

# Geochemical Characterization of Nyamyumba Hot Spring, Northwest Rwanda

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## Research article

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# Abstract

Hot spring is a hot water that is naturally occurring on the surface from the underground and typically heated by subterranean volcanic activity and local underground geothermal gradient. There are four main hot springs in Rwanda such as: Kalisimbi, Bugarama, Kinigi and Nyamyumba former name Gisenyi hot springs. This research focused on the geochemical analysis of Nyamyumba hot springs located near the fresh water of Lake Kivu. Nyamyumba hot springs are located in the western branch of the East African Rift System and they are located near Virunga volcanic complex, explaining the rising and heating of water. The concentrations of Sulfate, Iron, Ammonia, Alkalinity, Silica, Phosphate, Salinity, Alkalinity, and Conductivity using standard procedures were measured. The results showed that hot spring water has higher concentrations of chemicals compared to Lake Kivu water and the geochemistry of these hot springs maybe associated with rock dissolution by hot water. The measured parameters were compared with World Health Organization (WHO) standards for recreational waters and it has been identified that Nyamyumba hot spring are safe to use in therapeutic activities (Swimming).

## 1. Introduction

Hot spring is known as a geothermal spring is a spring produced by the emergence of groundwater that has been strongly heated geothermally below the earth surface. Hot spring water often contains large amounts of dissolved minerals. The chemistry of hot springs ranges from acid sulphate springs with a pH as low as 0.8, to alkaline chloride springs saturated with silica, to bicarbonate springs saturated with carbon dioxide and carbonate minerals. Some springs also contain abundant dissolved iron. The minerals brought to the surface in hot springs often feed communities of extremophiles, microorganisms adapted to extreme conditions, and it is possible that life on Earth had its origin in hot springs (Farmer, 2000).

Generally, the chemical composition of a hot spring varies from alkaline to acid sulphate to bicarbonate to iron-rich, and each of them defines an end member of a range of possible chemistry of that hot spring (Drake, et al., 2014). According to White, et al. (1956), Alkaline chloride hot springs are derived from the hydrothermal fluids that form when groundwater containing dissolved chloride salts reacts with silicate rocks at high temperature. These springs are saturated with silica ( $\text{SiO}_2$ ) but their pH is nearly neutral. Since silica solubility depends on temperature, upon cooling, the silica is deposited as geyserite, a form of opal (opal-A:  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) (White, Brannock, & Murata, 1956). On the other hand, acid sulphate hot springs are made when the hydrothermal fluids rich in hydrogen sulphide ( $\text{H}_2\text{S}$ ), is oxidized to form sulphuric acid,  $\text{H}_2\text{SO}_4$  (Drake, et al., 2014).

The resulted  $\text{P}^{\text{H}}$  in this formed fluid is lowered to an acidic value less than 0.8 (Cox, Shock, & Havig, 2011). The so formed acid reacts with the rock to change it to clay minerals and silica residue. In the case where carbon dioxide ( $\text{CO}_2$ ) and groundwater would react with carbonate rocks, this would lead to the formation of hydrothermal fluid of bicarbonate hot springs (Drake, et al., 2014). When these hydrothermal fluids reach the surface,  $\text{CO}_2$  is rapidly evaporated and carbonate minerals precipitate to form travertine, so that bicarbonate hot springs tend to form high-relief structures around their openings (Des Marais & Walter, 2019). The Iron rich hot springs are characterized by the presence of groups of microorganisms that produce the small groups of oxidized iron from the iron found in the hydrothermal fluids, and then feed the springs (Parenteau & Cady, 2010).

Recreational waters may contain chemicals of organic or inorganic source. Generally, chemicals get into hot spring water through rock dissolution where it passes, and soil in which water percolates (Zhang, et al., 2019).

This is due to the fact that dissolution increases with temperature. Other than temperature, low pH of water also causes greater leaching of inorganic materials from rocks and soil, increasing the chance that naturally occurring inorganic substances will accumulate at higher concentrations than expected (Van der Sloot et al., 1997).

The main sources of sulfate ion in the underground waters are: i) Fumarolic gas of sulfur dioxide, ii) Rock forming minerals gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and 3) Rock forming minerals of pyrite (Seki et al, 2004). However, pyrite needs much oxygen to form sulfate ion ( $\text{FeS}_2 + 4\text{O}_2 + 3\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 2\text{SO}_4^{2-} + 6\text{H}^+$ ) (Jolie, 2010). Geothermal water tends to reduce the resistivity and increase the conductivity of its host rock caused by high concentrations of dissolved particles in the fluid and secondary alteration minerals that are formed when the thermal waters interact with the host rock. The type of alteration minerals being formed depends on the type of the host rock and the temperature and salinity of the fluid (Jolie, 2010). In the complex circulation processes, water-rock interactions play an important part in hydro-geochemical indicators of the waters in the geothermal systems which can be used to examine the properties of geothermal reservoirs and the mixing behavior of groundwater (Capasso et al., 2001; Han et al., 2010; Baioumy et al., 2015; Shi et al., 2017). Mixing processes between thermal and non-thermal water can be enhanced by faults in a geothermal area (Han et al., 2010).

The minerals in hot springs have a detoxifying capacity and remedy for skin ailments including acne, eczema and psoriasis because of their dissolved chemicals including Sodium bicarbonate, chloride and sulfur (Gupta and Nicol, 2004; Levin and Miller, 2011). Nyamyumba hot springs attract many people for swimming purpose. This research aimed at studying the chemical composition of Nyamyumba hot springs and analyze its safety for recreation purpose.

## 2. Geological Settings

Different geodynamic processes including faulting and magmatism controlled the evolution of Lake Kivu. All these contributed to the formation of the lake and different structures like faults, fractures, joints, folds and the unconformities that occur along the margin of Lake Kivu. The tectonic uplift and an extension led to creation of the East African Rift (EAR) (Wood, 2014). The East African Rift system is the best example of an active rift system. The geological and geotectonic parameters of the East Africa Rift System (EARS) suggests that it is very potential for geothermal resource (Godfrey. B et al., 2005). The area of Nyamyumba hot spring is mainly composed of Mesoproterozoic rocks such as mica schist, highly weathered sandstone, travertine and basaltic rocks from volcanic eruption. The East African Rift System resulted from two mantle plumes beneath Afar and Kenyan Plateau (Ebinger and Sleep, 1998; Rogers et al., 2000; Furman et al., 2006). The plateaus are dynamically supported by the convective activity under the asthenosphere (Ebinger et al., 1989), providing heat transfer for partial melting of the lithospheric mantle. The western branch of the East African Rift System in which Rwanda belongs has a limited and localized volcanic products with diversifying chemistry than the eastern branch.

Kivu rift is the middle part of the western branch of the East African Rift System. The rift valley is composed of deep lacustrine basins and structural heights which are overlain by volcanic rocks. These features are Rungwe volcanic area, Rukwa and Tanganyika basins, South Kivu volcanic area, Kivu basin, Virunga volcanic area, Edward basin, Toro-Ankole volcanic area, and Albert basin from south to north (Poucllet et al., 2016). These are the indicators of the mantle plume beneath the lithosphere, and it is suggested to be the heating factor of hot

springs in this area. The faults around the mineral springs in the western part of Rwanda suggest that there rising of Nyamyumba hot spring water is structurally controlled.

## 3. Methods

### 3.1. Sampling procedure

Fourteen samples water samples were collected at six locations; hot spring emerging point or location 0, location 1, 2,3, 4, 5 and 6 using clean plastic bottles (Fig. 2).

### 3.2. Analytical Procedure

Conductivity as the measure of the ability of water to conduct the electricity increases with increasing salinity. The conductivity of water samples in six locations was measured using CTD Sonde. The concentrations of Sulfate, Iron, Ammonia, Alkalinity, Silica, and Phosphate were measured in water samples using Hach kits.

The measurement of silica was preceded by warming the samples at room temperature before analyzing. Silica and Phosphate in the sample reacted with molybdate ion under acidic conditions to form yellow silicomolybdic acid complexes and phospho-molybdic acid complexes. Citric acid was added to destroy the phosphate complexes. Silica was then determined by measuring the remaining yellow color. The method used was Silico-molybdate method (silica, high range (0 to 75.0 mg/L)).

Moreover, the alkalinity which is the capacity of water to resist to the acidification was measured by using digital titrator for Phenolphthalein and total alkalinity from 10 to 4000 mg/L as  $\text{CaCO}_3$ . Unlike other chemicals, sample bottles for phosphate analysis were first cleaned with 1:1 hydrochloric acid solution and rinsed with deionized water. The analysis method used was Phos Ver 3 (Ascorbic Acid), phosphorus reactive (0 to 30 mg/L  $\text{PO}_4^{3-}$ ).

The measurement of iron concentration was preceded by collecting water samples in acid-cleaned plastic containers. Since water samples were analyzed immediately, no acid was added. Ferro-Ver method for iron (0 to 3.00 mg/L) was used for the analysis.

CDC401 conductivity probe was used in the measurement of salinity of the water samples. The probe was rinsed with deionized water and after dried with a lint-free cloth. The shroud was installed. The probe was put in the sample with the sensor fully in the sample. Air bubbles were removed by shaking the probe. After shaking, it was stirred, and the salinity was read.

Furthermore, sulfate analysis was done using Sulfa-Ver 4 method for sulfate (0 to 70 mg/L). In this method, sulfate ions react with barium in Sulfa-Ver 4, sulfate reagent forming barium sulfate precipitate. The turbidity formed is proportional with sulfate concentration and the stabilizing agent in Sulfa-Ver 4 holds the suspended precipitates.

## 4. Results

The results from the chemical analysis of water samples taken at all the locations show that male site has higher concentrations of chemicals than female site (Fig. 3).

Chemicals in water samples from hot spring sources have higher concentrations than other locations. This is shown by the gradients of linear relationships of chemicals in Fig. 3.

Male site has a very high ammonia concentration of around 0.58 mg/l at location 2 compared to 0.15 mg/l at female site. The conductivity and the salinity are lower at the sources compared to the location 1 at all sites (Fig. 3b).

The alkalinity at location 4 show a decrease in concentration in female site than male site. The concentrations in lake are lower than the concentrations at the source of hot springs. The linear and curved relationships show the decrease in the concentration of chemicals. The conductivity of water at the source is higher than the conductivity in lake Kivu and other locations.

Table 1  
The concentrations of chemicals at 6 locations taken at the female site

Parameter/ Location	Ammonia(mg/l)	Silica(mg/l)	Conductivity( $\mu$ s/cm)	Salinity(ppt)	Alkalinity(eq/l)
0(hot springs)	0.145	47	2400	1.2	19
1	0.16	53.7	2550	1.4	20.7
2	0.15	49.6	2100	1.14	18.7
3	0.135	16	1450	0.8	17.0
4	0.087	7.5	375	0.6	4.6
5	0.08	5	210	0.56	4.0
6 (lake)	0.05	1.7	185	0.49	3.5

Table 2  
The concentrations of chemicals at 6 locations taken at the male site

Parameter/ Location	Ammonia(mg/l)	Silica(mg/l)	Conductivity( $\mu$ s/cm)	Salinity(ppt)	Alkalinity(eq/l)
0(Hot springs)	0.15	53.7	2470	1.3	22.0
	0.16	57.0	2450	-	23.8
1	0.41	55.3	2670	1.26	22.0
2	0.58	54	2600	1.3	21.4
3	0.28	36	2050	1.0	19.0
4	0.13	10	540	0.74	16.0
5	0.08	5	210	0.6	10.0
6 (Lake)	0	5	185	0.6	3.5

Table 3  
Average concentrations of the chemicals at the source of hot springs.

Parameter/ Location	Ammonia (mg/l)	Silica (mg/l)	Conductivity ( $\mu\text{s}/\text{cm}$ )	Salinity (ppt)	Alkalinity (eq/l)	Iron (mg/l)	Phosphate (mg/l)	Sulfate (mg/l)
Source	0.152	52.57	2440	1.25	21.6	0.2	0.31	75.7

The average concentrations calculated from Table 1 and 2 at the male and female sources in Table 3 show that the ammonia has a very low concentration compared to the other chemicals. Sulfate and silica have larger concentrations than other chemicals with 75.7 mg/l and 52.57 mg/l respectively (Table 3).

## 5. Discussion

The results show that most of the measured parameters have higher concentrations at the hot spring sources than other locations. This difference can be explained to be caused by the high temperature in which hot water dissolves the rocks through which it passes explaining why the concentration of chemicals in hot spring is very high compared to the lake water.

Alkalinity refers to the water's capacity of withstanding the change in pH. It also refers to the measure of buffering ability of water with the recommended level in swimming pool is 80-120 ppm. The increase in the concentration of ammonia at the location 2 of male site may have been caused by the decay of organic matter as the location is in the swamp area with water and bushes. The alkalinity at location 4, female site immediately decreases and continues constant at location 5 and 6. This is caused by the mixing of Lake water and hot spring water. The dilution of this water lead to the decrease in alkalinity (Hu et al., 2015).

Silica content in ground water is found in two forms such as dissolved particulate matter. Dissolved silica is an indicator of weathering and water circulation (Dobrzynski Dariusz 2005). Mostly, silica content in groundwater is from rock-water interaction (Drever and Vance, 1994). Weathering process which releases silica in underground water is controlled by water saturation deficit of the aeration zone, precipitation and temperature fluctuations, mineral stability and bed rock reactivity (Dobrzynski Dariusz 2005). Although the exact form of dissolved silica is not known, it is always measured as  $\text{SiO}_2$  (Al-Rehaili et al., 2003). It has been calculated that the average concentration of silica in natural water ranges between 1.0 and 30.0 ml/L (Davis et al., 1964). It has been also shown that water ascending from deep reservoirs contain higher silica values than shallow origin. Silica content in the studied hot springs has the average concentration of 52.57 mg/l. This concentration is higher than the average calculated by (Davis et al., 1964). This indicates that the source of water reservoir is deep. 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). The increase in conductivity infers to the increase in salinity of the water (Hategekimana et al., 2020). The higher conductivity of hot spring water result from salinity or simply the concentrations of dissolved ions. The concentration of salinity is higher at location 1 compared to the sources of hot springs, this led to the increase in conductivity at location 1. 3 factors affecting the conductivity include; the concentrations of dissolved ions (salinity), type of ions, and temperature. The temperature facilitates the mobility of ions. Hot springs water is hot and this allows the dissolution of rocks in which they percolate hence increasing the concentrations of ions in water and the conductivity.

People usually use hot springs water in therapeutic activities. When swimming in water, their skins are extensively exposed to chemicals. Two pathways have been suggested for transport of chemicals across the stratum corneum (outermost layer of skin): one for lipophilic chemicals and the other for hydrophilic chemicals (Raykar et al., 1988). The extent of uptake through the skin will depend on a range of factors, including the period of contact with the water, the temperature of the water and the concentration of the chemical. For these reasons, the chemical composition of hot springs must be analyzed to understand the safety related issues. All the parameters measured in this research are lower than the maximum values suggested by the WHO for recreational water (Fig. 4). Ammonia and iron have lower concentrations compared to the minimum WHO standard concentrations. This has no impact on the health of the people using Hot springs water for recreation.

Table 4  
The comparison of chemicals from Hot spring and WHO, (2003) standards

No	Chemicals	WHO(min)	WHO( max)	Hot Spring Data
1	Ammonia(mg/l)	0.2	3	0.152
2	Silica(mg/l)	0	75	52.57
3	Conductivity( $\mu$ s/cm)	560	3250	2440
4	Salinity (ppt)	0.3	1.7	1.25
5	Alkalinity (eq/l)	2.7	1668	21.6
6	Iron (mg/l)	0.5	50	0.2
7	Phosphate (mg/l)	0.01	0.75	0.31
8	Sulfate (mg/l)	23.45	353.65	75.7

Therefore, basing on the measured parameters, swimming in Nyamyumba hot springs is trusted. However, the detailed analysis and continuous monitoring are recommended for the safety of people.

## Conclusion

This research aimed at studying the concentrations of chemical compositions of Nyamyumba hot springs water and compare to those of lake Kivu water. The location of Nyamyumba hot springs in the East African Rift System play a great role in controlling the rising of hot spring water. The heating of water maybe caused by magmatic chamber in the underground. Most of the chemicals in hot springs water resulted from rock-water interaction. This have been influenced by the temperature of the hot springs. It has been identified that chemicals have higher concentrations at the source than lake water due to the dissolution of rocks by circulating hot water. The results also showed that the use of Nyamyumba hot springs in swimming effect is safe when compared to the WHO standard concentrations of chemicals in recreational waters. However, a detailed study is advised to consider other chemicals especially carcinogenic chemical elements and other infectious biological organisms.

## Declarations

### Availability of data and materials

All the data are given in this manuscript.

### **Competing interests**

Not applicable

### **Funding**

Not applicable

### **Authors' contributions**

All the authors participated in sampling, laboratory works and manuscript drafting.

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## Figures

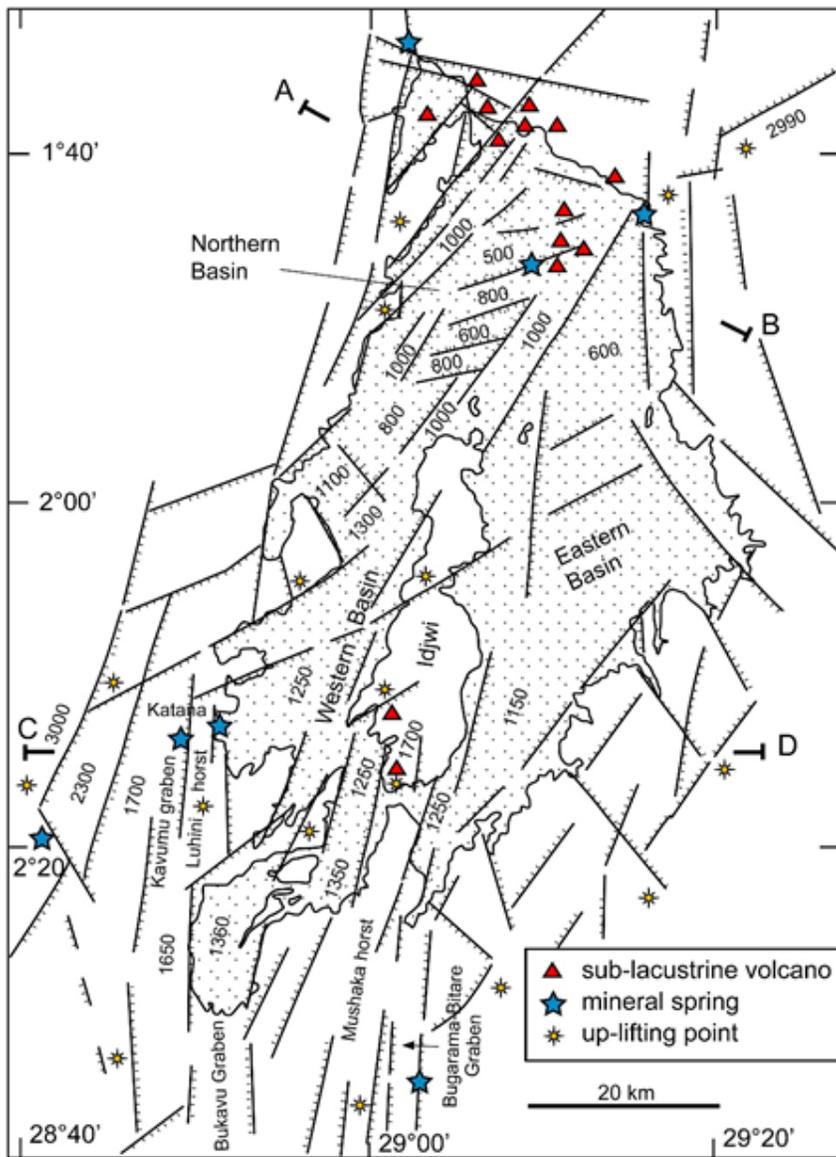
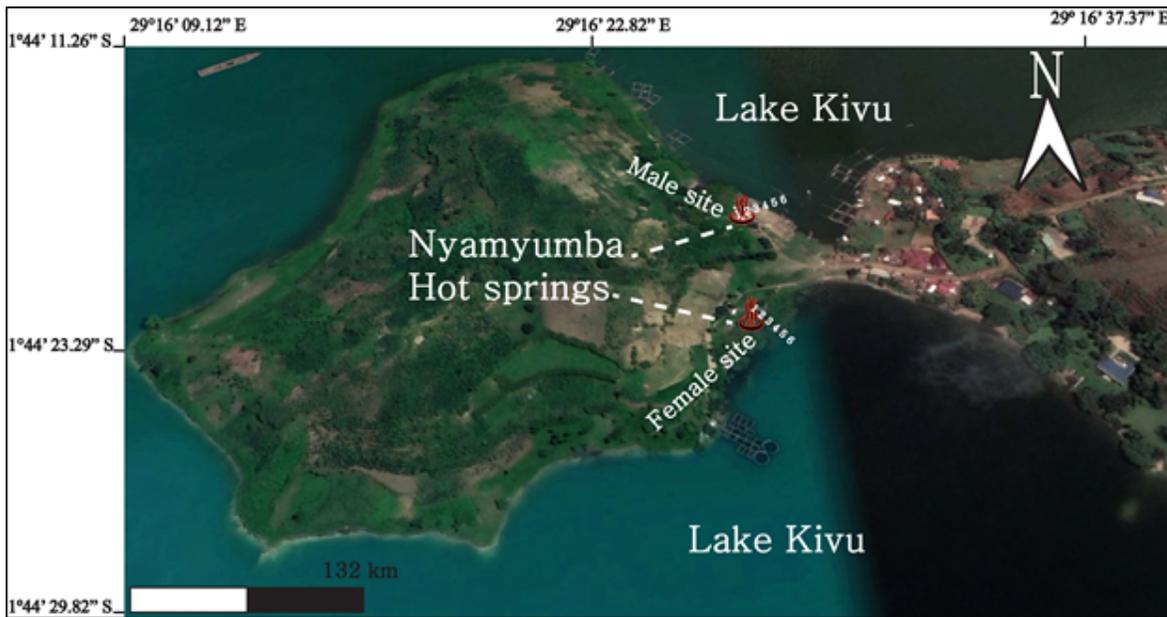


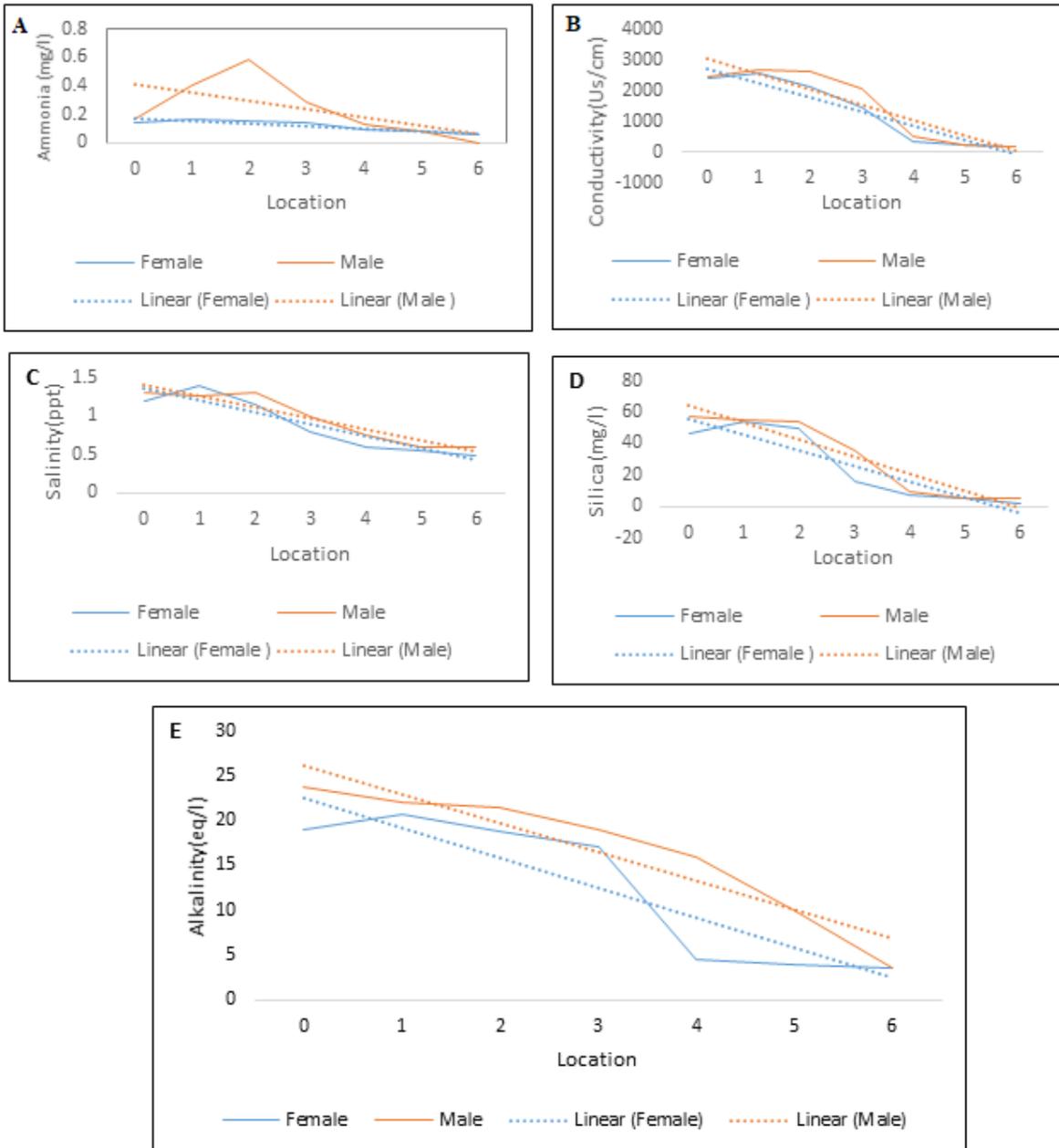
Figure 1

Structural map of the Kivu basin (Modified from Pouclet et al., 2016).



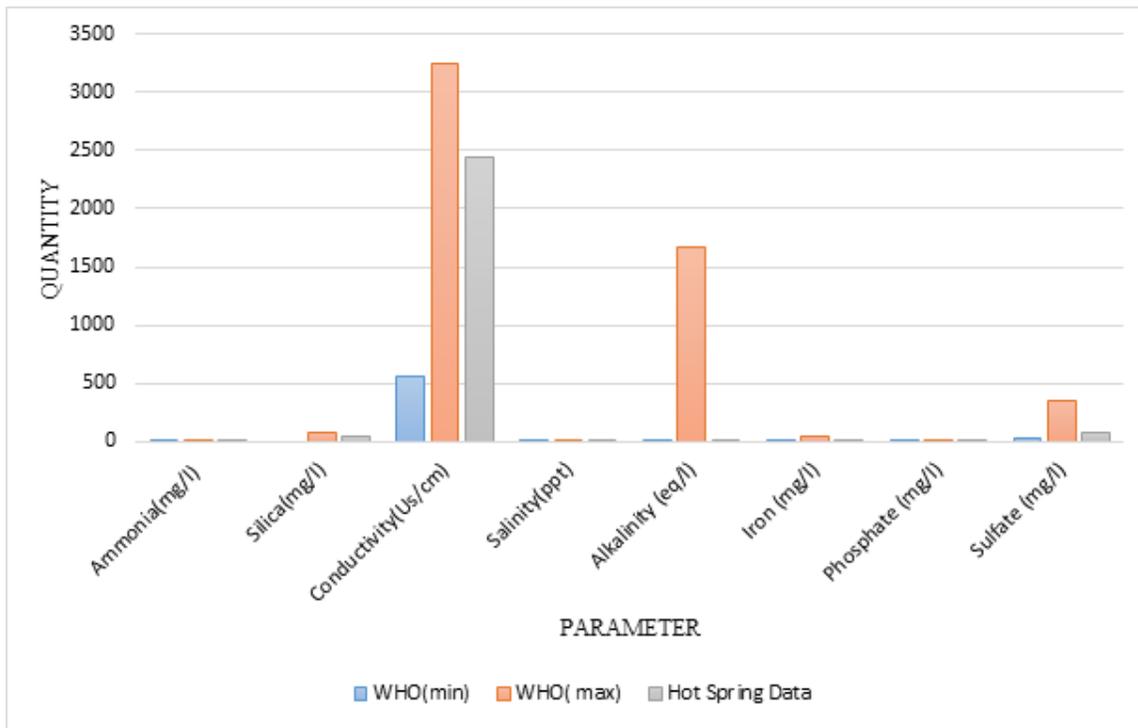
**Figure 2**

The location of Nyamyumba hot springs showing the location of the two sites (Female and Male) relative to Lake Kivu. Male and female names are based on the location reserved for male and female respectively. Numbers from 1 to 6 represents sampled locations.



**Figure 3**

Comparison of chemical composition of water samples taken at 6 locations at two sites (female and male). A, ammonia. B, conductivity. C, salinity. D, silica. E, alkalinity.



**Figure 4**

The comparison of the concentrations of chemicals at the hot springs and WHO standards for swimming water.