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HYDROCHEMICAL STUDY OF HOT SPRINGS OF KASWA IN MAHAGI TERRITORY (ITURI, DEMOCRATIC REPUBLIC OF CONGO)

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ABSTRACT

The waters of six hot springs at Kaswa in the Mahagi territory, in the province of Ituri, northeastern Democratic Republic of the Congo were analyzed in order to evaluate its physicochemical characteristics and detect substances with a therapeutic virtue contained therein. Sampling was done in four different campaigns from 2014 to 2017. Analyzes were performed using multiparameter probes (HANNA HI 83200, Water Proof PCST Tespr-35, Palintest, photometer 5000) and volumetry methods. The results showed that these waters are generally mesothermal or hyperthermal (temperature: 41.2±0.23 - 61±0.2°C), acid or neutral (pH: 6.48±0.03 - 7.25±0.01), soft that can harden in certain periods (THT: 23.96±1.3 - 285.5±0.5 mg/L of $CaCO_3$); its mineralization being important (EC: 885.7±0.2-1342.2±1.3µS/cm). These waters are sulphurous (total sulfur: 25.2±0.5-96.0±0.5 mg/L), with significant presence of H_2S. The analysis of major ions by the hydrochemical method (Schöeller Berkaloff diagram) reveals that the concentration of sulfates is high, followed by chlorides, calcium and magnesium. The valorization of these sources is essential for the benefit of the population.

KEYWORDS: Kaswa, Mahagi, hydrochemical, hot springs.

1. INTRODUCTION

From the first age of humanity, hot springs have been sought by people in the treatment of various pathologies. This old medicine dates back more than 2000 years and to this day it knows a new boom in a will of return to the sources (Sanders, 2006).

Many researchers around the world have studied the characteristics of hot springs. These waters are also discovered in some parts of the African continent but are not sufficiently valued. They can be of deep or superficial origin (Fekraoui, 2007) and are first classified according to the existence in their composition of a "remarkable" anion either by its concentration or by its chemical nature (Jaltel, 1984).

In the Democratic Republic of Congo, the presence of hot springs is reported in several provinces, most of which are in the eastern part of the country, crossed by the Rift valley in its western branch and attract thousands of visitors in search of hot baths. The obvious geothermal potential consists of geothermal sites and active volcanoes, but it is almost untapped (Kasemuana, 2009, Bagalwa et al., 2015, UNDP, 2016).

In the Ituri Province, in the Mokambo Chiefdom (Mahagi territory), the hot springs were first discovered in 1926 by the Belgian explorers (Messen, 1951). These waters spring from the mountain range of “*Mont Bleu*” and pour into Lake Albert at the Fishermen's Camp named "Kaswa" in the Ramogi entity. Kaswa is located at 2° 0'46.678 North and 31° 04'57.829 East at 735 m of altitude. It is bounded on the east by Lake Albert and on the west by the “*Mont Bleu*” mountains and the East Rift valley region of the Democratic Republic of Congo forming the Nile basin. The average temperature of the region varies between 25-30 °C. The Blue Mountains, is a real watershed of the Nile and Congo, the hydrographic networks of the eastern slopes of these Blue Mountains belong to the Nile river basin and those of the western slope are part of the Congo River basin. This country enjoys a humid tropical climate, with two distinct seasons: the dry season and the wet season (Messen, 1951).

The natives riparian give to these waters a virtue of curing many diseases. Being directly accessible and without cost, these hot waters have been used for a long time by this population to treat their various dermatological conditions. In addition to the curiosity of many people they attract, these springs are a place of pilgrimage for a local religious group through ancestral worship, granting divine power.

The study of the characteristics of thermo-mineral waters is often intended to specify the potential variations of their quality and their origins or to present their location. Their contamination may also be caused by meteoric waters, the pollution of which is often considered as the result of an important anthropogenic activity (Tardy, 1980, Djorfi, 1988, Chevalier-Lemire et al., 1990). Actually the hydrochemical quality of these hot springs of Kaswa remains unknown to users due to a lack of available data because no such study has been done on these waters. In the hypothesis that these waters could have therapeutic virtues, what are then the physico-chemical characteristics of the thermal waters of Kaswa? What are the chemical substances contained therein capable of conferring on them the said therapeutic properties? The present hydrochemical study made it possible to highlight these characteristics, which will allow enlightening the population on the hydrochemical quality of the water which it uses.

2. MATERIALS AND METHODS

The geographic location of the different hot springs studied (Figure 1) were taken from the GPS device, GARMIN "eTrex®10", 2.2 "monochrome screen feature, high sensitivity WAAS compatible GPS receiver with Hot Fix® and GLONASS technologies.

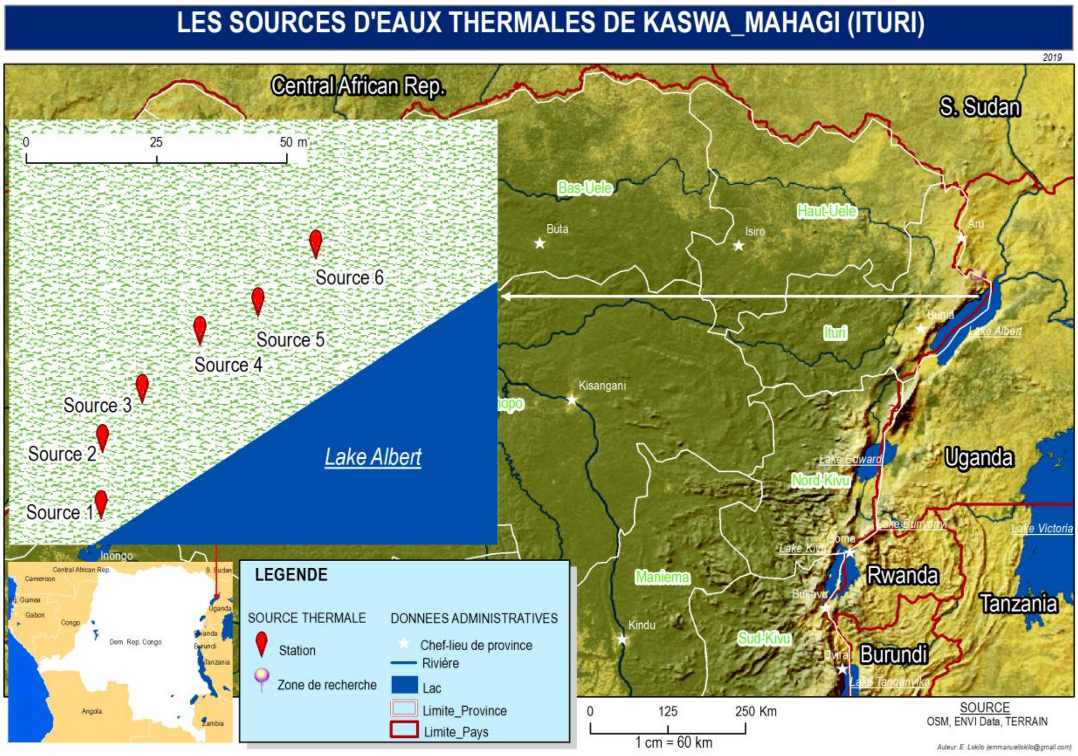

Figure 1: Sampling site for Kaswa-Mahagi thermal water samples (Ituri, DR Congo).

Legend: Source 1 = Kaswa α (Kα), Source 2 = Kaswa β (Kβ), Source 3 = Kaswa γ (Kγ), Source 4 = Kaswa δ (Kδ), Source 5 = Kaswa ε (Kε), Source 6 = Kaswa λ (Kλ)

Five water samples were collected and analysed for each source, in five-day steps, between 6:00 am and 12:45 pm and per campaign. The study was conducted from 2014 to 2017, in four different campaigns.

The samples were collected manually (instant sample), in polyethylene bottles, at the point of emergence. Sampling equipment was carefully cleaned and rinsed with distilled water, then inside three times and then with water analysed (Degremont, 1989 and Rodier et al. 2009). The started study focuses on the organoleptic analysis. This give place to the determination of 14 physicochemical characteristics of the waters of six hot springs.

In addition to the measurements in situ (temperature, pH and electrical conductivity (EC)), the other analyses were carried out in the laboratory within 6 to 48 hours after sampling, using Multi Parameter Probes and titrations. The parameters, materials and methods used are presented as Table 1.

Table 1: Parameters, materials and methods used for the hydrochemical study.

Parameters	**Packaging** Standards NF EN ISO 5667-3 (June 2004), (RODIER, 2009)	**Materials and methods**
T°, pH et EC	In situ	Water Proof PCST Tespr-35 Multi Parameter Probe
Alkalimetric Complete Title (ACT, HCO_3^-	4°C	Palintest, photometer 5000, reagent V40326 and V40327.
Oxydability	4°C, H_2SO_4 (pH<2)	Titration by the KMnO4 method - sulfuric acid (Rodier et al., 2009).
Hydrotimetric Title (THT)	4°C, HNO_3 (pH<2)	Titration by EDTA (Rodier et al., 2009).
Ca^{2+}	4°C, HNO_3 (pH<2)	Titration by EDTA (Rodier et al., 2009).
Mg^{2+}	4°C, HNO_3 (pH<2)	HANNA HI 83200 photometer, HI 937520-01 reagent (calmagite method, EGTA)
SO_4^{2-}	4°C	Gravimetry (Rodier et al., 2009).
NO_3^-,	4°C, H Cl (pH<2)	HANNA HI 83200 photometer, HI 93728-01 (cadmium reduction)
Cl^-	4°C	Mohr's method (Rodier et al., 2009)
PO_4^{3-}	4°C, H_2SO_4 (pH<2)	HANNA HI 83200 photometer, reagents HI 93713-01 (ascorbic acid).
Total sulphur (H_2S, S^{2-}, thiosulfates)	4°C, zinc acetate, pH 12 + sodium hydroxide	Titration by iodine N/10; after sulphate and carbonate precipitation of sulphurous water by saturated solution of $BaCl_2$ (Rodier et al., 2009).

Calibration was done in advance at the laboratory. Three tests were made per sample for each parameter and the average results with the respective standard deviations are transcribed in the table of the results. The hydrochemicalanalysis of data has been done by means ofaSchöellerBerkaloffdiagram and statisticsmethods, namely the study of means, standard deviations, coefficient of variation, student t test and analysis of variance (ANOVA), using the statistical software "PAST".

3. RESULTS AND DISCUSSION

3.1. Physical characteristics measured "in situ"

Temperature

Temperature is the most important factor to consider in this study because it accounts for almost all physical, chemical and biological responses in the aquatic environment. These hot springs at the emergence point show the temperature between 41.2±0.23 °C observed at the Kλ site in 2015 and 61±0.2 °C recorded at the Kδ site in 2014. Kaswa γ is essentially mesothermal, its average temperature varying between 41.2±0.23 °C and 44.2±0.36 °C. The five other sources are hyperthermal (46.4±0.07 - 61±0.2 °C) considering the classification suggested by Castany (1967). This temperature increases significantly with depth (Criaud and Vuataz, 1984).

These temperatures are close to the majority of the thermal waters of the Katana region in South Kivu (DRC) studied by Bagalwa et al. (2015) although some of them reach a temperature of 70°C. They are also close to the majority of thermal waters of Vernet-les-Bains in the eastern Pyrenees whose temperature varies between 40-60 and Sulfuric sodic waters of Luchon in the Pyrenees studied by Criaud and Vuataz (1984). The thermal waters of Kaswa, however, are warmer than those of the South Setian-East Algeria whose temperature, according to Boudoukha and Athanema (2012) oscillates between 25.1 and 43.1°C.

According to Louvier (1971), temperature does not have a therapeutic role in itself, but it is possible that a high temperature accelerates the beneficial action of certain compounds of the water on the deficient biological functions of the patient. The hot spring of Kaswa in Mahagi have a set of characteristics that are likely to provide health-enhancing properties and are therefore classified as medicinal waters (Jaltel 1984, Thomas 1995, Houti et al 2015).

According to Ouali et al. (2007), when the temperature of the water is lower than 100°C, the water is of low enthalpy. Thus, these geothermal resources can be used in the heating of the houses but also for the production of the electricity with binary cycle, this is the case of the use thermal waters of the Cheffia mountains in extreme northeastern Algeria studied by Alayat and Lamouroux (2007) and Zelfana's thermal water. In fact, the thermal energy of the geothermal fluid is converted into mechanical energy, and then into electrical energy by using a generator (Ouali et al., 2007). The energy obtained is then a clean energy.

Temperature variation study

The variation of temperature during the study period is presented as Figure 2.

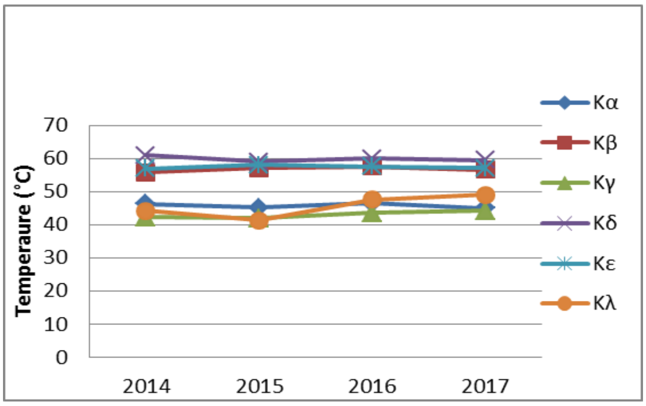

Figure 2: Temperature of Kaswa's thermal waters.

$$\text{Coefficient of variation, CV (\%)} = \frac{\text{Standard deviation}}{\text{Average}}\ x\ 100$$

The coefficient of variation between 0.96 % at Kε and 7.48% at Kλ shows a low dispersion around the mean temperature. According to D'hainaut (1975), if the coefficient of variation is less than 15%, the distribution is homogeneous, reflecting a low dispersion. From this, it is deduced that the temperatures of these waters practically varied at the same level during the period considered.

Temperature comparison

The comparison of temperature is represented as Table 2.

Table 2: Temperature comparison of Kaswa's hot spring using ANOVA (Analysis of Variance) Test.

	Sum of squares	df	Average of squares	F_{calc}	$F_{th.05}$	$p_{(same)}$	SS
From one to another groups	1099.02	5	219.804	**85.01**	2.77	7.033E-12	**S**
Within groups	46.54	18	2.58556				
Total	1145.56	23					

Legend: df = degree of freedom; SS = statistical significance; S = significant

F_{calc} = F calculated; $F_{th.05}$ = theoretical F at significance level α = 5%;

P = probability

Analysis of variance shows a significant difference (F_{obs} = 85.01> $F_{th.05}$ = 2.77). This means that the temperature of these hot waters differs significantly from one spring to another. However the temperature averages compared in pairs by means of student's t test shows that the difference is not significant between the waters of Kβ and Kε hot spring (t_{obs} = 1.411); Kα and Kλ (t_{obs} = 0.126); Kγ and Kλ(tobs= 1.3553),, the observed values being lower than the theoretical value ($t_{th.05}$ = 3.1824, df = 3); their temperatures are therefore practically the same during the study period. The observed differences can be attributed to random fluctuations in sampling. The thermal waters of the other sources show different temperatures, the Kδ hot spring being the hottest (maximum 61 ±0.2 °C) compared to the others.

pH and electrical conductivity

The pH ranging from 6.48±0.03 recorded at the Kα site in 2016 to 7.25±0.01 at the Kδ in 2014 and Kα sites in 2017 shows that these waters have a slightly acid character and sometimes neutral. These pH values are close to those obtained by Bagalwa et al (2015) for thermal waters in the Katana region of South Kivu, where the pH varies between 6.5 and 8. In these waters, the pH can be influenced by calco-carbonic equilibrium.

The electrical conductivity varies between 885.7±0.2 µS/cm noted at Kα in 2014 and 1342.2±1.3 µS/cm at Kδ in January 2016. It is 2 to 5 times higher than that of sodium sulphide water from Luchon in the Pyrenees, where the electrical conductivity, according to Criaud and Vuataz (1984) varies between 160 and 524 µS/cm.

The variation of the pH and electrical conductivity are presented as Figure 3 and 4.

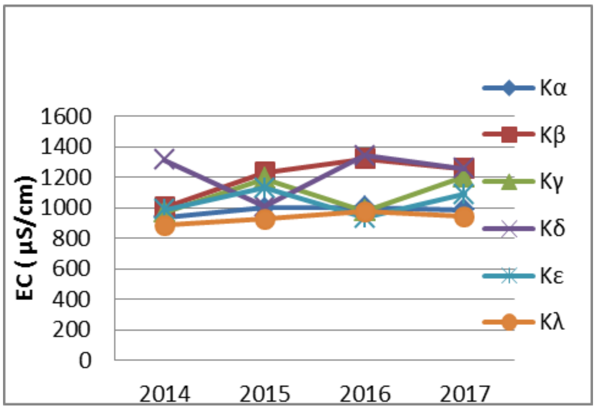

Figure 3: pH of Kaswa'' thermal waters.

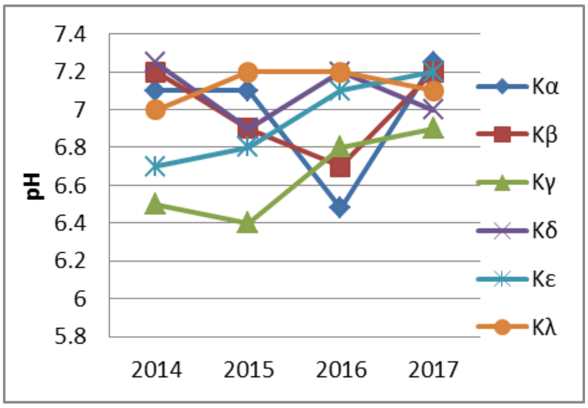

Figure 4: Electrical conductivity of Kaswa's thermal waters.

There is a close relationship between the total dissolved salt content (mineralization) and its conductivity (Martin et al, 1979, Rodier, 2009). Thus, high mineralization is recorded at Kβ, Kδ and Kε; the mineralization being important but sometimes high in certain periods for other springs. The electrical conductivity is directly related to the formations of the geological ground crossed, they can be little or strongly mineralized, depending on their course (Alayat and Lamouroux, 2007). During their transfer from the deep reservoirs to the surface, they undergo dilutions following mixtures in the liasic reservoir (Lakdar et al, 2007). The strong mineralization of the thermal waters of Kaswa is partly attributed to the nature of the terrain crossed during their journey.

3.2. Physicochemical characteristics of the thermal waters of Kaswa / Mahagi

3.2.1. Total sulfur

The total sulfur (hydrogen sulphide, sulphides and thiosulphates) ranging from 25.2±0.5 to 96±0.5 mg/L recorded at Kδ in 2016 and 2014 respectively show that these waters are sulphurous. The total sulfur concentration varies from one source to another and from one period to another. According to Boulegue (1979), the sulfur species are derived for some of the sulphates from meteoric waters and for the other, the leaching of pyrite (FeS_2) which supplies hydrogen sulphide (HS^-), sulphate (SO_4^{2-}) and traces of thiosulfates ($S_2O_3^{2-}$). Nevertheless the presence of basalts, a volcanic rock in the area suggests the presence of volcanoes in the depths and the possibility of an old eruption. The thermal waters of Kaswa are as sulphurous as those of Ax-les-Thermes (total sulfur content 31-34 mg/L) as well as those of Luchon in the Pyrenees whose concentration of total sulphides, according to Criaud and Vuataz (1984) can reach 60 mg/L.

3.2.2. Major Ions

The major ions in the thermal waters of Kaswa studied are nitrates, phosphates, sulphates, chlorides, calcium, magnesium and bicarbonates. They are represented by the Schöeller Berkaloff diagram (Figure 5, 6, 7 and 8).

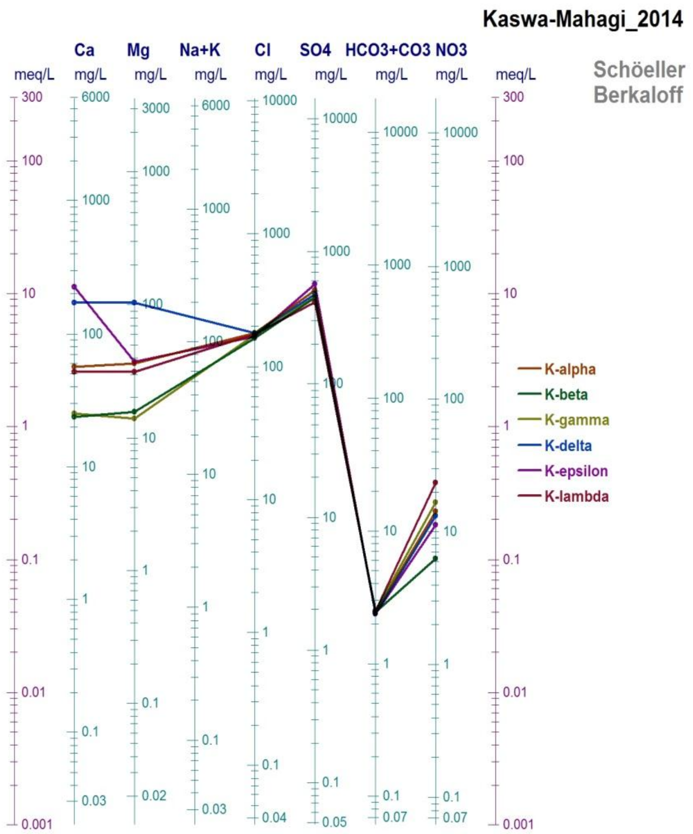

Figure 5: Schoeller-Berkaloff Diagram of Kaswa hot springs in 2014.

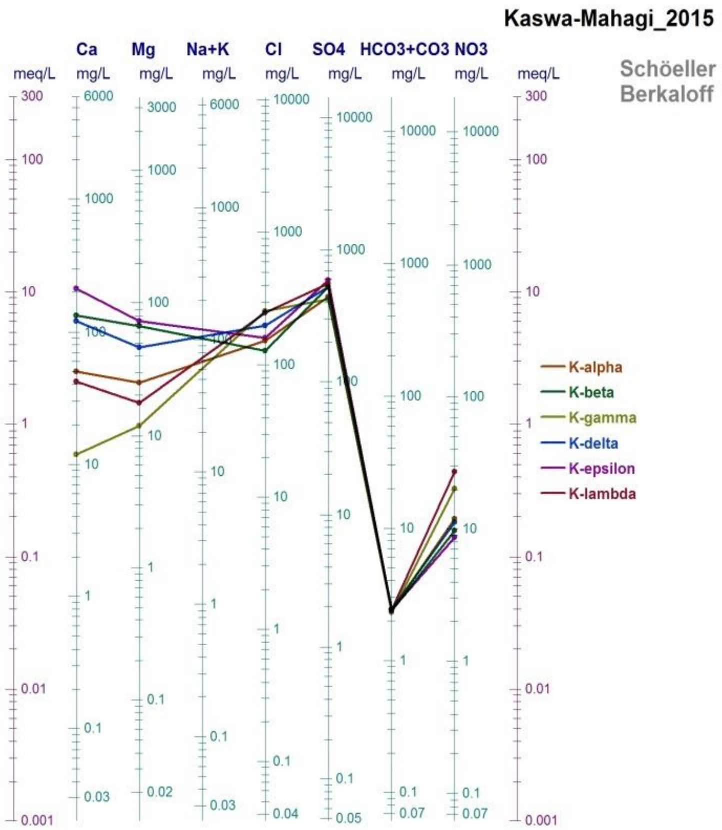

Figure 6: Schoeller-Berkaloff Diagram of Kaswa hot springs in 2015.

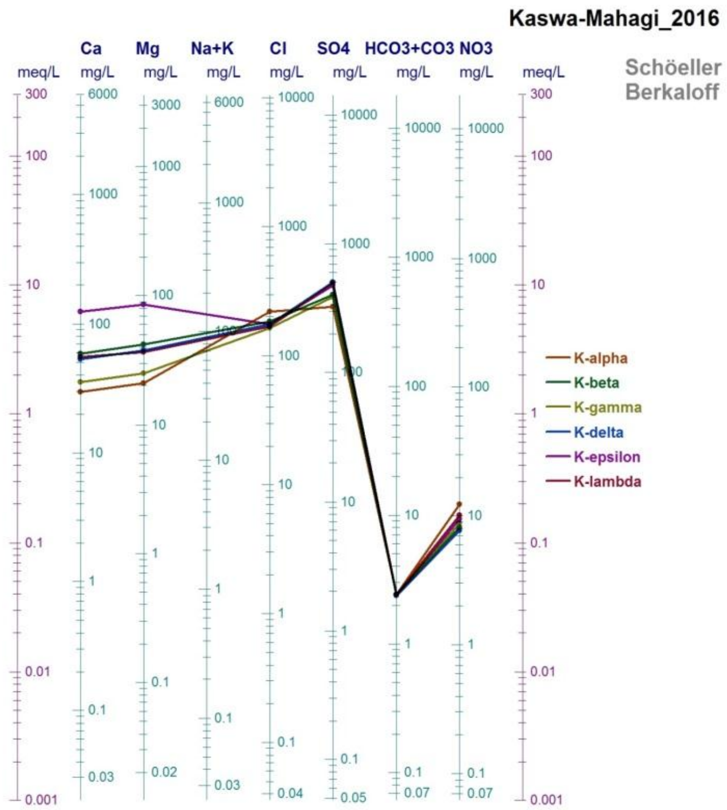

Figure 7: Schoeller-Berkaloff Diagram of Kaswa hot springs in 2016.

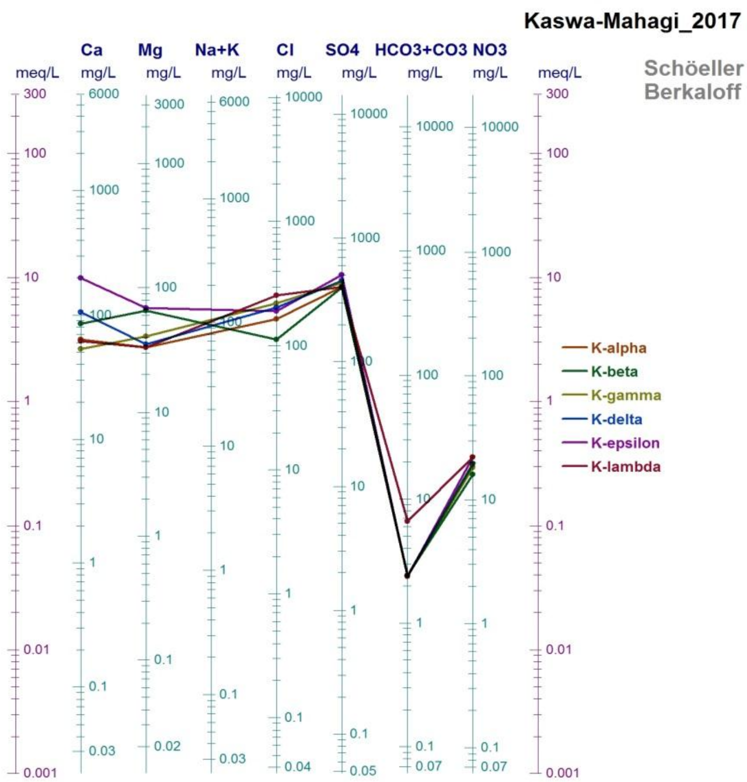

Figure 8: Schoeller-Berkaloff Diagram of Kaswa hot springs 2017.

The nitrate content is between 6.2±0.03 mg/L at the Kβ site in 2014 and 27.7±1.0 mg/L at the Kλ site in 2015. In groundwater, the concentration of NO_3^- generally ranges from 5 to 15 mg/L. However, the Kδ hot spring displays nitrate values above this margin in 2017. The PO_4^{3-} remains low. According to Bontoux (1983), the high nitrate content is characteristic of the degradation of organic compounds in progress and suspects pollution of organic origin. According to Bricha et al., (2007), groundwater, which is often geologically protected, is exposed to agricultural, industrial and / or urban pollution, which causes a change in their physicochemical composition. In the case of the thermal waters of Kaswa, the low pollution would be mainly due to agricultural activities around the hot spring and activities of natives or visitors in hot bathing.

The Schöeller Berkaloff diagram analysis shows that the sulphate content is high, varying from 324.44±0.9 and 589.4±0.6 mg /L, recorded respectively in the Kα site in 2016 and Kε in 2015. According to Tardat-Henri (1992), natural waters almost always contain sulphates in variable proportions, their presence resulting from the slight solubility of $CaSO_4$ in the gypsum rocks and the oxidation of the sulphides diffused in rocks like pyrite. The hot spring of Kaswa are also likely to be classified as sulphated waters.

In fact, sulphated waters heavily loaded with sulfur and also containing calcium and magnesium, may be involved in the treatment of dermatoses, eczema and after-effects of burns (Sanders, 2006). The thermal water of Kaswa should be used in the treatment of these diseases.

The minimum chloride (Cl^-) concentration is 112.1±0.7 mg/L recorded at the Kβ site in 2017 while the maximum concentration of 255.6±0.4 mg/L was noted at the Kγ site in 2015. Based on Tardat-Henri (1992), the waters of the sedimentary regions contain more chlorides. It is noted that the thermal waters of Kaswa are also charged with chlorides.

The concentration of the calcium ions varies between 11.9±0.7 mg/L at Kγ in 2015 and 224.7±0.7 mg/L at Kε in 2014. It varies from one hot spring to another and from one period to another. According to Bordat et al. (2000), the variation in Ca^{2+} concentration can be related to bicarbonate ions HCO_3^- but also to other anions present in the aquatic environment. Lakdar et al. (2007) have shown that hot spring waters with a high concentration of chloride, sulphate and calcium have undergone deep circulation through a calcaro-dolomitic crystalline basement affected by major tectonic activities.

The Mg^{2+} content is between 11.91±0.8 mg/L at Kγ in 2015 and 103.7±0.6 mg/L at Kδ in 2014. According to Tardat-Henri (1992), calcium can come from Gypsum ($CaSO_4.2H_2O$) and from igneous rocks, apatite ($Ca_5(PO_4)_3$(F, Cl, OH), fluorite (CaF_2), some feldspars, etc. Magnesium is also abundant in igneous rocks. Kaswa thermal springs originate or have crossed limestone areas or igneous rock areas. These rocks are much less attacked by natural waters, so it is not surprising that the Kaswa waters are relatively hard. The physicochemical characteristics of thermal water are related to its underground course, its depth and the mineral constitution of the rocks (Ezzaidi et al., 2006 cited by Ben Moussa et al., 2012). According to Vergini (1996), magnesium is beneficial because of its effects on muscle relaxation.

3.3. Other physicochemical parameters studied

The total hardness varies between 23.96±1.3 mg/L noted at the Kγ site and 285.5±0.5 mg/L of $CaCO_3$ at the Kε site in 2015. These thermal waters have a variable hardness. The waters emerging from the source Kε is hard throughout the study period, the other sources are spouting very mild or soft thermal waters. According to Bli-Effert and Perreau (2001), water can become more hardened with anthropogenic activities. Thus, the varying hardness of the thermal waters of Kaswa would be due in part to the nature of the rocks crossed as well as the bathing activities by the users.

Total complete alkalinity (TCA) remains low for all these sources. It varies between 2.32±0.00 mg/L recorded at the Kγ thermal spring in 2015 and 6.62±0.4 mg/L recorded at the Kλ source in 2017. The bicarbonate content is close to that of the complete alkalimetric titre considering the study period. These thermal waters are practically not bicarbonated or carbonated. The alkalinity of these waters is mainly attributed to the presence of bicarbonate ions (HCO_3^-) in very low concentration.

The oxidability at $KMnO_4$ shows a minimum value of 6.4±0.02 mg/L noted at the Kα site in 2017 while the maximum value of 14.2±0.15 mg/L was recorded at the Kλ site in 2015. The oxidability allows the estimation of the total organic pollution of water and the assessment of the effectiveness of oxidation treatments. Thus, an increase in the $KMnO_4$ oxidability may reveal the appearance of organic matter such as chemical pollution by nitrates for example. It should be noted that the thermal spring Kλ is polluted in 2015. For the most part, these thermal springs are free from organic pollution.

CONCLUSION

The aim of this work was to do the hydrochemichal study of the Kaswa hot spring waters and identify the elements capable to confer therapeutic power. The studied waters have different temperatures, mesothermal or hyperthermal. This property attracts the curiosity of locals and visitors looking for natural hot baths. They have all undergone significant mineralization, which explains their high electrical conductivity. They contain contain sulfur, sulphates and chlorides in important concentrations. This explains the use of this water by the indigenous population in order to relieve their dermatological, rheumatic and respiratory affections. Their composition in major mineral ions such as sulphates and chlorides, calcium and magnesium can also offer these waters the therapeutic power in the face of other pathologies. The presence of nitrogen compounds detected, in particular nitrates, indicates that these waters are exposed to pollution of external origin which can harm the health of the users. This study should stimulate researchers, specialized services as well as politico-administrative authorities to value the natural potential of the country for its development and management of hot spring in that region.

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