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Geochemical survey of the Nyamyumba and Bugarama hot springs in the western province of Rwanda

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RESEARCH ARTICLE

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ABSTRACT

The focus of the current study was to investigate the presence of selected trace metals (Pb, Cd, Mn, Ni, and Cu) and to determine the major cation and anion levels in Nyamyumba and Bugarama hot springs in the Western Province of Rwanda. The trace metals were determined using micro plasma atomic emission spectroscopy. The mean Cu concentrations in Nyamyumba and Bugarama were found to be 0.1 mg/L and were within the permissible limits of the World Health Organization (WHO) for potable water. Similarly, Mn concentrations were within acceptable WHO limits with mean concentrations being 0.04±0.02 and 0.11±0.03 mg/L in Nyamyumba and Bugarama, respectively. The lead concentration was found to be above the WHO limits with mean results of 0.01±0.001 and 0.013±0.01 mg/L in Nyamyumba and Bugarama, respectively. The mean concentration of cadmium was 0.01 mg/L in both sampling sites, which is observed to be above the allowed WHO limit. Nickel, on the other hand, was found to be below the detection limit. The fluoride concentration was determined using the SPADNS Ultra Violet Spectroscopic (UV-VIS) method and its mean levels were found to be 1.07±0.05 and 0.85±0.07 mg/L in Nyamyumba and Bugarama, correspondingly, which is within the acceptable limit of the WHO. Due to the potential pollution trends identified in this study, it is recommended that biosorption remediation techniques be applied for potable and therapeutic water usage to reduce the levels of Pb and Cd, which can have serious etiological risks to both flora and fauna due to possible trace metal bioaccumulation.

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1. Introduction

In the recent past, there has been an increase in feasibility studies and exploration activities to determine the viability and potential exploitation of geothermal resources in the northwest part of Rwanda. The results of various geophysical surveys have been quite promising and positive. This region is characterized by a host of active volcanoes and hot springs, making it a possible target for geothermal development [1,2]. Geothermal energy is a renewable energy resource that can be used as an alternative to rain-dependent hydropower, as well as to reduce overreliance on carbon-based fuels that are of concern to the environment. Geothermal energy has the ability to mitigate the effects of climate change while at the same time it can serve as a catalyst for rapid and sustainable development [3,4]. Geothermal water is suitable for multiple purposes depending on the various physical and chemical characteristics of the geothermal fluids. Its applications range from traditional therapeutic warm baths to modern use in agriculture, recreation, industry, and power production [5,6]. Since geothermal development is a capital-intensive project, collaboration among various stake holders is of primary importance in terms of carrying out feasibility studies, exploration, and exploitation to realize its full potential [7]. Scientific data encompassing geological information, geophysical and geochemical characteristics of a particular geothermal system is a critical component of successful geothermal development. Harnessing of the data creates synergy and leads to proper decision making in terms of resource management and risk mitigation [8].

It is important to emphasize that the utilization of geothermal energy has the potential to mitigate the effects of climate change arising from carbon-based fuels and accelerate the rate of economic growth toward the achievement of sustainable development goals. It is a renewable resource with versatile and unlimited applications that can be used in the energy sector, industry, agriculture, recreational activities, and tourism and health therapy with good investment returns. Rwanda is endowed with this form of green energy resources, but quite a number of geothermal systems are underutilized. It is necessary to unlock this potential by investing in research and development to optimize and efficiently utilize the geothermal resources available in the country.

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The geological and geophysical characteristics of geothermal reservoirs can be well understood through geochemical research. The process involves data collection through sampling of thermal water sources, statistical data analysis, and interpretation of the output. Geochemistry of a particular hydrothermal system can reveal the origin of thermal waters, predict the temperature of the reservoirs, and determine its minerology. This information can be used to determine whether a particular reservoir is viable for power production or can be put to alternative uses such as hospitality and horticultural production [9,10]. In order to estimate the temperature of deep reservoirs, geothermometers based on geochemical information are usually used. The isotopic composition of a given thermal water system can reveal its origin, while the high chloride concentration indicates its source as a high temperature deep water acquirer [11,12]. The classification of geothermal waters is usually based on anion and cation ratios, with sulfate, chloride, and bicarbonate anions playing an essential role [13,14]. Through speciation of geothermal fluids, the likelihood of scale formation and corrosion can easily be predicted [15,16]. Therefore, these aspects of geochemistry underscore its role in the provision of efficient and sustainable geothermal energy with minimal environmental and public health concerns.

The use of geothermal water leads to its contact and interaction with the flora and fauna of the ecosystem. Due to the diverse chemistry of geothermal fluids, it is necessary to monitor potential chemical hazards that may arise from their use and provide mitigation measures in order to reduce their etiological risks. The heat transfer from the interior of the earth to the impermeable subsurface rocks causes high pressure build-up, which enhances the constant circulation of water masses in the geothermal reservoirs. This phenomenon causes water-rock interactions that lead to the dissolution of some chemical components in rocks. It is these processes that cause geothermal fluids to acquire a unique chemical composition compared to normal surface waters. Mining and agricultural activities are some of the artificial sources that can enhance the presence of chemical pollutants in water systems [17]. The common toxic elements of geological origin that are usually present in geological fluids include B, Cd, Hg, F, Cl, Pb, Cu, and As. A considerable amount of non-condensable gases with concentrations below 10% are also witnessed and they include CO_2, H_2S, SO_2, SO_3, CH_4, and NH_3. Fibrous silicates as a result of volcanic eruptions are also deposited in water bodies and are present in the form of SiO_2. The concentration of Na and Cl ions, which are constituents of brine, will always be in greater amounts in surface waters. Ions such as HCO_3^-, SO_4^{2-}, Ca^{2+}, K^+, and CO_3^{2-}, may also be present, but in lesser amounts. The influx and magnitude of water circulation controls the concentration of these species in geothermal fluids, extracting them from either enclosing subsurface rocks or degassing magma [18].

Potentially toxic and ubiquitous metals such as Pb, Ni, Cd, Zn, and Cr can enter the ecosystem and remain concealed for years, and in the long run they can cause deleterious health effects to humans. These elements accumulate in the adipose tissues of humans and can cause adverse effects on the nervous, circulatory, and immune systems. Lead is a potential carcinogenic toxic metal that produces disorders such as kidney dysfunction, headache, nerve damage, and abdominal pain. Nickel affects the pulmonary system and causes significant dermal problems in humans, while Cd can damage the skeletal system and cause mental and growth retardation among children during chronic exposure cases. Similarly, Cr and Zn in high concentrations induce potential health problems for plants and human beings. On the other hand, chromium negatively affects the immune system, while Zn causes problems in the dermal and liver [19]. Toxicant and contaminant compounds formed by metals and organic species have been shown to be more toxic to man as a result of their long half-life and ability to dissolve in lipids [20,21]. Alkylated mercury ions are lipid-soluble compounds that are formed when mercury enters aquatic bodies and is consumed by organisms such as fish, among other aquatic organisms [22]. When larger fish consume microorganisms contaminated with mercury, alkylated mercury undergoes biomagnification and becomes bioconcentrated to lethal levels [23]. Consumption of fish contaminated with mercury by man can trigger damage to the brain and nervous system. In the years 1953-1960, more than 100 Japanese citizens died and then thousands of others were left with irreversible damage to nerves, reproductive systems, and other mutagenic diseases resulting from the consumption of fish contaminated with mercury in the form of methyl mercury [24].

The East African Rift valley consists of alkaline volcanoes that are usually rich in fluoride minerals such as fluorspar, which leads to elevated fluoride levels in groundwater in the region. Fluoride concentrations are also enhanced by the presence of siliceous igneous rocks and hydrothermal systems [25,26]. Regions with low calcium and high bicarbonate ions usually have increased fluoride concentrations in their groundwater systems due to the leaching effect [27]. Although fluoride in low concentrations is essential for preventing dental caries, excess intake can lead to dental and skeletal fluorosis due to its high affinity for Ca^{2+} ions contained in bone and teeth [28,29]. To reduce the levels of fluoride in drinking water, economically viable defluoridation techniques such as membrane adsorption and biosorption processes can be employed [30]. The safety of hydrothermal water potable with regard to fluoride levels should always be taken into account to protect public health and safety.

Geophysical and geological studies have been extensively carried out in Rwanda to determine the viability of various geothermal sites for power production. However, minimal geochemical studies have been done to assess public health concerns and environmental conservation in the exploitation of geothermal resources. The current study mainly focuses on the assessment of selected trace metals and fluoride levels in water samples whose presence in the environment can be deleterious. The concentrations of Pb, Cu, Ni, Mn, and Cd were investigated in geothermal water from Bugarama and Nyamyumba hot springs using micro plasma atomic emission spectroscopy. The samples were further subjected to major cation and anion analysis. Physical parameters measured during sampling included temperature, dissolved oxygen, conductivity, and total dissolved solids. These parameters were measured in situ using a multimeter. Calcium and Mg concentrations were determined using ethylenediaminetetraacetic acid (EDTA) titration, while K and Na were analyzed by flame emission spectroscopy. The SO_3^{2-}, F^-, PO_4^{3-} and NO_3^- ions were measured using UV spectroscopy. Titrimetric analysis was used to obtain the amount of hydrogen carbonate that was present in the thermal water. The study was intended to reveal the mineralogy of the springs of interest and identify potential chemical hazards. This research work will serve as a baseline for further research and possible mitigation measures to provide clean geothermal energy with minimal health and environmental hazards. In the long run, this will lead to efficient and diversified utilization of geothermal resources in new frontiers such as aquaculture, water mining, recreation, health therapy, drying of crops, horticulture, and power production. Ultimately, this is expected to eventually spur socioeconomic and sustainable development in Rwanda.

2. Experimental

2.1. Instrumentation

Spectroscopic determination of PO_4^{3-}, NO_3^-, SO_4^{2-} and F^- was carried out using a Hach DR6000 UV-Vis spectrophotometer.

Table 1. The coordinates of the sites sampled for analysis

Location	Coordinates	
Bungarama (B1)	2^{0} 40’09.5”S	28^{0}59’50.8”E
Bungarama (B2)	2^{0}40’02.1”S	28^{0}59’43.2”E
Bungarama (B3)	2^{0}40’20.3”S	28^{0}59’99.6”E
Bungarama (B4)	2^{0}40’15.8”S	28^{0}59’76.2”E
Nyamnyumba (N1)	1^{0}44’34.8”S	29^{0}16’46.1”E
Nyamnyumba (N2)	1^{0}44’17.4”S	29^{0}16’23.1”E
Nyamnyumba (N3)	1^{0}44’08.4”S	29^{0}16’32.2”E
Nyamnyumba (N4)	1^{0}44’01.2”S	29^{0}16’27.3”E

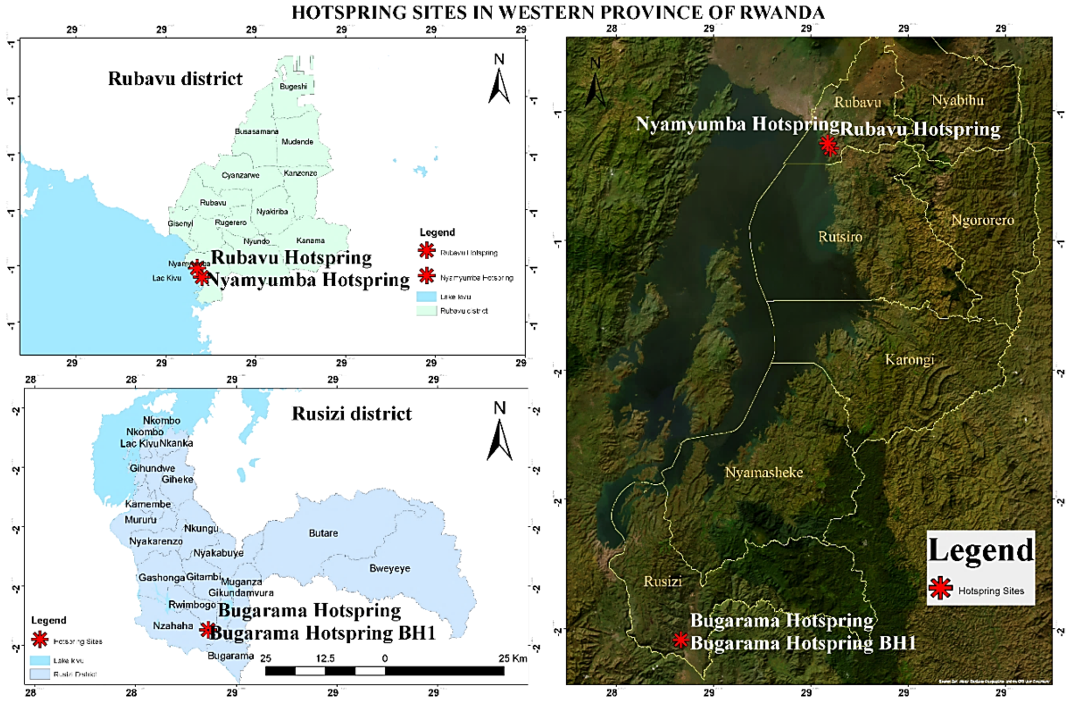

Figure 1. A map showing the sampling points in the Nyamnyumba and Bungarama hot springs in Rubavu and Rusizi districts in Rwanda.

Hanna bench top IC-HI5221-02 pH meter was used in the monitoring of pH. The *in-situ* measurement of temperature, conductivity, dissolved oxygen (DO), total dissolved solids (TDS), and pH was carried out using the HQ4Od multimeter, while the analysis of Pb, Cu, Ni, Mn, and Cd was performed using Agilent 4210 MP-AES instrument coupled with an SPS4 auto sampler and an external Agilent 4107 nitrogen generator for plasma production.

2.2. Sampling sites and sample collection

The samples were collected in Bugarama (Rusizi district) and Nyamyumba (Rubavu district), in the western province of Rwanda. Bugarama springs are located at coordinates (-2.669, 28.997) and 1995 m above sea level, while Rubavu Nyamyumba springs are located at coordinates (-1.734, 29.276) and 1470.40 m above sea level, as indicated in Figure 1. The actual locations of the sampled sites are reported in Table 1. Triplicate 1 L water/steam samples were collected from each sampling area in Bugarama and Nyamyumba in June 2023. Physicochemical parameters including temperature, pH, conductivity, dissolved oxygen, and total dissolved solids of the water/steam samples were measured in situ using a portable multimeter HQ40d before sealing the plastic containers. The samples for cation analysis were acidified using 1 mL of concentrated nitric acid. Samples were kept in cold boxes and then transported to the laboratory for further analysis.

2.3. Experimental procedures

The analysis was carried out according to the American Public Health Association standard procedures that are widely used for water quality assessments. Methods have been developed, validated, and proven to be quite reliable and accurate [31]. The methods used during the analysis included both titrimetric and instrumental methods. Some of the methods were modified in accordance with the availability of the reagents and the type of instrumental working mode and range. Titrimetric and various spectroscopic methods were employed in the determination of the analytes of interest.

2.3.1. Determination of anions

The determination of SO_4^{2-} was made using the turbidimetric method [32]. A stock solution containing 1000 ppm of SO_4^{2-} was prepared by dissolving 1.479 g of dried Na_2SO_4 in distilled water. The 100 ppm working standard was obtained by diluting the stock solution accordingly. A buffer solution was prepared by mixing 30 g of $MgCl_2\cdot6H_2O$, 5 g $CH_3COONa\cdot3H_2O$, 1 g of KNO_3 and 20 mL of CH_3COOH in 500 mL of distilled water. Serial dilutions ranging from 0 to 60 ppm calibration standards were obtained from the 100 ppm working standard. The contents were transferred to 250 mL beakers, then 20 mL buffer was added to each beaker and stirred using a magnetic stirrer. A spoonful of $BaCl_2$ was added and stirred for 1 min. The solutions were then transferred to cuvettes and the absorbance readings were measured within 5 min at 420 nm using the Hach

DR6000 UV VIS spectrophotometer. The samples were also subjected to the same procedure and using the calibration equation of the standards, their concentrations were obtained.

The analysis of PO_4^{3-} was performed using the mixed reagent ascorbic acid spectrophotometric method [33]. A mixture containing H_2SO_4 (2.5 M), ammonium molybdate, and antimony potassium tartrate was separately prepared. 12 g of ammonium molybdate was dissolved in 250 mL of warm distilled water, 0.291 g of antimony potassium tartrate was dissolved separately in 100 mL of distilled water and the two solutions were added to the 2.5 M H_2SO_4 and finally the mixture was made up to 2000 mL with distilled water. The solution was kept in the dark in a Pyrex glass bottle. For color development, the ascorbic acid reagent was freshly prepared by adding 2.108 g of ascorbic acid to 400 mL of an acidified mixture of ammonium molybdate/potassium antimony tartrate. Standard 1000 ppm phosphorous stock solution was prepared by dissolving 1.0967 g of KH_2PO_4 in distilled water (250 mL). The 10 ppm working standard was obtained by diluting the stock solution accordingly. Calibration standards ranging from 0 to 1.2 ppm were prepared from the 10-ppm working standard. 5 mL of each standard and samples were transferred to 50 mL volumetric flasks. This was followed by the addition of 20 mL of distilled water and 10 mL of mixed ascorbic acid reagent. The contents were then topped to the mark with distilled water. The solutions were allowed to stand for 1 hour and absorbance readings were performed using a Hach DR6000 UV VIS spectrophotometer at a wavelength of 880 nm.

The UV spectrophotometric screening method was used to quantify NO_3^- concentration levels in water samples [34,35]. During the analysis, 1 M HCl was added to the water samples to eliminate the interference of carbonate and hydroxide species. The calibration standards were prepared from a standard NO_3^- solution (10 ppm) and ranged from 0 to 2.5 ppm. This was followed by the addition of 1 mL of 1 M HCl. Absorbance measurements were performed simultaneously at 275 and 220 nm with distilled water as a blank using the Hach DR6000 UV VIS spectrophotometer. The difference in absorbance values obtained at the two wavelengths was used as a basis for quantifying the amount of NO_3^- in the standards and samples.

The amount of F^- in the water samples was determined using the SPADNS reagent UV spectroscopic method [36]. During the analysis, calibration standards ranging from 0.05 to 20 ppm were prepared from 100 ppm F^- standard in 50 mL volumetric flasks. 10.0 mL of each standard and sample were pipetted into test tubes and this was followed by the addition of 2 mL of SPADNS 2 reagent into each of the sample cells. The mixture was shaken and allowed to react for 1 min, and the absorbance readings were taken at 580 nm using a Hach DR6000 UV VIS Spectrophotometer starting with the blank.

Argentometric titration was used to determine the Cl^- concentration in water samples [37]. 100 mL of thermal water samples and distilled water (blank) were measured in 250 mL volumetric flasks. 1 mL of 30% H_2O_2 was added and the pH was adjusted to 8.0 using 0.1 M NaOH. This was followed by the addition of 1 mL of K_2CrO_4 indicator. Each sample was titrated with 0.01 M $AgNO_3$ to the tan red end point and the results were tabulated and subjected to further interpretation to quantify the amount of chloride in the sample.

Volumetric analysis was performed to determine HCO_3^-/CO_3^{2-} concentrations in water samples [38]. 50 mL of each sample was transferred to 250 mL Erlenmeyer flask and 5 drops of the phenolphthalein indicator were added. There was no color change in all samples that indicated that CO_3^{2-} ions were absent, which was attributed to low pH (< 8.3). To each sample solution, 5 drops of methyl orange were added and the solution was titrated with 0.01 M H_2SO_4 up to the end point of the red color. Replicate readings were taken for each sample and averaged accordingly.

2.3.2. Determination of major cations and trace metals

The evaluation of Ca in the water samples was performed by the EDTA titrimetric method [39]. 100 mL of each thermal water sample was transferred to a 250 mL Erlenmeyer flask. 2 mL of 1 M NaOH was added to raise the pH to about 12-13. This was then followed by the addition of two drops of the murexide indicator. The resultant solution was immediately but slowly titrated using 0.01 M EDTA to the red violet end point. The results for each titre were tabulated and the amount of Ca quantified.

The amount of total hardness of water (Ca + Mg) in the water samples was similarly determined using the EDTA titrimetric method [40,41]. 100 mL of each sample was transferred to a 250 mL Erlenmeyer flask. This was followed by the addition of 2 mL of buffer to adjust the pH to 10±0.1. Two drops of the Eriochrome Black T indicator were added followed by slow titration using 0.01 M EDTA to the red color end point. The total hardness obtained was used to evaluate the magnesium concentration in the samples.

The concentrations of K^+ and Na^+ ions were obtained by application of flame photometry [42]. The calibration standards of potassium ions were prepared from 100 ppm K^+ standard in the range of 0 to 100 ppm in 50 mL volumetric flasks. Similarly, sodium calibration standards were prepared from 100 ppm Na^+ standard in the range of 0 to 50 ppm. The standards were analyzed separately along with water samples for each analyte in a flame photometer. Standard calibration curves for K^+ and Na^+ were obtained and used to quantify the respective analytes in the samples.

Microwave plasma atomic emission spectroscopy was used to determine the presence of trace elements [43]. Two sets of standards in the range of 0.1-0.5 and 0.01-0.05 ppm were prepared from the 5-ppm mixed MP-AES multimetal standard containing the analytes of interest (Pb, Cd, Mn, Ni, and Cu). Highly purified deionized water was used during serial dilution. Each set of standards was analyzed concurrently with the water samples to determine the levels of the respective analytes. To ensure that the results obtained were reliable and fairly accurate, optimum operating conditions for each element were applied. Quantitation data, together with standard calibration curves for each analyte were automatically generated after analysis of the samples.

3. Results and discussion

The values of physical parameters and concentration levels of major anions and cations are relatively comparable to the data obtained in previous geochemical studies of geothermal fields in Rwanda [44]. The results of the analysis showed that there was no significant difference in the mean physicochemical parameters measured at Bugarama and Nyamyumba, $p = 0.81945$ ($(x \leq F) = 0.18055$), although the concentration levels of most ions at Bugarama were higher than those from Nyamyumba. This can be attributed to the effect of the different sources of geothermal waters and their geological origins of the thermal waters.

The pH values were between 6.40 and 6.95 in both areas of study. The pH is almost neutral and hence suitable for direct usage of water for drinking purposes, water bottling, and swimming. Temperatures were in the range of 38.8-60.2 °C, indicating that hot springs are likely to be low-enthalpy geothermal systems which may not be viable for power production. Since the hot springs are located in rich agricultural areas, the moderate hot temperature waters can be used for drying crops, establishment of green houses, aquaculture, and direct heating purposes. Additionally, they can be used in the construction of therapeutic commercial warm baths [45,46].

Table 2. Physico-chemical parameters, major cations, and anions obtained in Nyamyumba hot springs *.

Parameter	**Sampling site**				
	N1	**N2**	**N3**	**N4**	**Mean±SD**
pH	6.82±0.05	6.85±0.04	6.95±0.06	6.91±0.05	6.88±0.06
Temperature (°C)	56.30±2.62	59.50±2.37	60.20±2.45	54.80±2.55	57.70±2.57
Dissolved oxygen (mg/L)	2.63±0.27	2.71±0.19	2.30±0.25	2.11±0.30	2.44±0.28
Total dissolved solids (ppm)	1432.00±22.17	1398.00±15.97	1405.00±19.44	1443.00±20.56	1419.50±21.46
Conductivity (mS/cm)	4.83±0.09	4.78±0.08	4.67±0.12	4.61±0.06	4.72±0.10
Total hardness (mg $CaCO_3$/L)	135.78±5.43	139.74±4.11	140.22±5.06	148.4±4.95	141.04±5.30
Mg^{2+} (mg/L)	19.55±0.55	20.12±0.81	20.19±0.69	21.37±0.73	20.31±0.76
Ca^{2+} (mg/L)	49.45±1.21	49.14±1.11	51.73±0.97	50.37±1.13	50.17±1.16
Cl^- (mg/L)	213.72±0.95	214.35±1.12	216.10±0.94	215.58±0.79	214.94±1.09
CO_3^{2-} (mg/L)	nd	nd	nd	nd	nd
HCO_3^- (mg/L)	1066.28±9.45	1088.24±10.48	1063.84±12.04	1063.35±8.98	1070.43±11.94
NO_3^- (mg/L)	0.46±0.06	0.49±0.40	0.57±0.05	0.51±0.04	0.51±0.05
SO_4^{2-} (mg/L)	47.34±1.38	46.38±1.26	49.25±1.19	48.81±1.28	47.95±1.32
PO_4^{3-} (mg/L)	0.24±0.02	0.23±0.01	0.28±0.03	0.28±0.02	0.26±0.03
F^- (mg/L)	1.11±0.04	1.11±0.03	1.02±0.05	1.04±0.06	1.07±0.05
K^+ (mg/L)	49.62±1.74	47.05±1.65	45.50±1.57	47.05±1.70	47.31±1.10
Na^+ (mg/L)	214.85±7.26	291.58±8.72	301.49±9.95	311.39±9.75	301.49±9.91

***** N1, N2, N3, and N4 represent samples collected from Nyamyumba hot springs (Table 1).

Table 3. The physico-chemical parameters and major cations and anions obtained in Bugarama hot springs *.

Parameter	**Sampling site**				
	B1	**B2**	**B3**	**B4**	**Mean±SD**
pH	6.40±0.04	6.47±0.05	6.43±0.06	6.45±0.04	6.44±0.05
Temperature (°C)	46.50±3.23	40.20±3.89	45.10±3.75	38.8±3.62	42.65±3.73
Dissolved oxygen (mg/L)	1.45±0.70	2.21±0.62	1.23±0.81	2.61±0.48	1.88±0.65
Total dissolved solids (ppm)	1023.00±15.16	990.00±14.54	1016.00±16.10	997.00±15.73	1006.5±15.55
Conductivity (mS/cm)	2.93±0.19	2.65±0.12	2.85±0.16	2.56±0.21	2.75±0.17
Total hardness (mg $CaCO_3$/L)	357.86±13.43	377.90±15.01	350.76±12.89	379.02±14.34	366.39±14.25
Mg^{2+} (mg/L)	51.53±1.98	54.42±2.25	50.51±1.56	54.58±1.82	52.76±2.05
Ca^{2+} (mg/L)	96.43±5.31	102.24±4.87	89.36±4.92	96.62±4.68	96.16±5.28
Cl^- (mg/L)	117.68±2.86	117.66±2.98	123.44±3.49	123.42±3.45	120.55±3.33
CO_3^{2-} (mg/L)	nd	nd	nd	nd	nd
HCO_3^- (mg/L)	968.68±12.87	1005.28±15.61	956.48±13.82	939.4±14.34	954.85±14.71
NO_3^- (mg/L)	0.39±0.02	0.44±0.01	0.39±0.01	0.44±0.02	0.42±0.03
SO_4^{2-} (mg/L)	38.88±1.75	40.06±1.84	36.68±2.01	35.5±1.91	37.76±2.05
PO_4^{3-} (mg/L)	0.16±0.01	0.14±0.01	0.16±0.01	0.17±0.01	0.16±0.01
F^- (mg/L)	0.91±0.06	0.91±0.05	0.780±0.04	0.80±0.07	0.85±0.07
K^+ (mg/L)	29.5206±2.97	23.335±3.12	30.04±2.46	27.46±2.75	27.59±3.05
Na^+ (mg/L)	103.47±20.45	202.48±26.79	145.54±29.21	165.35±28.67	171.12±28.91

* Legend: B1, B2, B3, and B4 represent samples collected from Bugarama hot springs (Table 1).

In general, the temperatures in Nyamyumba are higher than those of Bugarama and directly correlate with other physicochemical parameters with a few exceptions, highlighting the influence of temperature on these species [47,13].

The total dissolved solids (TDS) values lie between 990 and 1443 ppm. These high values indicate a high amount of dissolved salts and the possible presence of trace metals which may make the water unsuitable for drinking without pretreatment. High TDS in drinking water makes it bitter, has a foul smell, and may cause health problems like kidney stones [48]. The results of previous geochemical studies in Rwanda indicated pH, TDS, and temperature ranges of 6.25-7.00, 2101.90-1836.78 ppm, and 33.0-70.6 °C, respectively. To a large extent, the current results were in agreement with the results of previous studies. The slight variation could be due to temporal variations over time and the instrumentation used in the analysis. In comparison to the hot springs in the Eastern arm of the Great Rift Valley, the TDS, pH, and temperature values in the Rwandan geothermal regime are generally lower. A case study of Lake Bogoria hot springs in Kenya showed surface temperatures of up to 100 °C [49]. This phenomenon coupled with high reservoir temperature makes the regimes have high enthalpy that is suitable for power production. Additionally, most of the hot springs are alkaline and saline in nature, exhibiting pH values as high as 10, which makes the geothermal water unsuitable for aquaculture. The hot springs also contain high amounts of total dissolved solids, rendering the water unsuitable for domestic use.

The concentration levels of various ions in both Nyamyumba and Bugarama are reported in Tables 2-4. The results of the main cations in Tables 2 and 3 showed the predominance of sodium ions with values ranging from 103.47 to 311.39 ppm. On the other hand, the bicarbonate anions were the highest with concentrations in the range of 939.40-1088.24 ppm. This indicates that the waters are mainly rich in sodium bicarbonate. There is also a significant presence of potassium (23.34-49.62 ppm), Magnesium (19.55-54.58 ppm), and calcium (54.31-151.61 ppm) cations, while the other predominant anions were chloride (117.66-216.10 ppm) and sulphate (35.50-49.25 ppm). The NO_3^-, PO_4^{3-}, and F^- ions were also present but in small quantities. Fluctuations in the concentration levels of various species show the influence of continuous boiling and mixing in deep reservoirs. The mean Na/K ratios for Nyamyumba and Bugarama are 6.37 and 6.20, respectively. These low values indicate the presence of up-flow structural systems in which the temperature-dependent fluid mineral equilibria reach to the surface quickly. The results are in agreement with previous investigations which have classified the geothermal waters in in other geothermal waters to be of Na-HCO_3-Cl-SO_4 type and mainly of volcanic origin [44,50]. Previous studies on Nyamyumba and Bugarama hot springs showed average conductivity, PO_4^{3-} and SO_4^{2-} values of 2440 µs/cm, 0.31 ppm, and 75.5 ppm, respectively [51]. The current study in the area showed an increased mean conductivity of 4072.0±10 µs/cm as reported in Table 2. This can be attributed to the increase in dissolved matter resulting from both natural and human activities over time. The mean concentrations of PO_4^{3-} and SO_4^{2-} were found to be 0.26±0.03 ppm and 47.95±1.32 ppm, respectively. These variations could be due to seasonal variations.

Table 4. The concentrations of selected trace metals obtained in Nyamyumba and Bugarama.

Metal	Sampling site									
	Nyamyumba					Bugarama				
	N1	N2	N3	N4	Mean±SD	B1	B2	B3	B4	Mean±SD
Pb^{2+} (mg/L)	0.01±0.001	0.01±0.001	0.01±0.001	0.01±0.01	0.01±0.00	0.01±0.001	0.02±0.01	0.01±0.01	0.01±0.01	0.013±0.01
Mn^{2+} (mg/L)	0.03±0.01	0.03±0.02	0.07±0.02	0.02±0.01	0.04±0.02	0.07±0.02	0.15±0.03	0.12±0.02	0.10±0.03	0.11±0.03
Cd^{2+} (mg/L)	0.01±0.01	nd	nd	nd	0.01±0.00	0.01±0.01	nd	nd	nd	0.01±0.00
Cu^{2+} (mg/L)	0.01±0.01	0.01±0.00	0.01±0.01	0.01±0.01	0.01±0.00	0.01±0.01	0.01±0.01	0.01±0.01	0.01±0.01	0.01±0.00

* Legend: N1, N2, N3, N4, B1, B2, B3, and B4 represent samples collected from Nyamyumba and Bugarama hot springs (Table 1).

The significant presence of magnesium and calcium makes the water suitable for portable use as they are macronutrients that are essential for animal nutrition, as they are needed for various metabolic and physiological processes. The highest fluoride concentration was found to be 0.11 ppm which is lower than the permissible WHO limit of 1.5 ppm fluoride in portable water. It is an important element in low concentrations due to its ability to prevent tooth decay. However, excess consumption of it can lead to fluorosis.

Hot springs in the eastern part of the East African Rift valley usually exhibit high concentrations of dissolved ions. This is partly associated with high temperature and pressures, which enhance water-rock interactions, resulting in more dissolution of minerals and the nature of origin of the thermal water. Investigation of physicochemical of Eritrean hot springs indicated higher values in some parameters compared to those found in this study. The SO_4^{2-} levels were as high as 979.7±75.5 ppm in some instances, while the highest chloride concentration was found to be 5946.0±33.8 ppm. The F^- concentrations were generally higher than the WHO limit of 1.5 ppm [52]. In a case study conducted in Lake Bogoruia hot springs, a very high F^- content was found with some spring samples having values above 100 ppm [53]. The high F^- and SO_4^{2-} concentrations of hot spring water renders it unfit for human consumption compared to the geothermal water in Bugarama and Nyamyumbba with respect to these ions.

The main focus of this study was to identify the inherent potential inorganic chemical hazards in the geothermal water samples and assess its quality for possible direct use. The results of the five trace metals that were analyzed are recorded in Table 4. Manganese was the most predominant trace metal with values as high as 0.15 ppm in sample B2. The Mn levels are within the acceptable WHO limit of 0.4 mg/L. Manganese is an essential element that is required for the physiological functioning of body organs as well as growth and development [54]. The mean concentration of Mn in Bugarama (0.11±0.03 ppm) was higher than the mean concentration in Nyamyumba (0.04±0.02 ppm). The mean concentration of copper in both regions was of 0.01 mg/L which is below the WHO limit of 0.05 mg/L. Manganese, however, is an essential element for various metabolic processes [55,56].

As can be seen in Table 4, the highest concentration of lead was 0.02 given by sample B2, which is above the threshold limit of 0.01 mg/L. The mean concertation of Pb in Bugarama (0.013±0.01 ppm) was slightly higher than in Nyamyumba (0.01 ppm). Lead is a non-essential element whose presence in the environment is deleterious because it is poisonous and bioaccumulative. Cadmium concertation levels in both samples, N1 and B1 was 0.01 which is above the WHO threshold limit of 0.005 mg/L, thus making it a threat to the environment. Cadmium is capable of competing with divalent cations such as calcium and zinc, and it can bind to specific proteins, making it toxic to humans and animals and being a non-essential element. There is more trace metal contamination in Bugarama than in Nyamyumba, as shown by the mean values of Mn and Pb. The cumulative phytotoxic effects of Cu, Cd, and Pb may lead to bioamplification depending on the physicochemical conditions of the aquatic environment that determine their bioavailability. For example, at low pH, the uptake of these elements by plants increases, leading to more toxicity not only for plants but also to the food chain of the ecosystem [57,58]. Therefore, it is necessary to apply measures that can minimize the presence of these trace elements in the geothermal water environment. Chemical precipitation, redox, ion exchange, and adsorption are some of the conventional methods that have been used to remove heavy metals from polluted aquatic systems [59]. The adsorption technique has proven to be quite useful in hydrometallurgical applications, because it can eliminate metal ions from very dilute solutions and has the capacity to process ions that are present in large volumes of solutions. The technique is also easy to operate and has higher recovery efficiency with low maintenance costs compared to other methods that are capital intensive and suffer high regeneration costs [60,61]. Bone char has been successively applied in the removal of various metal species such as Cu, Zn, Cd, Pb, As, Hg, and Ni. Calcium hydroxyapatite $[Ca_{10}(PO_4)(OH)_2]$, a major component of the inorganic phase of bone char, exhibits its adsorption behavior through an ion exchange reaction, surface complexation and co-precipitation [62]. The use of activated carbon adsorbents is one of the most effective and widely used techniques, but its large-scale application is restricted due to high cost [63].

The occurrence of trace metals in geothermal water is influenced by geological origin, pH, and temperature. Low pH enhances the bioavailability of elements such as Cd, Cu, Pb, and Ni due to leaching of rock minerals. High temperatures also lead to more dissolution of minerals resulting from increased water-rock interactions. In most geothermal springs around the world, trace elements occur in minute quantities in the range of ppbs. Although these elements may be present in small amounts, their bioaccumulation can affect the environment in the long run [64-66]. The level of trace metal contamination in the Nyamyumba and Bugarama hot springs is of concern due to the significant presence of Pb and Cd.

4. Conclusion

The pH values of both Bugarama and Nyanyumba are between 6.4 and 6.8 which makes the water in both areas suitable for direct use as potable water. The mean value of total dissolved solids is above the WHO limit of 500 mg/L for direct use of water. Fluoride and trace element concentrations are within WHO limits except for Pb and Cd. There are no significant differences in the mean physicochemical parameters measured in Bugarama and Nyamyumba. The results of the analysis showed some considerable inorganic contamination and hence there is a need for water treatment to reduce the total dissolved solids for potable use. Biosorption of lead and other trace element contaminants can be applied, because it is inexpensive and cost-effective. This study is expected to contribute to the public and community awareness of the hidden hazards of geothermal fluids based on research findings. This information will also serve as a benchmark for future research to unlock the enormous potential of geothermal assets to achieve green growth, decarbonization, and spur economic development through diversification. Due to dynamic geological changes and seasonal variations, continuous monitoring of geothermal water quality is needed. Further research is recommended on organic contaminants in geothermal water and the effect of trace metal contamination on fish in Lake Kivu.

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