Available online at www.kenyachemicalsociety.org

Journal of the Kenya Chemical Society 14-1 (2021), 9-16

JOURNAL OF THE KENYA CHEMICAL SOCIETY

Trace Elements in Carbonated Cold Springs of Eastern Mt. Kenya, Meru County

George N. Mungai[1, 2*], Hellen N. Njenga[1], Eliud M. Mathu[3] and Vincent O. Madadi[1]

[1]*Department of Chemistry, University of Nairobi, P.O. Box 30197-00100, Nairobi, Kenya*
[2]*Department of Physical Sciences, Meru University of Science and Technology, P.O. Box 972 60200, Meru, Kenya*
[3]*Department of Geology and Meteorology, South Eastern Kenya University, P.O. Box 170-90200, Kitui, Kenya*

Abstract

Carbonated spring waters are natural sources of trace minerals considered to have important biological and therapeutic functions. However, some trace elements are toxic to the human body upon exposure even at low concentration levels. Ten carbonated springs located in Meru County, on the Eastern Slopes of Mt. Kenya were investigated to determine the levels of trace elements. The host communities draw the carbonated mineral waters regularly for drinking, cooking, watering the livestock and selling. Cavity ring-down spectroscopy was used for the analysis of dissolved inorganic carbon in the spring waters and inductively coupled plasma-optical emission spectrometry for the determination of the following trace elements: As, B, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se and Zn. Host rocks analysis for major toxic elements As, Cd, Cr, Cu, Hg and Pb was done by X-ray fluorescence. The reported dissolved inorganic carbon in the waters was significant ranging from 39.2-89.0 mmol/kg and this enhanced dissolution of minerals from rocks due to the presence of carbonic acid. Levels of As in six springs ranged from 11.1 to 21.5 µg/L and exceeded the 10 µg/L WHO recommended limit for drinking-water. There was a strong positive correlation with r = +0.8, between As levels and dissolved inorganic carbon. The other elements were within the safe limit. Toxic elements in the rocks ranged from As 30-170 ppm, Cd <10 ppm, Cr <10-100 ppm, Cu 40-180 ppm, Hg <10 ppm and Pb <10-370 ppm. Therefore, water-rock interaction contributed significantly to the presence of toxic elements in the carbonated waters. Arsenic (As) is a well-known carcinogen and poses many other health risks to humans. An epidemiological study on clinical manifestations of As toxicity in the region as well as removal of As from the waters prior to consumption are recommended.

Keywords: Arsenic toxicity, carbonated springs, mineral waters, trace minerals

1. Introduction

Some springs in Eastern Mt. Kenya region discharge cold waters containing high concentrations of dissolved CO_2 and mineral content. The apparent sources of CO_2 in mineral springs include the mantle and sedimentary carbonate rocks (Cartwright *et al*., 2002; Mungai *et al*., 2014). Intake of carbonated water enhances digestive solubility of food and improves intestinal physiology by stimulating secretion and motility of the digestive tract. Such waters are suitable remedy for conditions such as dyspepsia (indigestion) and irritable bowel syndrome. Studies have shown that bicarbonated mineral waters minimises cardiovascular risks through breakdown of cholesterol into bile salts and their subsequent removal from the body (Gasbarrini *et al.*, 2006; Schoppen *et al.*, 2004). Trace elements occur in various environmental matrices at concentrations ranging from 1 ppb to 100 ppm (Skoog, 2004). Some trace elements such as B, Co, Cr, Cu, Fe, Mn, Mo, Ni, Se and Zn are essential trace or micronutrients because their requirement in the body is less than 100 mg/day and deficiency leads to serious disorders. These elements regulate crucial biological pathways by acting as cofactors for various enzymes and forming centers for stablisation of enzymes and proteins (Vinha *et al*., 2019; Prashanth *et al.*, 2015). However, trace elements such as As, Cd, Cr, Cu, Pb and Hg are highly toxic to humans even at low concentrations. These metals interfere with functioning of body cells by binding to enzymes, structural proteins and nucleic acids. They are known to affect the nervous and circulatory systems, causes multiple organ damage and some of them are human carcinogens (Golekar *et al.*, 2013).

*Corresponding author e-mail: georgenmungai@gmail.com
Received: 05 February 2021
Revised: 31 March 2021
Accepted: 19 April 2021

A study on CO_2-rich waters in Iceland showed that water-rock interaction is responsible for elevated trace elements above the World Health Organization (WHO) guidelines for drinking-water, especially As and Mn at <0.01-1.08 µmol/kg and 0.1-184 µmol/kg, respectively (Thomas *et al.*, 2016). Groundwater in Bangladesh was found to contain excessive levels of As with an average of 84.7 µg/L in the sedimentary aquifers. The occurrence was associated with the reduction of iron and manganese oxides containing adsorbed As. The process allows the release of As species into the groundwater (Nwankwo *et al*., 2020). Mt. Kenya with summit elevation of 5,199 m (Batian peak) is an extinct volcano which lies outside the East Africa Rift System. The major rock types found in Mt Kenya region are basalts, kenytes, trachytes, phonolites and rhomb porphyrites (Baker, 1967). The commonest minerals in this area are magnetite (Fe_3O_4), rutile (TiO_2), augite [$(CaNa)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$], mica flakes and garnet (Mason, 2007). Volcanic CO_2 degassing in the region is manifested by occurrence of widespread carbonated mineral springs called '*muonyo'* in the local dialect which emerge through point sources along the eastern slopes of the volcano.

As CO_2 gas rises through fractures or point sources, it mixes with groundwater to form weak carbonic acid, H_2CO_3. The acid increases the capacity of water to dissolve minerals from the underlying rocks which increases the risk of contamination. For example, siderite mineral ($FeCO_3$) dissolves in carbonic acid to form aqueous iron (II) bicarbonate $Fe(HCO_3)_2$ as shown in equation 1 (Andrews *et al.*, 2004).

$$FeCO_{3\,(s)} + H_2CO_{3\,(aq)} \rightarrow Fe(HCO_3)_{2\,(aq)} \qquad (1)$$

The local communities in the study area use the carbonated mineral waters directly for drinking, cooking, watering livestock and selling. According to the consumers, the water is claimed to have a pleasant soda taste and provide therapeutic relieve for stomach discomforts. This study involved chemical investigation on the levels of trace elements in the spring waters as well as toxic elements in the host rocks. The purpose of the study was to create awareness of the potential health benefits and risks that may arise from drinking the carbonated spring waters. Ten springs were investigated which included Gikumene, Kathathantu, Kiambogo, Mbwinjeru, Nthungu, Mulathankari, Rwarera-A, Rwarera-B, Tharu and Ukuu.

2. Methodology

2.1 Study area

The study area is located in Meru County on the Eastern Slopes of Mt. Kenya which is about 250 km North-East of Nairobi, Kenya. Fig. 1 shows the geological map and the sites of the carbonated springs in the study region. The volcano flanks have distinct craters and vents. The occurrence of multiple lineaments is a sign of underlying buried faults through which passive CO_2 degassing takes place from the magma. The springs are bound within latitudes 00^o 13.401' N and 00^o 05.004' S and longitudes 37^o 35.620' E and 37^o 40.763' E as shown in Table 1.

Table 1: Sampling sites GPS coordinates and elevation above sea level

Spring	GPS Coordinates	Elevation (m)
Gikumene (GIK)	N 00^o 01.154' E 037^o 38.983'	1566
Kathathantu (KAT)	S 00^o 04.799' E 037^o 39.639'	1491
Kiambogo (KIA)	S 00^o 05.004' E 037^o 40.763'	1410
Mbwinjeru (MBW)	S 00^o 01.545' E 037^o 37.905'	1647
Mulathankari (MUL)	N 00^o 02.449' E 037^o 40.584'	1425
Nthungu (NTH)	N 00^o 00.668' E 037^o 38.629'	1601
Rwarera-A (RWA)	N 00^o 13.333' E 037^o 37.534'	1413
Rwarera-B (RWB)	N 00^o 13.401' E 037^o 36.759'	1414
Tharu (THA)	S 00^o 04.467' E 037^o 35.620'	1938
Ukuu (UKU)	S 00^o 02.616' E 037^o 38.322'	1614

2.2 Sampling

Ten carbonated springs regularly used by the local communities were selected for sampling. The sampling was done during a dry season to avoid runoff mixing with the spring waters. Three water samples for dissolved inorganic carbon (DIC) analysis were collected from each spring using 13 mL glass vials. One drop of saturated $HgCl_2$ was added to each vial to preserve the samples. For trace element analysis, three water samples were collected from each spring and filtered through 0.45 µm filters into clean 300 mL PET bottles. The samples were treated by adding a drop of concentrated HNO_3 in each bottle to adjust the pH (<2). They were then preserved at approximately 4 ^oC in a refrigerator. Grab sampling of host rocks on the surface was done within an area of approximately 10 m^2 around the springs. Three rock samples were collected from each site and the weathered surface was scrapped off.

2.3 Chemicals

All the chemicals used were analytical grade obtained from Sigma-Aldrich. They included: Mercury (II) chloride ($HgCl_2$), nitric acid (HNO_3), calcium carbonate ($CaCO_3$), phosphoric acid (H_3PO_4) and TraceCERT® 100 mg/L multi-element ICP-OES standard solution.

2.4 Dissolved inorganic carbon measurement

Dissolved inorganic carbon (DIC) was determined by Cavity Ring-Down Spectroscopy (CRDS) method (Dickinson *et al.*, 2017). Six $CaCO_3$ standards ranging from 0.3 to 2.0 mg were weighed into 13 mL vials. The vials were tightly closed and evacuated for five seconds. A volume of 2 mL of each sample was transferred with a syringe into an evacuated and weighed vial. The vial was reweighed. Similarly, a method blank was

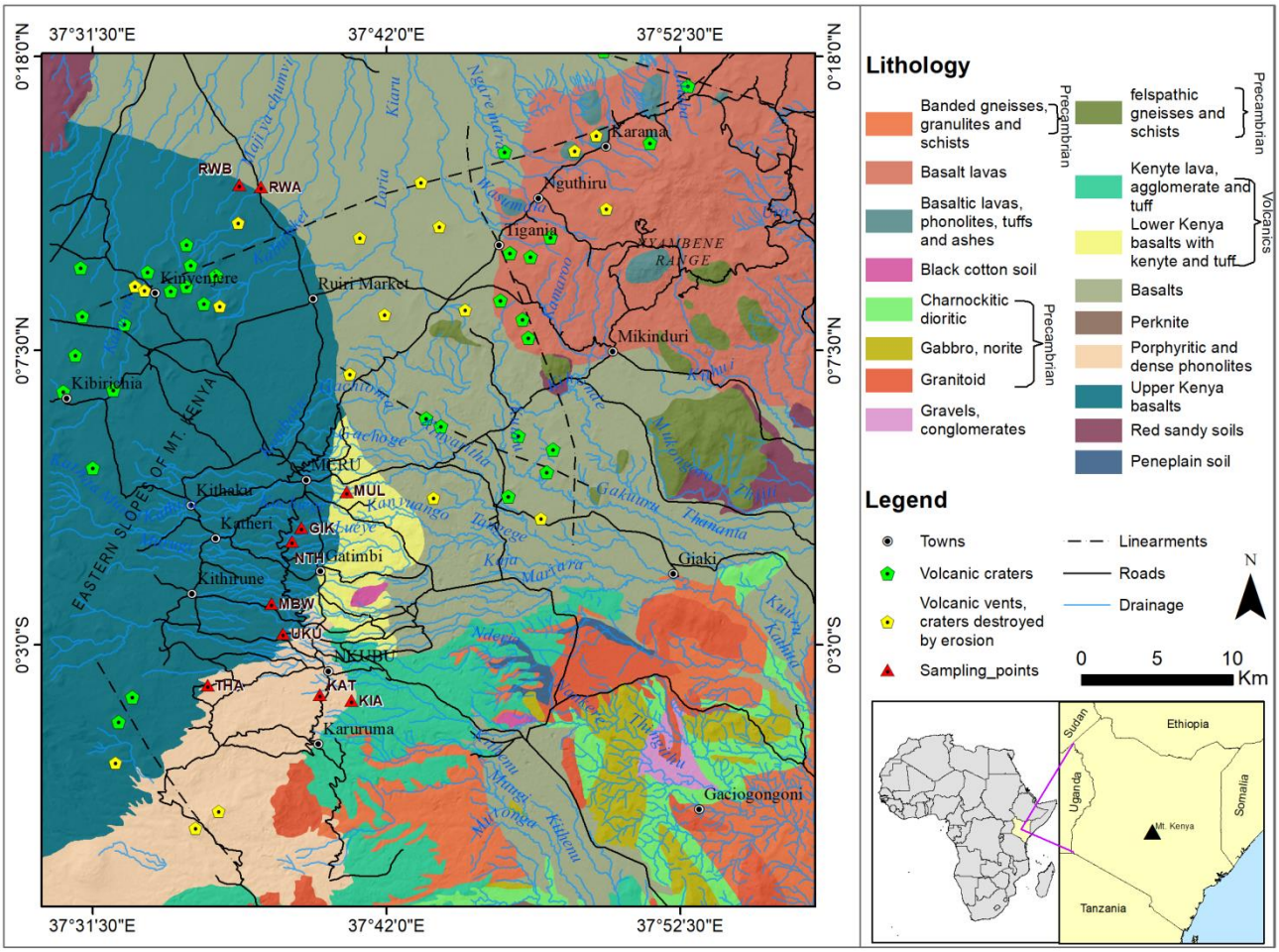

Figure 1: The geological map of the Eastern Slopes of Mt. Kenya. The carbonated springs are shown on the map trending North-South. (Courtesy of Department of Geology, University of Nairobi)

prepared by transferring 2 mL of reagent water into a pre-weighed and evacuated vial. To each standard, sample and blank, 2 mL of 25% H_3PO_4 was added. The released CO_2 gas was directed into the Picarro CRDS system (Picarro CRDS G2101-i Isotopic CO_2 Analyzer). The DIC measurement of the sample was obtained by comparison with a reference CO_2 gas released from the calibration standards.

2.5 Trace elements analysis in the water

Samples were digested with concentrated HNO_3 in a microwave digester in order to dissolve all the elements of interest prior to analysis using inductively coupled plasma-optical emission spectrometer (ICP-OES Agilent Technologies: 5110) as per US EPA Method 200.7 Revision 5.0 (US EPA, 2001). External calibration standards were prepared from a 100 mg/L multi-element standard stock solution. The following quality control measures were adopted to check the performance of instrument and analytical procedures employed. Precision was ensured by analysis of three replicates. Acceptable (<±0.5%) relative standard deviation (RSD) range was established which showed reliable reproducibility of the measurements. To ensure that the elements were reliably detected and quantified, their limits of quantitation (LOQ) were established by analysing ten replicates of calibration blanks and multiplying the obtained standard deviation by ten.

2.6 Heavy metals analysis in the rocks

The samples were dried in an oven at 110 ^oC for 24 hours. They were ground into fine powder and filtered through a 100 micron mesh. About 2 g of each ground rock sample (~100 microns) was transferred into the sample holder and scanned with a portable energy dispersive X-ray fluorescence (EDXRF) spectrometer (BRUKER S1 TITAN) to a maximum potential of 50 keV. Three replicate samples were analysed for each spring.

3. Results and Discussion

The results for dissolved inorganic carbon (DIC) and trace elements analysis in the waters followed by the results for toxic elements determination in the rocks are reported in this section. The results are accompanied by their respective relative standard deviations (RSD).

3.1. Dissolved inorganic carbon (DIC)

The DIC concentrations in the spring waters are shown in table 2. The springs are identified with their first three letters e.g. GIK for Gikumene.

Table 2: DIC levels (mmol/kg) in the spring waters

Spring	DIC(mmol/kg)
GIK	39.2±2.7
KAT	54.0±3.1
KIA	47.6±3.6
MBW	81.3±2.9
MUL	66.8±3.5
NTH	70.2±1.5
RWA	89.0±3.2
RWB	72.4±2.6
THA	87.3±2.8
UKU	72.6±3.5

The DIC values obtained from the study region ranged from 39.2 to 89.0 mmol/kg and indicated a large amount of carbon species in the system which may increase dissolution of minerals from the host rocks. The slight variations in RSD values may be attributed to the loss of some CO_2 from the samples. The DIC is possibly linked to CO_2 degassing from the mantle and carbonate rocks deep in the crust. DIC concentrations in natural waters usually range from 0.02 mmol/kg in acidic soft waters to 5 mmol/kg in highly alkaline hard waters (Cole and Prairie, 2014). DIC composition can be expressed as shown in equation 2 (Andrews *et al.*, 2004).

$$DIC = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad (2)$$

Kanakiya *et al*. (2017) established that carbon dioxide (CO_2)-rich fluids react with rock-forming minerals in volcanic environments dominated with basalt rocks and the approach can be applied in sequestration of anthropogenic CO_2. Similarly, the mechanism may explain how the carbonated waters found in the Eastern Slopes of Mt. Kenya interact with volcanic rocks raising the mineral content in such fluids. This can lead to pollution of the spring waters by toxic elements derived from the basalt and other types of rocks in the region.

3.2. Trace elements in the waters

The average levels of 14 trace elements found in the carbonated mineral waters are shown in table 3 and are compared with the WHO guidelines for drinking-water quality (WHO, 2011). The limits of quantitation (LOQ) for the respective parameters are given.

3.3. Toxic elements in the host rocks

Table 4 shows the concentration of toxic heavy metals in the host rocks. Levels of Cd and Hg were below the XRF instrument detection limit (<10 ppm) in all the springs. Levels of As, Cu and Pb were significant except for KAT whose Pb levels were below levels of detection. Chromium (Cr) was only detected in RWB, THA and UKU springs. Hence, these volcanic rocks have the potential to contaminate the spring waters with toxic elements.

The results in Tables 3 and 4 indicate significant levels of trace minerals in both water and rock matrices, respectively. The high quantity of DIC largely contributes to the elevated mineralisation of the waters by the host rocks. Mercury which was below detection limit in the rock samples was also below quantitation limit in all the spring waters. Arsenic which was relatively high in the rock samples was found to be high in the spring waters even though there was no direct correlation. The As concentration in the rocks was highest at KIA (170±0.002 ppm) but relatively low in the water compared to the other springs. This disparity could be due to the low amount of DIC at KIA hence low rate of As dissolution from rocks. Lead levels were high in the rock samples but not correspondingly high in the spring waters. Similarly, Cr was not detected in the rocks in most springs but it was found in the waters. This may indicate that besides water acidity and rock types, there are other factors that affect the transfer of trace elements from the rocks into the waters such as ion exchange. The distribution and levels of the elements in the waters also depends on the types of aquifer supplying water to the springs (Sidibé *et al.*, 2019). While most of these elements are useful or harmless to the body, long term ingestion of some of them may trigger human health complications (Wada, 2004).

3.4. Essential trace elements in the waters

The concentration of Boron (B) was found to range from 35 to 837 µg/L and was below the recommended WHO maximum limit of 2400 µg/L. Boron helps in bone formation and functioning of the central nervous system, promotes hormonal action, has anti-inflammatory effects which reduce arthritic symptoms and minimise risk for some types of cancer. However, excessive intake of B is associated with toxicity of the male reproductive system (Nielsen, 2014). There are no WHO guidelines for cobalt (Co) whose levels ranged from <1.6 (below LOQ) to 15.1 µg/L. Cobalt is an essential trace metal in humans. It is a vital component of vitamin B_{12} which is involved in healthy functioning of blood cells, nerve cells,

Table 3: Trace minerals (µg/L) in carbonated springs of Eastern Mt. Kenya

	GIK	KAT	KIA	MBW	MUL	NTH	RWA	RWB	THA	UKU	LOQ	WHO
As**	<3.7	8.8±0.4	6.5±0.3	**14.4±0.7**	5.1±0.2	**11.1±0.6**	**16.5±0.4**	**19.7±0.3**	**21.5±0.8**	**13.9±0.4**	3.7	10
B	35±0.7	210±1.3	193±0.6	387±1.5	44±0.8	241±1.0	335±1.4	302±0.9	837±2.2	414±1.7	6.8	2400
Cd	0.5±0.6	0.3±0.6	<0.1	0.7±0.5	0.5±0.8	0.6±0.4	0.5±0.6	0.2±0.5	0.3±0.7	0.2±0.4	0.1	3
Co	15.1±0.4	<1.6	<1.6	<1.6	9.8±0.1	<1.6	2.4±0.5	2.6±0.3	<1.6	<1.6	1.6	-
Cr	0.6±0.9	0.6±0.5	0.8±0.5	2.5±0.4	1.2±0.7	1.3±0.1	1.3±0.4	0.8±0.5	0.6±0.2	0.7±0.1	0.2	50*****
Cu	4.2±0.7	6.1±0.8	6.4±0.1	10.8±0.3	7.8±0.5	8.4±0.9	11.1±0.4	10.9±0.2	11.5±0.5	11.9±0.3	0.1	2000
Fe	7077±3.2	8757±2.8	8077±3.4	7070±3.1	1972±1.4	6678±2.7	4207±2.1	2538±2.2	2602±1.5	6079±2.5	1.5	-
Hg	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	0.8	6
Mn	1347±1.2	920±1.6	1069±2.0	135±0.5	1041±1.7	531±0.8	444±1.1	329±0.5	224±0.9	522±1.4	0.2	-
Mo	1.5±0.8	1.4±0.3	1.8±0.5	1.8±0.2	2.4±0.7	1.9±0.1	2.2±0.5	<1.0	<1.0	2.6±0.3	1	-
Ni	23±0.5	<5.8	<5.8	<5.8	25.5±0.2	8.0±0.2	9.6±0.1	9.1±0.5	<5.8	<5.8	5.8	70
Pb	<1.2	<1.2	<1.2	4.3±0.6	<1.2	<1.2	3.2±0.6	4.1±0.5	3.1±0.8	2.6±0.4	1.2	10*****
Se	<4.9	<4.9	7.5±0.8	<4.9	9.2±0.7	6.0±0.4	10.8±0.5	14.7±0.5	20.6±0.4	6.0±0.7	4.9	40
Zn	15.7±0.3	4.5±0.1	5.5±0.6	16.4±0.4	7.2±0.2	13.7±0.5	5.6±0.4	<3.0	4.0±0.1	6.2±0.5	3.0	-

- Occurs in drinking water at concentrations well below those of health concern.
*****Provisional guideline value.
******Above WHO guidelines for drinking-water quality (GDWQ) of 2011.

Table 4: Levels of toxic elements (ppm) in the rocks

Spring	As	Cd	Cr	Cu	Hg	Pb
GIK	30±0.002	<10	<10	160±0.003	<10	310±0.005
KAT	170±0.002	<10	<10	140±0.003	<10	<10
KIA	50±0.002	<10	<10	40±0.002	<10	250±0.005
MBW	50±0.001	<10	<10	40±0.002	<10	190±0.004
MUL	30±0.002	<10	<10	100±0.003	<10	310±0.005
NTH	50±0.001	<10	<10	90±0.002	<10	270±0.005
RWA	30±0.001	<10	<10	70±0.003	<10	370±0.006
RWB	30±0.001	<10	80±0.005	180±0.003	<10	280±0.005
THA	40±0.002	<10	40±0.004	120±0.002	<10	310±0.005
UKU	80±0.002	<10	100±0.004	160±0.003	<10	240±0.004

amino acid metabolism and DNA synthesis (Czarnek *et al.*, 2015). Iron (Fe) levels were significant varying from 1972 to 8757 µg/L. There is no WHO limit for Fe. Its functions in the body include oxygen transport, electron transport, enzymes cofactor and DNA synthesis. Iron deficiency in the body leads to anaemia; however, excess Fe has ability to form damaging free radicals (Abbaspour *et al.*, 2014). Figure 2 shows a photograph of Tharu spring. The brown precipitates indicated occurrence of insoluble $Fe(OH)_3$ which usually form due to air oxidation of aqueous Fe^{2+} to the less soluble Fe^{3+} when the water gets aerated at the surface, as shown in equation 3 (Andrews *et al.*, 2004).

$$4Fe^{2+}_{(aq)} + O_{2\,(g)} + 10H_2O_{(l)} \rightarrow 4Fe(OH)_{3\,(s)} + 8H^{+}_{(aq)} \qquad (3)$$

Figure 2: Tharu spring and the host rocks

Manganese (Mn) levels varied from 135 to 1347 µg/L. According to WHO, Mn levels generally found in drinking water is not of health concern although some epidemiological studies have associated high levels of Mn in drinking water with neurotoxicity such as tremors (Chen *et al.*, 2018). It acts as a cofactor for various enzymes involved in digestion, reproduction, antioxidant defense, immune response, respiration and neuronal activities. Molybdenum (Mo) ranged from <1.0 to 2.6 µg/L and there is no maximum limit provided for Mo by WHO. Mo is an essential trace element with an estimated daily requirement of 0.1–0.3 mg for adults. It is present in enzymes such as sulphite oxidase, aldehyde oxidase and xanthine oxidase/dehydrogenase (Wada, 2004).

Nickel (Ni) levels (<5.8-25.5 µg/L) were below WHO limit of 70 µg/L. Nickel is involved in hormonal activity and lipid metabolism. The most common adverse effect of Ni is allergic contact dermatitis (Zdrojewicz *et al.*, 2016). Selenium (Se) levels of <4.9 to 20.6 µg/L were below the WHO provisional guideline value of 40 µg/L. Selenium is an essential trace mineral in humans. Selenium constitutes selenoproteins whose functions include providing anti-oxidant and anti-inflammatory effects in the body. Selenium deficiency is associated with severe cardiomyopathy (Keshan disease). The effects of selenium toxicity (selenosis) include gastrointestinal disturbances and dermatological effects (skin discolouration, hair and nail loss). Other effects are decayed teeth, degeneration of motor neurons and prevalence of cancers (Rayman, 2012). The levels of Zinc (Zn) ranged from <3.0-16.4 µg/L and it has no WHO limit. It is an essential trace mineral in humans and its requirement in adult males is 15–20 mg/day. Zinc enhances normal growth and development during pregnancy, childhood and adolescence. Reproductive (spermatogenesis), nervous, immune, dermatological and gastrointestinal systems are the most affected by Zn deficiency. However, excess absorption of Zn interferes with Cu and Fe uptake (Roohani *et al*., 2013).

3.5. Toxic trace elements in the waters

Arsenic (As) levels varied from <3.7 to 21.5 µg/L against WHO guideline value of 10 µg/L (WHO, 2011). The following springs exceeded As safe limit: MBW (14.4 µg/L), NTH (11.1 µg/L), RWA (16.5 µg/L), RWB (19.7 µg/L), THA (21.5 µg/L) and UKU (13.9 µg/L). The source could be As-bearing sulphide and sedimentary mineral deposits such as arsenopyrite-FeAsS (Herath *et al*., 2016). Figure 3 shows a strong positive linear relationship (r = +0.8) between As levels and DIC. Hence, high amount of CO_2 in the waters enhances leaching of As from the underlying rocks.

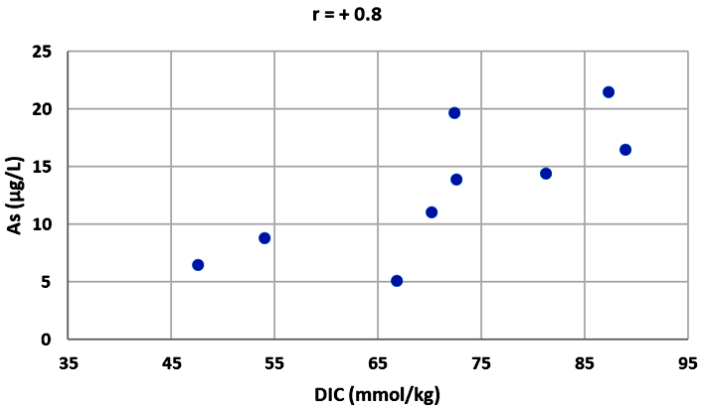

Figure 3: Correlation of As with DIC

Carbonation of arsenic sulphide minerals helps in leaching of As into the groundwater under anaerobic conditions by forming stable arseno-cabonate complexes such as $As(CO_3)(OH)_2^-$, $As(CO_3)_2^-$ and $AsCO_3^+$ (Kim *et al*., 2000). Arsenic is a metalloid of great public health concern in some natural waters as it is considered to be carcinogenic. It induces changes in DNA which have been linked with cancer development on the skin, prostate, lungs, liver, bladder and kidney. It is also associated with skin lesions, diabetes and cardiovascular disease (Abdul *et al*., 2015; WHO, 2011, IARC, 2019). A study in Bangladesh by Ahmed *et al.* (2016) on groundwater revealed clinical manifestations of arsenic poisoning (arsenicosis) among the residents, such as neuropathy and dermatology. There was lack of proper awareness about arsenic toxicity among the people. Arsenic can be removed from the waters prior to consumption using available methods such as flocculation followed by microfiltration (Han *et al*., 2002) and electrocoagulation (Kumar *et al*., 2004). Cadmium (Cd) levels of <0.1 (below LOQ) to 0.7 µg/L were below the WHO permissible limit of 3 µg/L. While the waters may be considered safe with respect to Cd toxicity, it is important to note that Cd accumulates in the human kidneys causing damage (Liu *et al*., 2015). It is a probable carcinogen according to the International Agency for Research on Cancer (IARC, 2019).

Chromium (Cr) levels (0.6-2.5 µg/L) were below the WHO provisional guideline value of 50 µg/L. The ratio of Cr^{3+} to Cr^{6+} in natural waters varies widely and significant high

concentrations of toxic Cr^{6+} may occur. In the gastrointestinal tract, Cr^{6+} is reduced to the less toxic Cr^{3+} which is an essential trace nutrient and its deficiency leads to impairment of glucose tolerance (WHO, 2011). Chromium toxicity causes dermatitis, renal failure and pulmonary cancer (Cefalu and Hu, 2004). Copper (Cu) level which ranged from 4.2 to 11.9 µg/L, were below the WHO maximum limit of 2000 µg/L. Copper helps in the synthesis of blood haemoglobin, bone development and connective tissue metabolism. In high doses it can cause kidney dysfunction, stomach and gastrointestinal bleeding (Uauy *et al.*, 2008). Mercury (Hg) was below the LOQ (<0.8 µg/L) and also below WHO set limit in all the springs implying that this element is not a significant contaminant of the spring waters. It is nevertheless bioaccumulative and highly toxic, capable of causing neurological disorders, kidney damage, benign tumours and genotoxicity (Davidson *et al.*, 2004). Lead (Pb) concentrations ranged from <1.2 (below LOQ) to 4.3 µg/L while the WHO provisional guideline value for Pb is 10 µg/L. Hence, all the springs were below the permissible level. Lead accumulates over time in the brain, kidney, liver and bones. It causes low intelligence quotient (IQ) in children, behavioural disorders, kidney damage, impaired fertility, adverse pregnancy outcomes and hypertension (Wani *et al.*, 2015).

4. Conclusions

The investigated waters were characterised by large amounts of DIC which accelerates the acid dissolution of minerals from the host rocks. The waters contained substantial levels of essential trace elements (B, Co, Cu, Fe, Mn, Mo, Ni, Se and Zn) which have important biological functions in humans. However, highly toxic elements such as As, Cd, Cr and Pb were present in varying amounts. The level of As was particularly high and exceeded the WHO guideline value of 10 µg/L in drinking-water at Mbwinjeru, Nthungu, Rwarera-A, Rwarera-B, Tharu and Ukuu. The results showed a strong positive correlation between DIC and As concentrations which resulted in water contamination. The rocks had significant levels of As, Cu and Pb in all the springs while Cr was reported in three sites. Through water-rocks interaction in the aquifer and the surrounding rocks which is aided by the dissolved CO_2, these toxic elements could get leached into the waters. Intake of the As-contaminated waters may have long term health effects such as development of various types of cancers. Therefore, As should be lowered to permissible level before using the polluted waters. Results for Gikumene, Kathathantu, Kiambogo and Mulathankari were within the acceptable range and people can enjoy the associated health benefits. However, the waters should be taken in moderation to avoid overexposure to significant levels of B, Fe, Mn, Ni and Se. Further biochemical and epidemiological studies should be carried out to ascertain the potential health risks of these spring waters on human population especially the threat by arsenic toxicity. An extended geochemical study of the springs covering several dry and wet seasons is also recommended to monitor the variability of the chemical composition with time and seasons.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

We thank the National Commission for Science, Technology and Innovation (NACOSTI) and Meru County Government, Kenya, for authorising this research. We are sincerely grateful to Geoffrey Murira and Jacob Hare of the Kenya Bureau of Standards; Edward Mwangi and Joram Wambua of the Ministry of Petroleum and Mining in Kenya; Jens Hartmann, Gibran Romero-Mujalli and Peggy Bartsch of the Institute for Geology, University of Hamburg in Germany, for working with us during the analysis.

References

Abbaspour, N., Hurell, R., and Kelishadi, R. (2014) Review on iron and its importance for human health. *Journal of Research in Medical Sciences*, **19**:164-174.

Abdul, K. S. M., Jayasinghe, S. S., Chandana, E. P. S., Jayasumana C., and De Silva, P. M. C. S. (2015) Arsenic and human health effects: A review. *Environmental Toxicology and Pharmacology*, **40**:828–846.

Ahamed, S., Sengupta, M. K., Mukherjee, S. C., Pati, S., Mukherjeel, A., Rahman, M. M., Hossain, M. A., Das, B., Nayakl, B., Pal, A., Zafar, A., Kabir, S., Banu, S. A., Morshed, S. A., Islam, T., Rahman, M. M., Quamruzzaman, Q., and Chakraborti, D. (2006) An eight-year study report on arsenic contamination in groundwater and health effects in Eruani village, Bangladesh and an approach for its mitigation. *Journal of Health, Population and Nutrition*, **24**:129-41.

Andrews, J. E., Brimblecombe, P., Jickells, T. D., Liss, P. S., and Reid, B. (2004) An Introduction to Environmental Chemistry, Second edition. Oxford UK: Blackwell Publishing, p151-153, 179-180.

Baker, B. H. (1967) Geology of the Mount Kenya Area. Geological Survey of Kenya. Ministry of Natural Resources, Kenya. https://edepot.wur.nl/ Accessed 10 Dec 2019.

Cartwright, I., Weaver, T., Tweed, S., Ahearne, D., Cooper, M., Czapnik, K., and Tranter, J. (2002) Stable isotope geochemistry of cold CO_2-bearing mineral spring waters, Daylesford, Victoria, Australia: sources of gas and water and links with waning volcanism. *Chemical Geology*, **185**:71–91.

Cefalu, W. T., and Hu, F. B. (2004) Role of chromium in human health and in diabetes. *Diabetes Care*, **27**:2741-51.

Chen, P., Bornhorst, J., and Aschner, M. (2018) Manganese metabolism in humans. *Frontiers in Bioscience (Landmark Ed.)*, **23**:1655-1679.

Cole, J. J., and Prairie, Y. T. (2014) Dissolved CO_2 in Freshwater Systems. Reference Module in Earth Systems and Environmental Sciences. doi.org/10.1016/B978-0-12-409548-9.09399-4

Czarnek, K., Terpilowska, S., and Siwicki, A. K. (2015) Selected aspects of the action of cobalt ions in the human body. *Central European Journal of Immunology*, **40**:236-242.

Davidson, P. W., Myers, G. J., and Weiss, B. (2004) Mercury exposure and child development outcomes. *Pediatrics* **113**:1023–9.

Dickinson, D., Bode, S., and Boeck, X. P. (2017) Measuring ^{13}C enriched CO_2 in air with a cavity ring-down spectroscopy gas analyser: Evaluation and calibration. *Rapid Communication in Mass Spectrometry*, **31**:1892-1902.

Gasbarrini, G., Candelli, M., Graziosetto, R. G., Coccheri, S., and Di, Iorio, F. (2006) 'Evaluation of thermal water in patients with functional dyspepsia and irritable bowel syndrome accompanying constipation', *World Journal of Gastroenterology*, **12**:2556–2562.

Golekar, R. B., Patil, S. N., and Baride, M. V. (2013) Human health risk due to trace element contamination in groundwater from the Anjani and Jhiri river catchment area in northern Maharashtra, India. *Earth Sciences Research Journal*, J **17**:17 – 23.

Han, B., Runnellsb, T., Zimbron, J., and Wickramasinghea, R. (2002) Arsenic removal from drinking water by flocculation and microfiltration. *Desalination*, **145**:293–298.

Herath, I., Vithanage, M., Bundschuh, J., Maity, J. P., and Bhattacharya, P. (2016) Natural Arsenic in Global Groundwaters: Distribution and Geochemical Triggers for Mobilization. *Current Pollution Reports*, **2**:68-89.

IARC. (2019) International Agency for Research on Cancer. Agents classified by IARC Monographs. https://monographs.iarc.fr › uploads › 2018/09 › ClassificationsAlphaOrder. Accessed 28 Aug 2019.

Kanakiya, S., Adam, L., Esteban, L., Rowe, M. C., and Shane, P. (2017) Dissolution and secondary mineral precipitation in basalts due to reactions with carbonic acid. *Journal of Geophysical Research: Solid Earth*, **122**: 4312–4327.

Kim, M. J., Nriagu, J., and Haack, S. (2000) Carbonate Ions and Arsenic Dissolution by Groundwater *Environmental Science and Technology*, **34**: 3094–3100.

Kumar, P. R., Chaudhari, S., Khilar, C. K., and Mahajan, S. P. (2004) Removal of arsenic from water by electrocoagulation. *Chemosphere*, **55**:1245-1252.

Liu, Y., Xiao, T., Baveye, P. C., Zhu, J., Ning, Z., and Li, H. (2015) Potential health risk in areas with high naturally-occurring cadmium background in southwestern China. *Ecotoxicology and Environmental Safety*, **112**:122–131.

Mason, P. (2007) Geology of the Meru - Isiolo Area Report No.31: 3-5, 24. https://s3-eu-west-1.amazonaws.com/.../geology/Geology+of+the+Meru+Isiolo.pdf Accessed 23 Aug 2019.

Mungai, G. N., Njenga, L. W., Mathu, E. M., Kamau, G. N. (2014) Study of minerals in the water and source rocks of Rurii spring in Meru County, Kenya. *International Journal of Biochemiphys*, **22**:11-19.

Nielsen, F. H. (2014) Update on human health effects of boron. *Journal of Trace Elements in Medicine and Biology*, **28**:383-387.

Nwankwo, C. B., Hoque, M. A., Islam, M. A., and Dewan, A. (2020) Groundwater Constituents and Trace Elements in the Basement Aquifers of Africa and Sedimentary Aquifers of Asia: Medical Hydrogeology of Drinking Water Minerals and Toxicants. *Earth Systems and Environment*, **4**: 369–384.

Prashanth, L., Kattapagari, K. K., Chitturi, R. T., Baddam, V. R., and Prasad, L. K. (2015) A review on role of essential trace elements in health and disease. *Journal of Dr. NTR. University of Health Sciences*, **4**: 75-85.

Rayman, M. P. (2012) Selenium and human health. *Lancet* **379**:1256-68.

Roohani, N., Hurrell, R., Kelishadi, R., and Schulin, R. (2013) Zinc and its importance for human health: An integrative review. *Journal of Research in Medical Sciences*, **18**:144-157.

Schoppen, S., Pérez-Granados, A. M., Carbajal, A., Oubina, P., Sanchez-Muniz, F. J., GomezGerique, J., and Vaquero, M. P. (2004) 'A sodium-rich carbonated mineral water reduces cardiovascular risk in postmenopausal women'. *Journal of Nutrition*, **134**:1058–1063.

Sidibé, A. M, Lin X., and Koné, S. (2019) Assessing Groundwater Mineralization Process, Quality, and Isotopic Recharge Origin in the Sahel Region in Africa. *Water*, **11**: 1-19.

Skoog, D. A, West, D. M, Holler, F. J., and Crouch, S. R. (2004) Fundamentals of analytical chemistry, 8th edition. USA: Thomson Brooks/ Cole, p771-772.

Thomas, D. L., Bird, D. K., Arnorsson, S., and Maher, K. (2016) Geochemistry of CO_2-rich waters in Iceland. *Chemical Geology* **444**: 158-179.

Uauy, R., Maass, A., and Araya, M. (2008) Estimating risk from copper excess in human population. *American Journal of Clinical Nutrition*, **88**:867S-871S.

US EPA. Method 200.7 Revision 5.0 (2001) Trace elements in water, solids, and biosolids by inductively coupled plasma-atomic emission spectrometry. U.S. Environmental Protection Agency. Washington, D.C. 20460. https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P1002CW0.TXT Accessed 4 Jan 2019.

Vinha, A. F., Sousa, C., Moutinho, C., and Matos, C. (2019) Trace Minerals in Human Health: Iron, Zinc, Copper, Manganese and Fluorine. *International Journal of Science Research and Methodology*, **13**: 57-80.

Wada, O. (2004) What are trace elements? Their deficiency and excess states. *Japan Medical Association Journal*, **47**:351-8.

Wani, A. L., Ara, A., and Usmani, J. A. (2015) Lead toxicity: a review. *Interdisciplinary Toxicology*, **8**:55-64.

WHO. (2011) Guidelines for drinking-water quality 4th Ed. Geneva, World Health Organization, Geneva. ISBN 978 92 4 154815 1. apps.who.int/iris/bitstream/10665/44584/1/9789241548151_eng.pdf Accessed 21 Aug 2019.

Zdrojewicz, Z., Popowicz, E., and Winiarski, J. (2016) Nickel-role in human organism. *Polish Medical Journal*, **41**:115-8.