Tanzania. In

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this study, it was pointed out that heavy metals and sulfide from the mining industry may cause the contamination of soil, surface water, and groundwater sources in areas close to the mining sites of Tanzania. It is also pointed out that mercury (Hg) use and cyanidation during gold processing and refinery may lead to further contamination in the mining areas. The author identifies leachate and mine tailings emanating from refinery facilities as the major point sources of these pollutants (Mwegoha 2008). Additionally, samples of soils collected from Geita gold mines, a large-scale mine also located in the Lake Victoria greenstone belt and about 200 km from the North Mara mines, indicated high concentrations of Pb, Zn, and Cu (Mkumbo et al. 2012). Compared to pristine soils, the concentration of heavy metals in these soils were higher by a factor of up to 21 (Mkumbo et al. 2012). Almås and Manoko (2012) studied trace element concentrations in waters, sediments, and soils in the vicinity of Geita and North Mara gold mines and concluded that the high concentrations of As and associated elements in the North Mara were attributable to the mining tailings dam (MTD). They pointed out that cyanidation and the resulting alkaline transport of contaminated water from the tailings storage facility contributed to the elevated concentrations of As and other elements in the collected environmental samples (Almås and Manoko 2012). Furthermore, in one of the studied areas (the North Mara mine), there was evidence of acid mine drainage (Almås and Manoko 2012).

In the present study, the spatial distribution of trace elements in groundwater samples was investigated. The objective of this study was to examine the extent of trace element pollution in the groundwater in one of the large-scale gold mines of Tanzania and to determine the principal sources and controlling geochemical factors.

Materials and Methods

Sampling Area

The North Mara gold mining area is located within the Lake Victoria greenstone belt in Tarime district, Tanzania (Figure 1). At the North Mara, there is a sulfide ore system rich in gold (Au) as well as arsenic (As), containing minerals and other base metal deposits (Bowell et al. 1995). The greenstone is geologically characterized by the lower Nyanzian and the superimposed Kavirondian successions (Kabete et al. 2012). Volcanic rocks in the Nyanzian, which contain the mineralized gold, have been hydrothermally altered to lower green schist facies. Quartz veins and scattered sulfides represent a large portion of the gold mineralization. The primary sulfide ore present in the Lake Victoria gold fields is pyrite (FeS_2) with smaller portions of arsenopyrite (FeAsS), galena (PbS), and sphalerite ((Zn,Fe)S) (Bowell et al. 1995).

There is inadequate information available with regard to groundwater flow and geological mapping as well as aquifer characteristics in the East Africa region. Few studies have been carried out in the Mara River Basin, in which the North Mara mines are located, but these studies give little emphasis to the subterranean hydrological features of the region (Mati et al. 2008; Mango et al. 2011). Not only has the Mara River Basin geology been understudied, but the whole Lake Victoria goldfields region is comparatively underexplored and poorly understood (Vos et al. 2009). This greenstone belt is a granitic and cratonic setting, geologically similar to Archean provinces elsewhere (e.g., the Abitibi province in Quebec, Canada or the Yilgarn province in the Western part of Australia). Its sub-terrain geological formation has the following characteristics: mainly felsic-mafic volcanics mixed with sediments that are intercalated with granitoid-gabbroic plutonic rocks (Figure 1c). In this region, mineralization occurs as diffused gold-sulfide, with a sulfide portion of up to 3% (Vos et al. 2009). The Mara region, and Tanzania in general, is underlain by complex fractured crystalline aquifers of varying composition and age (Kashaigili 2010). Generally, little is known about the African aquifers, and little has been published about these aquifers and their management (Altchenko and Villholth 2013). More details of the underlying geological features of the Lake Victoria goldfields are given in Kabete et al. (2012).

For the present study, a geochemical survey was carried out during August in 2012, which is usually a dry season in that area of Tanzania. In the Mara region, there are two wet seasons, peaking in the months of April and November, with an average annual rainfall of ~ 1200 mm. In this region, dry season is between June and September (Hoffman et al. 2011). Average annual temperature in the North Mara and surrounding areas ranges between 14 and 28 °C (Ngowi et al. 2008). Soils in this region are often dark-colored, high in clay content (vertisols), and are commonly referred to as "black cotton soil" (Mati et al. 2008). In a previous study (Almås and Manoko 2012), soils close to the core mining area of the North Mara were found to contain high levels of As, Co, Ni, Cr, Cu, and Zn. Almås and Manoko (2012) also found that water samples collected from sites close to the mining operations had high SO_4^{2-} concentrations. A study carried out in a mining site in the Serengeti Reserve, located a few kilometers south of the North Mara mining area, found that water from the tailings were characterized by a high concentration of sulfate SO_4^{2-} and trace element enrichment (Bowell et al. 1995). Thus, the North Mara mining area was selected as it has raised significant interest, speculation, and controversy regarding the impact mining activities may have on the groundwater, soils, and plants located close to the mining operation.

Samples were collected from 14 different sites: TRM1-TRM14 (Figure 1d). For statistical purposes, samples from the North Mara mining area were divided into two groups—Group 1 and Group 2. Group 1 (impact zone) consisted of samples collected within 7 km of the MTD, and Group 2 (control zone) consisted of samples collected beyond 7 km from the MTD. Samples were collected from community– and privately-owned boreholes of varying depths (from 10 to 40 m). At each sampling site, water was used for multiple purposes: from the washing of clothes and drinking to the watering of livestock and cultivated plants (Table 1).

Sample Collection

Global positioning system (GPS) location for each groundwater sampling site was taken using a handheld GPS device (Garmin GPSMAP®, Kansas City, Kansas). The water pH at each sampling site was taken using a portable pH meter

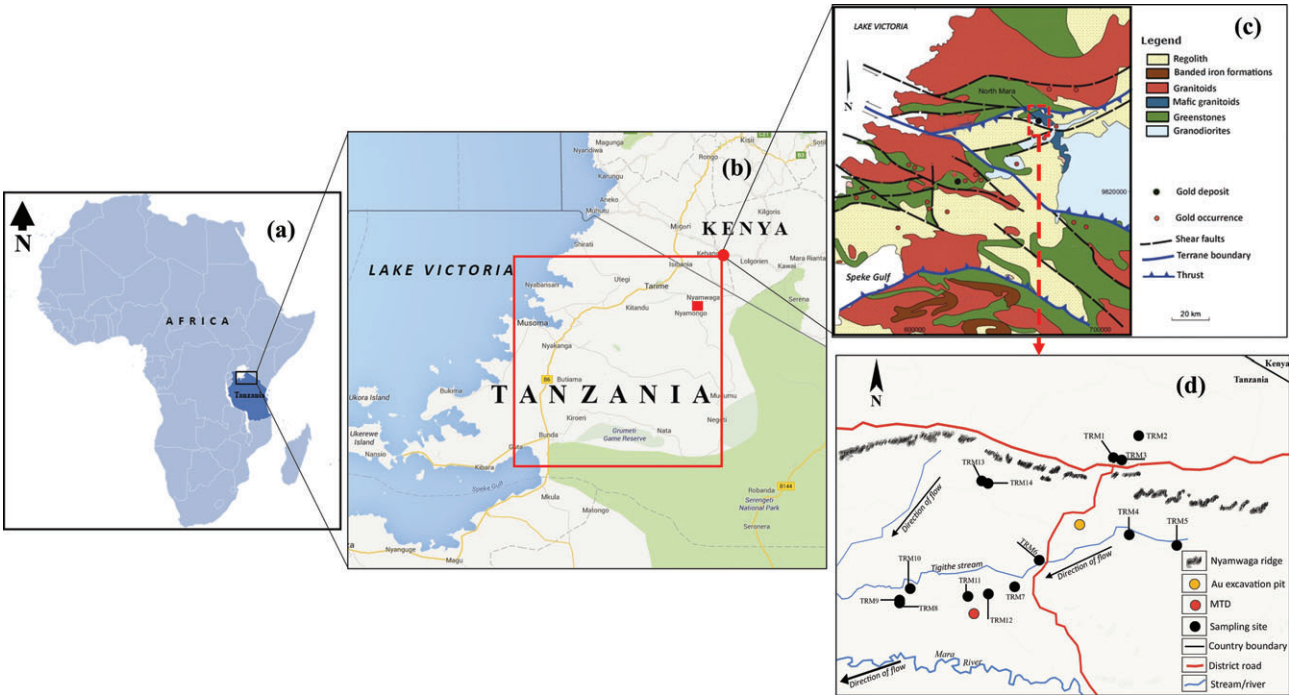

Figure 1. Map of the study area indicating: (a) Tanzania with respect to Africa, (b) the Lake Victoria Greenstone Belt, (c) the geological formations underlying the North Mara gold mining area, and (d) the sampling locations and topographic features of the North Mara area, including the direction of water flow. The geological map was modified from Kabete et al. (2012), whereas other maps were obtained through a Google™ search and/or compiled in Google™ maps/earth. TRM8 and TRM9 (d) are at the same location.

(pHep®, Hanna Instruments, Villafranca Padovana, Italy). At each sampling site, two samples were collected and stored in 50 mL sterilized polyethylene bottles (SPL Labware, Gyeonggi-do, Korea). One sample was used for analysis of total trace elements and the other for dissolved elements (filtered sample). During the filtration, a 0.45-µm filter (Puradisc™ 25 NYL Syringe Filters, Whatman®, Waltham, Massachusetts) was used. Samples were acidified on site to pH ≤ 2.0 using analytical grade HNO_3 (Sigma-Aldrich, Gillingham, Dorset, UK) and stored in a chest packed with ice until transported to the Nelson Mandela African Institute of Science and Technology (NM-AIST) in Arusha, Tanzania, where they were stored at 4 °C. The samples were then transferred to Gwangju Institute of Science and Technology (GIST) in the Republic of Korea for further analysis. For samples collected from a hand-pumped or tapped facility, water was allowed to flow for at least 5 min before sampling. All sampling, storage, and transfer protocols were conducted as previously described (APHA 1998).

Sample Analysis and Quality Assurance

All chemical analyses for 11 elements (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were carried out using inductively-coupled plasma mass spectrometry (ICP-MS, Agilent 7500ce, Agilent, Santa Clara, California). These elements were selected as other studies have suggested a link between the mine site and the concentration of these elements in groundwater (Kitula 2006; Marwa et al. 2012). In order to prepare the working standard solutions, a multi-element standard solution containing 20 µg/L of each element was obtained from Agilent. Calibration standards ranging from 0 to 100 µg/L for all target elements were prepared from the multi-element stock solution and 2% (v/v) HNO_3, prepared from 18.2 M /cm deionized water (Millipore Milli-Q purification system, Billerica, Massachusetts). A standard reference material (SRM 1640a) for trace elements in natural water (National Institute of Standards and Technology, Maryland) was analyzed in the same manner as the samples to verify the accuracy and precision of analytical methods.

A routine ICP-MS optimization procedure was performed for 30 min prior to injecting the samples. Detection limits (µg/L, in brackets) for each element were as follows: Al (0.18), As (0.01), Cd (0.01), Co (0.01), Cr (0.06), Cu (0.02), Fe (0.07), Mn (0.01), Ni (0.06), Pb (0.01), and Zn (0.08). In order to ensure analytical quality assurance, the reagent blank, instrument calibration standards, and standard reference material for trace element in natural water were analyzed after each 10th sample. The ICP-MS performance for all target elements was between 83.7% and 103.1% recovery of the calibration standards and between 77.5% and 125.4% recovery of SRM 1640a.

Statistical Analyses

Statistical analyses were performed using IBM SPSS Statistics for Windows, Version 21.0 (IBM Corp., Armonk, New York), Origin (Origin Lab, Northampton, Massachusetts), and Sigma Plot 12 (Systat Software Inc., San Jose, California). Total element concentration was used for the majority of the statistical analyses. Cluster analysis (CA) was performed according to Burns et al. (2008). As normality assumptions were not met by the distribution of our data, the current study applied Friedman's analysis of variance (ANOVA) to test the differences between trace element concentrations in water from sites close to the MTD and

Table 1

Detailed Characteristics of Sampling Sites in the North Mara Gold Mining Area

Site	Dist.[1] (km)	pH	Depth (m)[2]	Site Characteristics
TRM1	11.47	7.3	28	Nyamwaga village community borehole 1, a drinking water source (0675328/9846129).
TRM2	13.36	6.3	10	Borehole 2 in Nyamwaga village. Owned by community and used for washing, cleaning, and drinking (0676782/9847376).
TRM3	11.67	6.9	33	Privately owned hand pump. Used for drinking, washing, and gardening for one family (0675807/9845992).
TRM4	9.29	6.0	15	A relatively shallow community borehole used for washing, farm watering, cleaning, livestock watering, and drinking (0676233/9841720).
TRM5	11.53	6.3	10	Another shallow community borehole used for washing, cleaning, and drinking (0678959/9841116).
TRM6	4.26	8.4	12	A borehole next to Tigithe stream and adjacent to the main gold mining pit. Water at this site was used for cleaning, washing, drinking, and farm and livestock watering (0671064/9840277).
TRM7	2.17	7.2	40	Kewanja village community hand pump. Water was mainly for domestic use: cooking, cleaning, and washing (0669644/9838754).
TRM8	5.12	7.5	12	A locally drilled borehole in Matongo village, located next to the community borehole (TRM9) and used at mid-day when the community borehole is usually closed. Water is used for washing, cleaning, drinking, and for livestock watering (0663034/9837840).
TRM9	5.12	7.3	35	A community borehole in Matongo village, a few meters from TRM8. Open only for a few hours in the morning and in the evening, usually closed at mid-day (9837840/0663034).
TRM10	4.69	7.1	40	Another community borehole in Matongo village. Community-owned but serviced by the mining company (Barrick Gold Mines). Used for drinking, cooking, animal watering, and washing (0663651/9838659).
TRM11	1.52	8.1	10	A community borehole in Nyangoto village. It was located adjacent to the MTD. Water used for cleaning, washing, and livestock watering (0666966/9838208).
TRM12	1.14	8.2	n.a	Nyangoto village community-tapped water source, piped the Mara River. The tap was a few meters from the gold processing plant of North Mara gold mine. Water used mainly for domestic purposes (0668134/9838348).
TRM13	7.45	6.8	n.a	A community borehole in Nyakunguru village. Water flows from the nearby springs in the adjacent hills and is collected at this borehole. Used for drinking, washing, and cleaning (0668122/9844661).
TRM14	7.60	7.3	28	A community borehole located at Nyakunguru Primary School. Water is used for drinking, cooking, cleaning, and gardening (0667756/9844807).

Note: Characteristics given pertain to site name or landmark (where given), borehole ownership type (community or privately-owned), water use type, and the boreholes' respective GPS locations (UTMX/UTMY).

[1]Distance from the MTD.

[2]The depths were given as an estimate by a village leader and/or a borehole caretaker; n.a=not available.

those in water from sites further away from the MTD. For *post hoc* analysis, we used the Mann–Whitney test, with a p-value=0.05 chosen to infer significance. Following the Mann–Whitney test, we calculated the effect size (r) for each trace element analyzed using the following Equation 1:

$$r = \frac{Z}{\sqrt{N}} \quad (1)$$

where Z represents the z-score values from the Mann–Whitney analysis, and N represents the sample size (Field 2007). All effects are reported at the significance level of 0.05 without a Bonferroni correction. Finally, we performed Spearman correlation analysis for each element separately in both filtered and unfiltered groundwater samples. The correlations were examined using total concentrations, pH, and distance from the MTD across the 14 sampling sites.

Metal Pollution Index

To compare trace element enrichment at different sampling sites and to support the statistical analyses, the metal pollution index (MPI) was calculated as previously described (Usero et al. 1996 2005). The MPI is obtained using Equation 2:

$$\mathrm{MPI} = (\mathrm{Cf}_1 \times \mathrm{Cf}_2 \ldots \mathrm{Cf}_n)^{1/n} \quad (2)$$

where Cf_i=concentration for the metal i in the sample. Results of the CA were considered to be true if confirmed by the Friedman's ANOVA and the MPI.

Results

ICP-MS results for the concentration of trace elements in the groundwater samples are summarized in Table 2.

Table 2

Concentration of Trace Elements in the Groundwater from North Mara with Their Respective Drinking Water Regulatory Guidelines

Element Concentration (µg/L)	Unfiltered		Filtered		Unfiltered	Filtered	Drinking Water Standard (µg/L)		
	Min	Max	Min	Max	Median	Median	Tanzania	WHO	USEPA
Al	5.84	5313	0.05	2203	137.62	31.55	2000	n.r	200[2]
As	0.47	12.05	<dl[1]	9.93	1.15	0.67	50	10	10
Cd	0.02	0.17	<dl[1]	0.09	0.08	0.04	50	3	5
Co	0.12	2.05	0.03	0.65	0.33	0.23	1000	n.r	n.r
Cr	4.25	47.08	0.03	32.92	18.58	9.94	50	50	100
Cu	5.28	27.6	2.11	20.24	13.16	9.24	3000	2000	1000[2]
Fe	62.5	4524	0.5	2526	376.8	277.55	1000	n.r	300[2]
Mn	6.3	332.4	0.03	238.2	68.76	44.76	500	400	50[2]
Ni	3.05	51.2	0.03	25.64	16.26	9.14	500	70	n.r
Pb	2.05	16.82	0.02	5.87	5.65	3.13	100	10	15
Zn	17.92	3845	0.1	2886	83.01	51.10	15000	n.r	5000[2]

Note: Data are given as minimum, maximum, and median concentration obtained for each element across 14 sites. n.r=not regulated.
[1]Below detection limit.
[2]Secondary USEPA regulation.

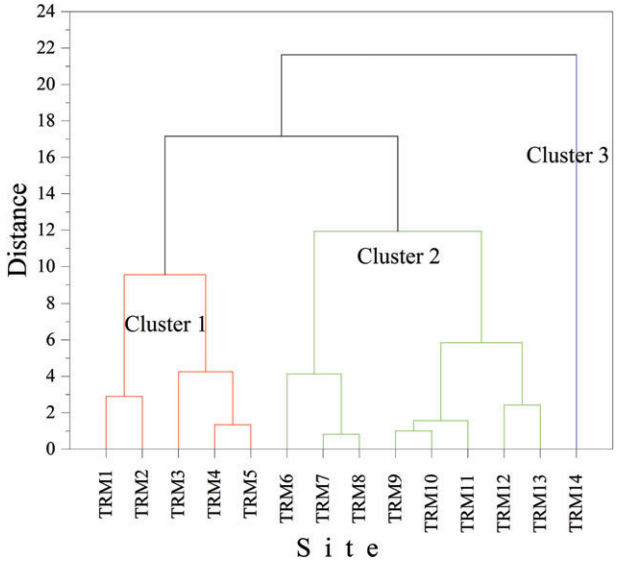

Figure 2. Dendrogram depiction of the clusters in the sampling sites of the North Mara gold mining operation, resulting from a hierarchical agglomeration classification on the trace element concentrations in the sample water for 14 sites (cases).

Results for CA are presented in Figure 2 as a dendrogram. CA results are divided into two major clusters and one minor cluster. Cluster 1 aggregates sites TRM1-5, whereas cluster 2 comprises sites TRM6-13. Cluster 3 represents only a single site, TRM14.

Data rankings generated by the Friedman's ANOVA are given in Table 3. Rankings represent the concentration of trace elements at the respective sampling site (higher ranking represents a higher trace element concentration). The highest-ranking site was TRM6 (12.9) at 4.3 km from the MTD and between the gold mining pit and the MTD. The lowest-ranking site was TRM2 (2.9) at 13.4 km from the MTD. The concentration of trace elements differed significantly among the 14 sites ($\chi^2(13)=55.22$, $p<0.001$). Following these significance results, a *post hoc* analysis was carried out, and the ranking values for the Mann–Whitney *post hoc* analysis are given in Table 4. These values are more salient than those from the Friedman's ANOVA because they result in classified ranks based on the distance of the site from the MTD. Except for Cd, the concentration of trace elements in samples close to the MTD had higher mean rank values than those in sampling points located further away.

By using the outcomes of the Mann–Whitney analysis, the effect size was calculated. Effect size values are given in Table 5. The element-by-element effect size values ranged from −0.05 to −0.70. Using these data, we constructed a graph depicting relative positions of trace elements on a correlation plane (Figure 3). An effect size value of 0.1, 0.3, and 0.5 implies that element concentrations are less, moderately and significantly affected by the distance from the MTD, respectively (Field 2007).

Spearman correlation results for both unfiltered and filtered water are given in Tables 6 and 7, respectively. A strong inverse correlation between distance from the MTD and the pH of the water was found. Groundwater pH was also strongly correlated with the concentration of As and Co in the unfiltered water samples. A strong positive correlation was also found between the pH and the concentrations of As and Ni in the filtered water samples. Except for Cd and Fe (unfiltered samples), all trace element concentrations were negatively correlated with the distance from the MTD, with strong correlations found for As, Mn, and Ni. In the unfiltered water samples, Al was strongly correlated with Fe, whereas in the filtered water samples, Al was significantly correlated with Co, Cu, Fe, and Pb ($r>0.5$, $p=0.01$).

Table 3

Friedman's Test Ranks for 14 Sampling Sites in the North Mara Gold Mining Area of Tanzania

Site	TRM1	TRM2	TRM3	TRM4	TRM5	TRM6	TRM7	TRM8	TRM9	TRM10	TRM11	TRM12	TRM13	TRM14
Mean Rank	6.2	2.9	4.9	6.1	9.8	12.9	7.9	10. 7	8.7	7.6	9.3	6.2	6.3	5.6

Note: Trace element concentrations in water samples were used to obtain the mean rank values.

Table 4

Mann–Whitney Ranks for the Concentration of Trace Elements between Sampling Sites from Group 2[1] and Group 1[2] in North Mara Mining Area, Tanzania

Element	Group	*N*	Mean Rank	Sum of Ranks
Al	2	7	7	49
	1	7	8	56
	Total	14		
As	2	7	4.57	32
	1	7	10.43	73
	Total	14		
Cd	2	7	7.86	55
	1	7	7.14	50
	Total	14		
Co	2	7	5.29	37
	1	7	9.71	68
	Total	14		
Cr	2	7	5.29	37
	1	7	9.71	68
	Total	14		
Cu	2	7	6	42
	1	7	9	63
	Total	14		
Fe	2	7	7.29	51
	1	7	7.71	54
	Total	14		
Mn	2	7	5	35
	1	7	10	70
	Total	14		
Ni	2	7	6.71	47
	1	7	8.29	58
	Total	14		
Pb	2	7	4.86	34
	1	7	10.14	71
	Total	14		
Zn	2	7	5.71	40
	1	7	9.29	65
	Total	14		

[1] > 7 km from the MTD.
[2] ≤ 7 km from the MTD.

It was also found that As was strongly correlated with Ni in the filtered water samples and with Co and Mn in the unfiltered water samples. In general, trace element concentrations were more correlated to each other in the filtered water samples than those in the unfiltered water samples.

Samples of TRM1–3, TRM13, and TRM14 showed the lowest MPI, with a range of 4.9 to 9.9. The highest MPI value (39.93) was found at TRM6 followed, in decreasing order, by TRM8, TRM5, TRM11, TRM9, TRM10, TRM7, TRM4,

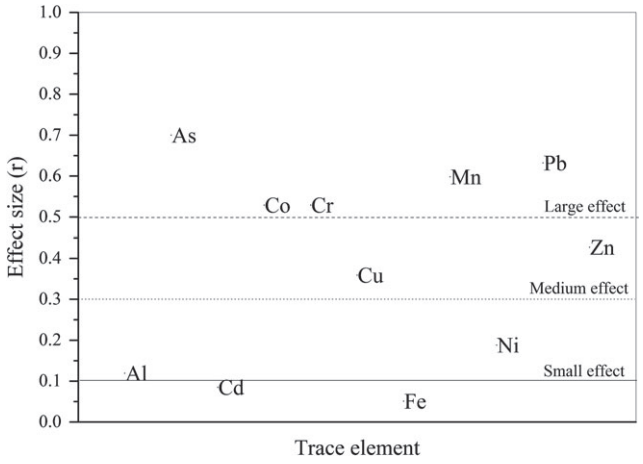

Figure 3. The effect of distance from the MTD on the levels of individual trace elements in groundwater samples from North Mara mining area, Tanzania.

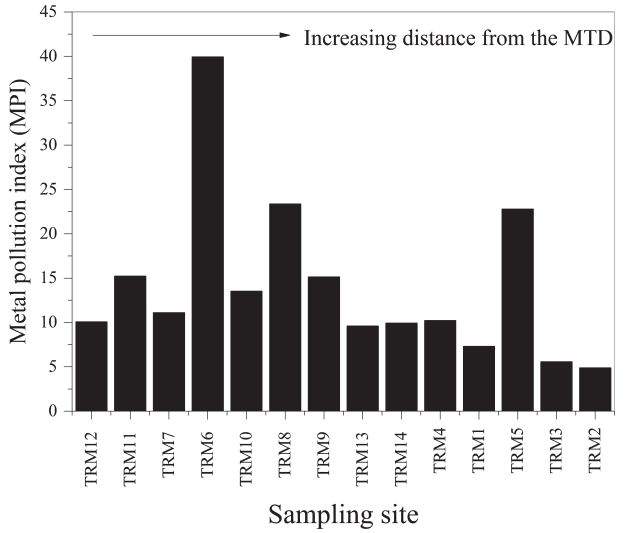

Figure 4. Metal pollution index (MPI) for each of the 14 sampling for 11 trace elements examined in the groundwater samples from the North Mara gold mine.

Table 5

Mann–Whitney *U* and Friedman's ANOVA *Z* Test Statistics Values[1] for Trace Element Concentrations in Water Samples Taken from the North Mara Mining Area, Tanzania by Element

	Mann–Whitney *U*	*Z*	Effect Size (*r*)	Asymp. Sig. (2-Tailed)	Exact Sig. (2-Tailed)
Al	21	−0.45	−0.12	0.655	0.710
As	4	−2.62	−0.70	0.009	0.009
Cd	22	−0.32	−0.09	0.749	0.830
Co	9	−1.98	−0.53	0.048	0.050
Cr	9	−1.98	−0.53	0.048	0.053
Cu	14	−1.34	−0.34	0.18	0.209
Fe	23	−0.19	−0.05	0.848	0.902
Mn	7	−2.24	−0.60	0.025	0.026
Ni	19	−0.70	−0.19	0.482	0.535
Pb	6	−2.36	−0.63	0.018	0.012
Zn	12	−1.60	−0.43	0.11	0.128

Note: Also given are effect sizes and significance values. For this study, we used the Exact Significance (2-tailed).
[1]Grouping variable: Distance from MTD.

and TRM12 (Figure 4). The MPI values represent geometric means of the site-to-site trace element concentrations in the samples. High MPI values at a particular site are indicative of its trace element enrichment compared to other sites.

Discussion and Conclusions

Concentrations of As and Pb exceeded the World Health Organization's (WHO) guideline for drinking water of 10 and 15 µg/L, respectively. While not an international standard, a proportion of sites had concentrations of trace elements that exceeded the United States Environmental Protection Agency (USEPA) guidelines. The USEPA drinking water guidelines for Mn, Fe, Al, As, and Pb are 50, 300, 200, 10, and 15 µg/L, respectively (USEPA 2012). Levels of Al and Fe were higher than the Tanzanian drinking water guideline thresholds of 2000 and 1000 µg/L, respectively (Tanzania 2007; GoT 2011). These high levels of Al and Fe could pose a toxic threat to drinking water systems (Mitchell et al. 2011; Willhite et al. 2012). However, the concentrations of Al and Fe did not change significantly with the distance from the MTD (Tables 6 and 7 and Figure 3). This indicates that levels of Al and Fe in the analyzed samples were probably of geological formation origin rather than being caused by mining activities.

CA yielded two major homogenous clusters: (1) sampling sites close to the MTD and (2) sampling sites further away from the MTD, as well as one minor group consisting of only one case (Figure 2). Generally, our Group 1 (≤7 km from the MTD) samples were aggregated in Cluster 2, while Group 2 (>7 km from the MTD) samples were aggregated in Cluster 1, that is, sites with lower trace element concentrations aggregated in Cluster 1, whereas sites with higher trace element concentration aggregated in Cluster 2. Previous studies on the mobility of As in the environment around MTDs indicate a similar pattern, where As concentration is high in the vicinity of the mine tailings and tends to level off with distance (Kreidie et al. 2011; Larios et al. 2012). When considering only distance, TRM14 should cluster with sites in Cluster 1 (>7 km from MTD). However, TRM14 (7.6 km) did not cluster with its peer sites of similar distance values. The concentration of trace elements in the samples from TRM14 was, most likely, not low enough for the CA method to place it in Cluster 1. It may also be explained by the fact that groundwater trace element concentration at TRM14 was not high enough for it to be placed in Cluster 2. Therefore, TRM14 formed a one-membered cluster, Cluster 3. From a distance perspective, TRM13 (7.5 km) was supposed to aggregate in Cluster 1. However, TRM13 aggregated in Cluster 2. Although distance from the MTD is an important factor in trace metal enrichment of groundwater, it is not the only factor affecting the system. Other factors such as local mineralogy, geomorphological features,

Table 6

Spearman Linear Correlation Matrix Using Trace Element Concentrations, pH, and Distance of the Sampling Site from the MTD for Unfiltered Groundwater Samples from the North Mara Mining Area

	pH	Dist.[1]	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb
Dist.[1]	–0.72**											
Al	–0.06	–0.06										
As	0.71**	–0.75**	0.12									
Cd	–0.04	0.21	0.09	0.22								
Co	0.62*	–0.49	0.42	0.70**	0.48							
Cr	0.45	–0.40	0.06	0.28	0.12	0.36						
Cu	0.15	–0.34	0.41	0.15	0.09	0.42	0.64*					
Fe	–0.02	0.15	0.64*	–0.10	0.16	0.35	0.10	0.37				
Mn	0.50	–0.61*	0.36	0.78**	0.17	0.72**	0.44	0.44	0.35			
Ni	0.50	–0.22	–0.06	0.46	0.51	0.51	0.37	0.26	–0.30	0.11		
Pb	0.40	–0.51	0.26	0.39	0.23	0.64*	0.57*	0.65*	0.48	0.66*	0.03	
Zn	0.38	–0.43	0.01	0.13	–0.06	0.30	0.43	0.46	0.42	0.46	–0.25	0.79**

[1]Distance from the MTD.
**Correlation is significant at the 0.01 level (2-tailed). *Correlation is significant at the 0.05 level (2-tailed).

Table 7

Spearman Linear Correlation Matrix Using Trace Element Concentrations, pH, and Distance of the Sampling Site from the MTD for Filtered Groundwater Samples from the North Mara Mining Area

	pH	Dist.[1]	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb
Dist.[1]	–0.72**											
Al	–0.06	–0.25										
As	0.82**	–0.79**	0.02									
Cd	0.28	–0.47	0.34	0.27								
Co	0.48	–0.35	0.53*	0.42	0.43							
Cr	0.34	–0.26	0.22	0.35	0.44	0.38						
Cu	–0.18	–0.18	0.64*	0.01	0.40	0.38	0.30					
Fe	0.12	–0.09	0.57*	–0.09	0.37	0.61*	0.20	0.21				
Mn	0.25	–0.43	0.48	0.39	0.41	0.63*	0.37	0.44	0.56*			
Ni	0.69**	–0.71**	0.34	0.60*	0.82**	0.60*	0.60*	0.29	0.27	0.35		
Pb	0.27	–0.37	0.63*	0.24	0.76**	0.72**	0.58*	0.67**	.61*	0.65*	0.72**	
Zn	0.37	–0.43	0.33	0.21	0.74**	0.51	0.49	0.33	0.67**	0.60*	0.68**	0.84**

[1]Distance from the MTD.
**Correlation is significant at the 0.01 level (2-tailed). *Correlation is significant at the 0.05 level (2-tailed).

climatic conditions, borehole depth, and water pH may affect the concentration of trace elements in the groundwater (Nicolli et al. 2010; Larios et al. 2012).

pH and borehole depth play a role in trace element mobility and enrichment in groundwater systems. In the present study, groundwater pH ranged from slightly acidic (6.0) to slightly alkaline (8.4), with a mean pH value of 7.2 ± 0.7. The studied borehole depths ranged from approximately 10 m to 40 m. A similar study conducted in the Salı´ River Basin, Argentina in groundwater of a similar pH range found that in shallow aquifers, As accumulation was controlled by near-surface evaporation and that deeper groundwater had comparatively low As concentrations (Nicolli et al. 2012). These authors also found, as in this case, that As had a poor correlation with dissolved Al, Fe, and Mn (Table 7). Additionally, in the present study, both Al and Fe were present in high concentrations. The presence of Al and Fe oxides and hydroxides in the groundwater would, therefore, be most likely. Under neutral or near-neutral pH environment, As would be expected to be adsorbed onto Al and Fe oxides and hydroxides. However, high pH and oxic conditions cause sorption of As and less favorable related elements (Nicolli et al. 2012), and this may have contributed to the observed high concentrations. This also explains a strong positive correlation between pH and As concentrations (Tables 6 and 7).

MPI results (Figure 4) show that the sampling site TRM5 (11.5 km from the MTD) had concentrations characteristic of sampling sites close to the MTD. These results suggest that trace element concentrations at this site were higher than expected. This may be explained by the fact that TRM5 was a shallow borehole (10 m deep), locally constructed by villagers as a source of drinking water on a short-term basis after their hand-pumped borehole was recently broken (pers. comm.). This is consistent with previous research by Larios et al. (2012), which concluded that local mineralogy of the area coupled with atmospheric deposition could contribute to the escalation of trace elements in shallow wells. More importantly, shallow groundwater is highly vulnerable to contamination by surface water containing mine wastes, such as tailings and mine drainage (Larios et al. 2012). A study on the feasibility of decentralized potable water systems by Peter-Varbanets et al. (2009) indicated that apart from natural causes of groundwater contamination, in countries like Tanzania, industrial, agricultural, and domestic activities may also contribute to groundwater pollution. The authors also added that in low income communities, contamination of groundwater sources may occur if wells are placed in close proximity to sources of contamination or if the wells are shallow (Peter-Varbanets et al. 2009). Generally, MPI values for the various sampling sites in the present study were in agreement with the CA results.

Friedman's ANOVA analysis (Table 3) indicates that TRM6 had the highest rank value (12.9) followed by TRM8 (10.7). However, TRM6 was not the closest sampling site to the MTD. Similar reasons as given above may explain this phenomenon. TRM6 was located within a short distance downstream of the main mining pit and adjacent to the Tigithe stream that flows through the intensive mining area (Figure 1d). Proximity not only to the MTD but also to the most intensive mining locality probably contributed to the increasing concentrations of trace elements detected in samples collected at this particular site. This site also had the highest pH level (8.4). Alkaline conditions at TRM6 could cause desorption of elements that form oxyanions such as As (Mitchell et al. 2011). These results, as confirmed by post-hoc analysis (Table 4), suggest a relationship between the concentration of trace elements in water and the distance from the MTD. This is a typical phenomenon within a semi-arid climate (Razo et al. 2004). However, other factors may also play a role in elevating trace element concentrations. MPI results were also consistent with our Friedman's ANOVA analyses. It is important to note that although the MPI is a powerful agglomeration tool and provides an easy product to make site-to-site comparisons, it does not have a value to denote the extent of pollution (Roychoudhury and Starke 2006).

The present study demonstrates clear distance-based effect size values for each element examined in the groundwater samples from the North Mara mining operation (Figure 3). Results in Figure 3 suggest that the levels of Cd, Fe, and possibly Al and Ni in our groundwater samples may be related with natural causes. These results were also corroborated by Spearman correlation values (Table 6), with a strong positive correlation between Al and Fe, whereas Cd and Ni lacked a good correlation with other elements. Concentrations of Cu and Zn indicated an intermediate effect—a medium to large effect—suggesting a combination of natural and anthropogenic sources. However, As, Co, Cr, Mn, and Pb levels in the water samples may be associated with anthropogenic enrichment. This is also in agreement with the Spearman correlation results, where As, Co, Cr, Mn, Ni, and Pb indicated a good positive correlation (Table 6). Based on our effect size findings (Figure 3), future research on the levels of trace elements in groundwater in the North Mara area may focus on the aforementioned five trace elements. As distance from the MTD decreases, the concentration of trace elements in the North Mara gold mining operation seems to be decreasing in the following order:

$$As > Pb > Mn > Cr = Co.$$

Accordingly, Zn and Cu could be given a secondary surveillance priority as distance seemed to have a medium-size effect on the concentration of these metals in water sources. In the North Mara area, contamination of groundwater is attributable to the cyanide-rich alkaline waste water. Cyanide-driven leaching seems to be more prominent during the dry season and may carry with it high concentrations of dissolved trace elements (Bowell et al. 1995; Williams 2001). Although not generalizable, these results may apply to sites in Sub-Saharan Africa, where environmental and geological conditions are similar to those prevailing at the North Mara mines.

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Supporting Information

The following supporting information is available for this article:

Table S1. Trace element concentration in the samples from North Mara gold mine, Tarime district, Tanzania.

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