Physical and Chemical Characteristics of Five Hot Springs in Eritrea

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Abstract
Eritrea has a number of hot springs whose physicochemical characteristics are not documented. This study examined the thermal and chemical features of five hot springs located in the eastern escarpment of Eritrea. Field data and water samples were collected from five hot springs namely; Akwar and Maiwooi near Gahtelai, Garbanabra and Gelti near Irafayle at the Gulf of Zula and Elegedi in Alid volcanic center. The water temperatures at source varied from 49.5°C to 100°C while pH levels ranged from 6.97 to 7.54. Elegedi had significantly higher temperature ($p < 0.05$) than the other four hot springs. Strong correlation was observed between electrical conductivity (EC), total dissolved solid (TDS), salinity, sodium, potassium, calcium and chloride ($R^2 > 0.9$) as well as between temperature and sulphate levels ($R^2 = 0.96$). Evident clustering was noted at $p < 0.05$, using Non-metric multidimensional scaling (NMDS), between the three locations of the hot springs. Akwar and Maiwooi, situated close to each other, clustered together, Garbanabra and Gelti, which were characterized by higher salinity levels, formed a separate cluster. Elegedi, characterized by high temperature (100°C), sulphate (979.7 mg/l) and NH_4^+ (196.33 mg/l) levels, clustered separately. Akwar and Maiwooi had high bicarbonate (345 mg/l and 393 mg/l) and fluoride (8.20 mg/l and 6.48 mg/l) levels which are above WHO limits. Electrical conductivity (23,133 mS/cm), total dissolved solid (15,552 mg/l), sodium (3,800 mg/l), potassium (198 mg/l), calcium (1,653 mg/l) and chloride (5,946 mg/l) levels in Garbanabra and Gelti hot springs exceeded WHO limits. Bromine (74.8 mg/l in Garbanabra and 45.2 mg/l in Gelti) and boron (2.21 mg/l in Garbanabra and 1.55 mg/l in Gelti) levels were also above standard limits set for potable water. Maiwooi (1.20) and Elegedi (1.10) were depositional while Akwar water (-0.71) was slightly corrosive. The corrosive nature of the water sample from Akwar, is a public health concern. The waters from the five Eritrean hot springs are thus not fit for human consumption. In addition, the use of thermal spring water for recreational purposes should be closely monitored.

Keywords: key words, hot springs, physicochemical, Eritrea

1. Introduction

In the past few decades, there has been an unprecedented resurgence of interest in thermal springs due to diversification in their utilization. Thermal spring waters are increasingly being used for industrial processing, agriculture, aquaculture, bottled water and the extraction of rare elements (Shevenell *et al.*, 2002). Hot spring waters are suitable for medical purposes especially for skin therapy owing to the presence of sulphur and sulphate ions (Lund, 1996). The mineral composition of the thermal waters reflects the geological formations found at the site and possibly the depth of its origin (Olivier *et al.*, 2008). The physical and chemical attributes of water can be used in the classification and assessment of water quality in determining its use for irrigation, agriculture, drinking and industrial purposes (Lakshmi *et al.*, 2016).

Physicochemical analysis of water from hot springs from different parts of the world has been widely reported. In India, assessment of water quality has been conducted in several hot springs including the terrestrial thermal spring of Atri in Khurda District (Dash *et al.*, 2013), Vashisht in Manali region of Kullu District (Naresh *et al.*, 2013), Markanday region of Hamirpur District in Himachal Pradesh (Kumar and Surinder, 2013) and Tatapani in the Kalakote region of Rajouri District (Vardhan *et al.*, 2015). The biological and physicochemical properties of spring waters of Mahapelessa in Sri Lanka have been documented (Rajapaksha *et al.*, 2014). Thermal and chemical features of eight thermal springs located in the northern part of the Limpopo Province, South Africa were studied in order to establish their optimal use (Olivier *et al.*, 2011). The physicochemical properties of water from seven Ethiopian hyperthermal springs were analyzed and the pH, turbidity, chlorine, sulphate, nitrate, nitrite and ammonia were within the range stipulated for drinking water by WHO. However, the bicarbonate and sodium ions including conductivity in the Ethiopian springs were high (Haki and Gezmu, 2012).

In Eritrea, there are considerable low temperature-thermal springs that have potential for recreation, health and mineral water bottling. They occur at along the Asmara-Massawa highway, close to Gulf of Zula and within the Danakil Depression (Abraha, 2005). International and domestic standard hot spring recreational resorts are available at Akwar and Maiwooi, respectively. Other hot springs require further investigation to determine whether they are suitable for recreational development. Spring water is believed to heal various ailments, but the suitability of the water for drinking is unknown. Physicochemical analysis of waters from hot springs in Eritrea has been reported previously to evaluate the geothermal potential of Alid volcanic center. Groundwater samples in the surrounding lowlands and adjacent highlands were taken to determine regional stable isotope and chemical variations that might provide clues to sources of recharge for the Alid hydrothermal system (Clynne *et al.*, 1996). The present study, therefore, determined the water quality of five Eritrean hot springs in terms of physicochemical characteristics.

2. Materials and Methods

2.1 Study Site

Samples analyzed in this study were collected from five hot springs in Eritrea (Figure 1).

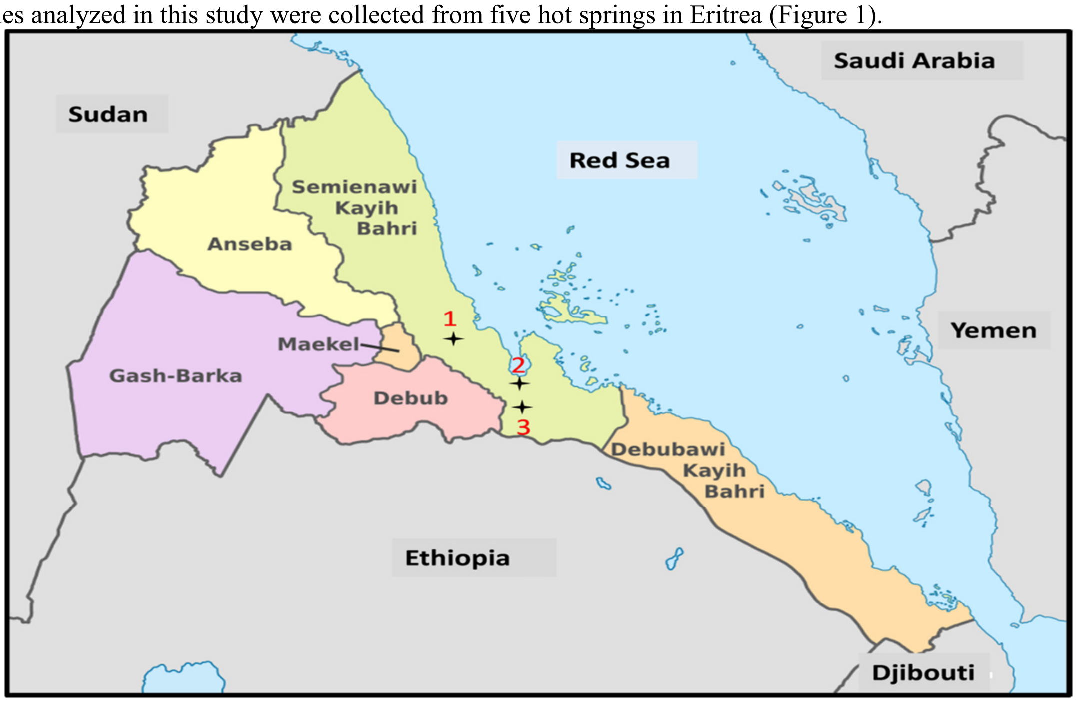

Figure 1. The location of five hot springs in Eritrea. Maiwooi and Akwar from Location 1 (Gahtelai area), Garbanabra and Gelti from Location 2 (Irafayle) and Elegedi from Location 3 (Alid area).

Two hot springs; Maiwooi (15° 32′ 53″N 39° 06′ 38″ E) and Akwar (15° 33′ 34″N 39° 05′ 37″ E) are located near Gahtelai at elevations of 330.1 and 344.5 m. Two other hot springs Garbanabra (15° 03′ 38″N 39° 46′ 27″ E) and Gelti (15° 03′ 39″N 39° 46′ 46″ E) are near Irafayle in the shore of Gulf of Zula at sea level. The fifth hot spring; Elegedi (14° 52′ 55″N 39° 55′ 37″ E) is located in Alid volcanic center at elevation of 512.7 m. From each hot spring, triplicate samples of 1000 ml water samples were taken for chemical analysis and stored at 4ºC until analysed.

2.2 Measurement of Physicochemical Parameters

The geographical position of each site including latitude, longitude and elevation was recorded using Global Positioning System (Garmin eTrex 10). Water temperature and salinity of the hot springs were recorded using a digital thermometer (Oregon Scientific) and an optical refractometer (E-Line ATC). The pH, electrical conductivity and total dissolved solids for each hot spring was measured with a portable pH-meter (HI 98185, Hanna Instruments) and confirmed using indicator strips (Merck, range 5–10) during sampling. Analyses of phosphate, potassium, calcium, magnesium, sulphate, sodium, iron, manganese, copper, boron and zinc were conducted at the Crop Nutrition Laboratory Services Ltd (Cropnuts, Nairobi, Kenya).

2.3 Statistical Analysis

Pearson Correlation Coefficient, principal component analysis, non-metric dimensional scaling (NMDS) and Piper diagram were used to analyse and determine relationships among the various physicochemical parameters and the hot springs using R programming language (Team, 2012). The corrosion and scaling potential of water were calculated by Langelier saturation index (LSI) (Langelier, 1936).

3. Results

Physicochemical parameters varied considerably among the three locations; Gahtelai, Irafayle and Alid. Water temperature was the highest at Elegedi (100°C), a boiling hot spring in Alid. The pH values of all water samples were within the range of 7.02–7.54 (Table 1).

Table 1. The mean values of the physicochemical parameters of the water sample from five hot springs in Eritrea

Parameter	Akwar	Elegedi	Garbanabra	Gelti	Maiwooi	WHO standards*
EC (mS/cm)	9060±116	2203±122	23133±696	15717±148	1317±117	No guideline
TDS (mg/l)	628±26	1546±58	15552±585	9290±336	543±38	500
Temperature (°C)	49.2±0.9	99.6±0.9	51.3±0.6	52.6±1.4	51.4±0.5	No guideline
pH (actual)	7.22±0.0	7.44±0.0	7.30±0.0	7.00±0.0	8.05±0.0	No guideline
pH_s	7.9±0.0	6.40±0.0	7.3±0.0	7.4±0.0	7.00±0.0	No guideline
SiO2 (mg/l)	100.3±1.5	97.4±0.9	121.7±1.8	112±2.1	76.0±3.1	No guideline
Na^+ (mg/ L)	188±7	12±1	3800±101	2378±229	227.0±10	200
K^+ (mg/ L)	104±3	12±2	198±7	119±3	13±2	50
Ca^{+2} (mg/ L)	19±2	157±8	1653±87	943±13	52±4	75
Mg^{+2} (mg/ L)	0.5±0.2	39.0±3.1	151.0±15.9	89.0±3.1	5.6±1.1	30
NH_4^+ (mg/ L)	0.11±0.01	196.33±7.36	0.03±0.01	0.06±0.01	0.03±0.00	No guideline
NO_3^- (mg/ L)	1.60±1.26	0.01±0.00	54.83±1.20	56.33±1.01	0.19±0.05	50
Fe (mg/ L)	0.00±0.00	0.83±0.15	0.00±0.00	0.00±0.00	0.10±0.01	0.3
Mn (mg/ L)	0.01±0.00	3.24±0.31	0.09±0.00	0.00±0.00	0.10±0.00	0.5
As (mg/ L)	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.01
Cl^- (mg/ L)	17.3±1.7	0.84±	5946.0±33.8	5183.7±28.9	71.3±2.2	250
SO_4^{-2} (mg/ L)	44.0±3.5	979.7±75.5	272.7±12.7	220.3±7.5	75.3±1.2	500
CO_3^{-2} (mg/ L)	22.3±0.3	21.3±0.3	28.7±1.5	23.0±0.2	20.3±0.4	90.2
HCO_3^- (mg/ L)	341.0±9.5	174.7±6.3	27.7±0.7	29.3±1.8	394.3±9.8	90.2
F^- (mg/ L)	8.20±1.30	1.18±0.20	2.87±0.40	2.87±0.70	6.48±1.10	1.5
B (mg/ L)	0.33±0.02	0.02±0.00	2.21±0.13	1.55±0.07	0.25±0.03	1.00
Br^- (mg/ L)	0.90±0.01	0.00±0.00	74.8±6.76	45.2±2.21	0.38±0.04	0.01

* Water quality standards provided by the WHO (World Health Organisation, 2011) for drinking water.

According to Langelier saturation index, water samples from Maiwooi (1.20) and Elegedi (1.10) were depositional while Akwar water (-0.71) was slightly corrosive. Water samples from Garbanabra (-0.02) and Gelti (-0.36) were neither depositional nor corrosive. Garbanabra and Gelti (both from Irafayle) registered significantly higher levels ($p < 0.05$) of electrical conductivity (EC), total dissolved solids (TDS), salinity, sodium, potassium, calcium, magnesium, chloride (Cl^-) and carbonates (CO_3^{-2}) levels. Significantly higher levels ($p < 0.05$) of bicarbonates (HCO_3^-) were detected in Akwar and Maiwooi and were characterized by having relatively high bicarbonate (341 and 394 mg/l, respectively) and fluoride (8.20 and 6.5 mg/l, respectively) levels above the WHO limit (Table 1). Sulphate, ammonium and manganese levels were significantly higher in Elegedi ($p < 0.05$). A principal component biplot of the hot springs and physicochemical parameters showed evident clustering between the three locations of the hot springs (Figure 2).

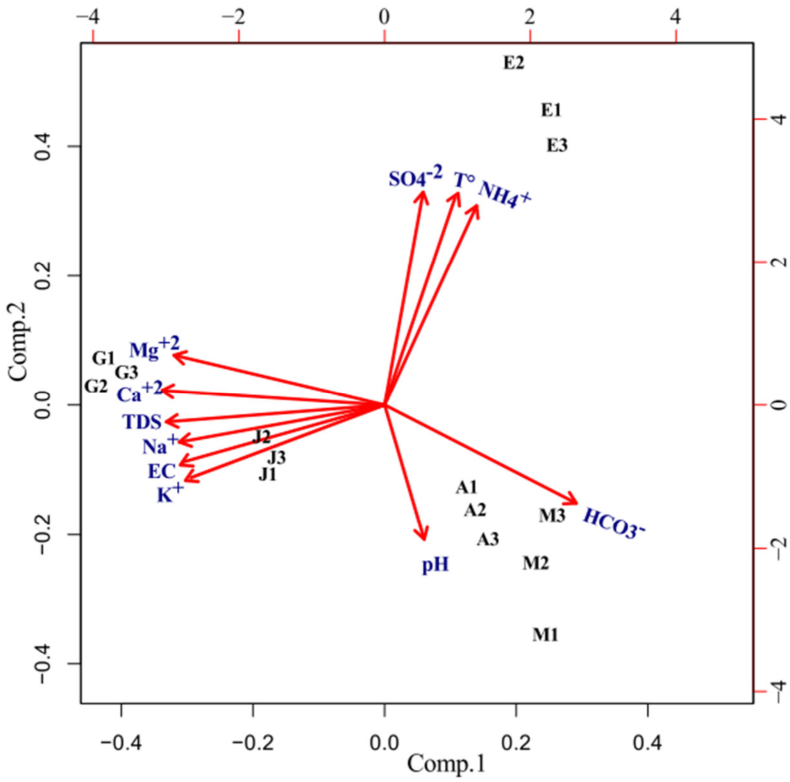

Figure 2. Principal component analysis biplot of environmental variables of the water samples. Letters refer to the five hot springs (A = Akwar, E = Elegedi, G= Garbanabra, J = Gelti and M = Maiwooi), while numbers are for the sampling stations for each hot spring.

The EC, TDS, sodium, potassium, calcium, magnesium, chlorides and carbonates showed similar patterns. These physicochemical parameters were significantly higher ($p < 0.05$) in the two hot springs from Irafayle; Garbanabra and Gelti. The variable bicarbonate concentration showed high correlation ($r = 0.9$, $p < 0.05$) with those hot springs located in Gahtelai. Temperature, ammonium and sulphate levels, which had similar response patterns, correlated ($r = 0.98$, $p < 0.05$) strongly with the boiling hot spring.

Pearson correlation was performed between the physicochemical parameters of water samples from the hot springs (Table 2). Strong correlation was observed between electrical conductivity, total dissolved solid (TDS), salinity, sodium, potassium, calcium and chloride ($R^2 > 0.9$). Temperature and sulphate levels also showed strong correlation ($R^2 = 0.96$).

Table 1. Pearson correlation between the physical parameters of the five hot springs in Eritrea

	EC	TDS	S (‰)	pH	T (°C)	Na	K	Ca	Mg	SO_4^{-2}	CO_3^{-2}	HCO_3^-	Cl^-
EC	1												
TDS	**0.93**	1											
S(‰)	**0.92**	**0.92**	1										
pH	-0.24	-0.14	-0.09	1									
T (°C)	-0.46	-0.30	-0.41	-0.34	1								
Na	**0.94**	**0.99**	**0.95**	-0.08	-0.40	1							
K	**0.96**	0.86	0.85	-0.27	-0.55	0.87	1						
Ca	**0.92**	**0.99**	**0.93**	-0.14	-0.28	**0.99**	0.85	1					
Mg	0.88	**0.95**	0.88	-0.18	-0.12	**0.94**	0.76	**0.95**	1				
SO_4^{-2}	-0.27	-0.08	-0.22	-0.39	**0.96**	-0.19	-0.37	-0.06	0.09	1			
CO_3^{-2}	0.85	0.88	0.74	-0.34	-0.30	0.85	0.88	0.89	0.78	-0.08	1		
HCO_3^-	-0.76	-0.85	-0.86	0.32	-0.09	-0.81	-0.64	-0.85	-0.89	-0.30	-0.66	1	
Cl^-	**0.91**	**0.96**	**0.99**	-0.07	-0.38	**0.97**	0.83	**0.96**	**0.92**	-0.17	0.77	-0.87	1

R^2 values above 0.9 are in bold and represent strong correlation between the parameters

A non-metric dimensional scaling (NMDS) analysis was performed to test differences among the five hot springs or the three locations. Evident clustering based on location of the hot springs was observed ($p < 0.05$), implying that the physicochemical parameters between the three locations are different (Figure 3). Akwar and Maiwooi, situated close to each other, clustered together while Garbanabra and Gelti, which are characterized by higher salinity levels, due to influx of seawater from the nearby seashore, were grouped together. Elegedi, characterized by high temperature and sulphate levels, clustered separately from the other hot springs.

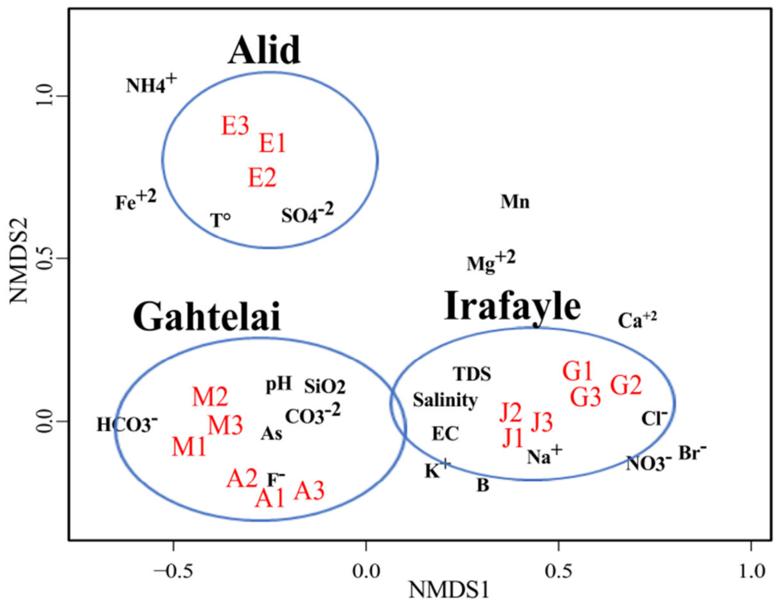

Figure 3. Non-metric multidimensional scaling (NMDS) based on Euclidean dissimilarities between the physicochemical parameters of the water samples. Letters refer to the five hot springs (A = Akwar, E = Elegedi, G= Garbanabra, J = Gelti and M = Maiwooi), while numbers are for the sampling stations for each hot spring.

Water from Akwar and Maiwooi (from Gahtelai) had similar hydrochemical characteristics in terms of composition of major ions (Figure 4). Waters issuing from the thermal springs at Garbanabra and Gelti also seemed to share a common origin. The dominant anion in hot springs from Gahtelai was bicarbonate (HCO_3^-). Chloride was the dominant anion in the water samples of the two saline hot springs whereas samples from Elegedi were dominated by sulphate. Sodium was the dominant cation in water samples from Gahtelai and Irafayle, while in Elegedi calcium was observed to be the dominant cation.

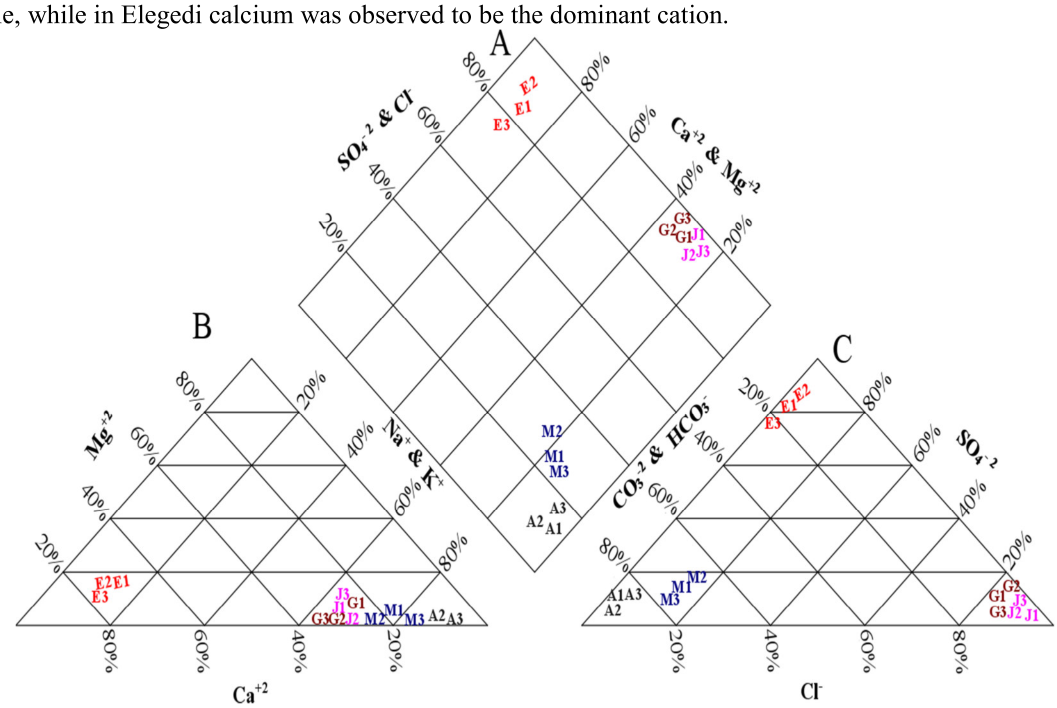

Figure 4. Piper diagram of the physicochemical parameters of the water samples from the five hot spring in Eritrea. Field A shows the compositon of major ions. The sample cation and anion concentrations are represented by the two base triangles B and C, respectively. Letters refer to the five hot springs (A = Akwar, E = Elegedi, G= Garbanabra, J = Gelti and M = Maiwooi), while numbers are for the triplicate samples from each hot spring

4. Discussion

Five hot springs in Eritrea were selected based on distinct characteristics such as temperature, salinity and location. The concentrations of major ions (sodium, potassium, calcium, magnesium, chloride and sulphate) in the five hot springs were fairly similar with the previous investigation conducted about 20 years before (Clynne *et al.*, 1996). In South Africa, concentrations of the major ions of the thermal springs remained remarkably consistent over 50 to 60 years (Olivier *et al.*, 2008).

The physicochemical parameters of the water samples were shown to cluster according to the location of the hot springs. Maiwooi and Akwar, located at the main eastern escarpment in Gahtelai along the Asmara-Massawa highway, were shown to register higher levels of bicarbonates. These hot springs, made up of precambrian rocks, were previously characterized as low energy hot springs which discharge near-neutral bicarbonate waters with low chemical content (Yohannes, 2010). The high concentration of bicarbonates and nearly neutral pH could be attributed to the mixing of volcanic CO_2 gas, instead of SO_2, with water (Homma and Tsukahara, 2008). Gelti and Garbanabra are located on the seashore in the Red Sea near the Gulf of Zula. Salinity of these hot springs is much higher than Maiwooi and Akwar due to mixing with the sea water. The physicochemical attributes of water samples between these two hot springs, located near Irafayle, were shown to be more similar than other hot springs. Electrical conductivity, total dissolve solids, salinity, sodium, potassium, calcium and chloride levels were much higher in these hot springs exceeding the maximum tolerable limits determined for drinking water (World Health Organisation, 2011). Chloride may be present naturally in groundwater and may also originate from diverse sources such as weathering, leaching of sedimentary rocks and infiltration of seawater (Vardhan *et al.*, 2015). Bromine and boron levels in these hot springs were also above the WHO limits set for drinking water.

Strong correlation was observed between electrical conductivity and total dissolved solid (TDS), salinity with $R^2 = 0.92$, sodium, potassium, calcium and chloride. TDS is a measure of the amount of material dissolved in water. Usually solids can be found in nature in a dissolved form then break into positively and negatively charged ions. The presence of these dissolved solids directly increases the value of salinity and conductivity as salinity is a measure of the amount of salts in the water and conductivity is the ability of water to conduct an electrical current with dissolved ions as conductors (Dahaan *et al.*, 2016).

Elegedi is located about 30 km South of the Gulf of Zula and is associated with a high temperature geothermal system underlying the Alid volcanic center in the Northern Danakil depression of Eritrea (Yohannes, 2010). The bubbling water discharged from this hot spring is typical of the fumarolic steam condensate with high temperatures (Clynne *et al.*, 1996). Water samples from Elegedi were relatively rich in dissolved sulphate (979.7 mg/l) and ammonium (196.3 mg/l). Waters rich in ammonium are generally found where steam separates at high temperature from boiling water in sedimentary rocks and the ammonium ion appears to be generated from the high-temperature distillation of organic material (Clynne *et al.*, 1996). Elegedi was the only hot spring with high sulphate levels (949 mg/l) surpassing the acceptable WHO limit. The sulphate ion can cause diarrhea at elevated concentrations (Kempster *et al.*, 1997). The sulphate ion could originate from the weathering of pyrite or the leaching of other sulphide (S_2) by hypothermal waters of deep origin (Drogue *et al.*, 2000). There is a special interest in sulphur-rich hot spring water because of its dermatological effects. Sulphur-compounds are able to penetrate the skin and sulphur-rich balneotherapy is known to be effective in the treatment of psoriasis and T-cell-mediated autoimmune diseases of the skin (Carubbi *et al.*, 2013). In the deeper layers of the epidermis, sulphur interacts with oxygen radicals, producing sulphur and hydrogen disulphide, which may subsequently be transformed into pentathionic acid, which could be responsible for the antibacterial and antifungal activity of sulphur water (Matz *et al.*, 2003).

The water sample from Akwar was slightly corrosive. Corrosive water tends to dissolve minerals which could be deleterious as it dissolves toxic metals such as lead and copper from plumbing utilities. Corrosion control is an important aspect of safe drinking water supplies. Water corrosion which may not be evident without monitoring is an important issue concerning both public health and economical aspects (Hoseinzadeh *et al.*, 2013).

5. Conclusion

The present study expands the knowledge on the physical and chemical characteristics of five hot springs; Akwar, Maiwooi, Garbanabra, Gelti and Elegedi in Eritrea. It provides current information on the physical and chemical characteristics of five hot springs located in the Eastern escarpment of Eritrea. The mineral composition of the thermal waters probably reflects the surface geology, since adjacent springs (Maiwooi and Akwar as well as Garbanabra and Elegedi) had similar physicochemical properties.

Waters from the hot springs investigated in the present study cannot generally be regarded as "pure". Unacceptably high levels of fluoride are present in Akwar and Maiwooi. Bromine and boron levels in Garbanabra and Elegedi were also above the WHO limits set for human consumption. The water quality of Elegedi seems better, though it had sulphate levels above the acceptable level. The waters from the five Eritrean hot springs are thus not fit for human consumption. In addition, the use of thermal spring water for recreational purposes should be closely monitored. It is thus important that the physical and chemical composition of thermal springs be monitored on a regular basis.

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