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Chapter

Characterization of Lake Kivu Water Chemistry and Its Environmental Impacts

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Abstract

Among the world's lakes, Lake Kivu, a rift lake in the western branch of the Eastern African Rift System, has significant reserves of dissolved chemicals. However, no research has been done on their vertical variation in lake and how they affect the environment. This proposed chapter will review earlier research to better understand the origin of Lake Kivu's chemical composition and its effects on the aquatic environment. Water samples were collected using Niskin bottles at various depths, as well as in various locations away from Nyamyumba hot spring sources. Hach kits and procedures were used to conduct chemical analyses on water samples. This study found that the majority of chemical concentrations rise with depth, primarily as a result of the deposition of organic matter. The sewage water from residential buildings, hospitals, runoff from agricultural activities, and rock-water interaction through dissolution process are the possible sources of chemicals discovered in Lake Kivu water. The levels of chemicals in the water of Lake Kivu at this time are less polluting and damaging to the aquatic environment. Therefore, it is important to implement a continuous monitoring strategy to stop eutrophication and other diseases linked to water pollution in humans.

Keywords: Lake Kivu, chemicals, water stratification, environment, eutrophication

1. Introduction

Over the last few decades, global awareness of lake eutrophication and aquatic ecological degradation has grown. The process of eutrophication refers to the change in the chemical properties of water caused by the accumulation of excess nutrients such as nitrogen and phosphorus. In this process, phytoplankton and other microorganisms are rapidly produced leading to the deterioration of water quality which is detrimental to aquatic ecology [1–3].

Water body chemistry results mainly from the interplay between diverse hydrological, geochemical, and biological processes controlled by either natural

or anthropogenic factors such as: lithology, climate, vegetation, relief, agricultural activities, and domestic or industrial discharge [4–7].

In this research, Lake Kivu which is a rift lake located in the western branch of the East African Rift System was considered (**Figure 1**). Like other lakes, Lake Kivu contains marine organisms (e.g. fishes) that should be environmentally protected through continuous monitoring of its water chemistry.

It is well known that the chemistry of water bodies varies with depth [8]. Numerous studies (e.g., [9–11]) were conducted to comprehend the chemistry of Lake Kivu while only focusing on surface chemistry; however, none of these studies ever made the connection between the vertical variation in chemistry and environmental pollution.

The water of East African rift lakes contains large amounts of dissolved gases such as carbon dioxide and methane, especially in Kivu Lake which is located between Rwanda and the Democratic Republic of Congo (DRC) (**Figure 1**). Lake Kivu is one of the largest carbon dioxide and methane gas reservoirs on earth [12, 13]. It was observed that the amount of CO_2 and CH_4 dissolved phase in Lake Kivu is 300 km^3 and 55 km^3 at standard temperature and pressure (gas volume at 0°C and 1 atm [14]. According to ref. [15], Methane is formed in three ways: (1) mantle-derived, (2) thermal maturation of organic matter, and (3) bacterial degradation of organic matter at the shallow depths. In the case of methane in Lake Kivu water column, the dominant methane-forming process is bacteria-mediated methanogenesis of CO_2 which is originated from volcanic activities.

Other than those gases, Lake Kivu contains several other chemicals including silica, phosphate, iron, sulfide, and ammonia which vary with depth [8, 9, 16]. Lake Kivu water is stratified where the divide between mixolimnion and monomolimnion occurs at a depth of around ~65 m [17] and ~ 45 m [8], respectively.

Lake Kivu waters are drained by different fluid sources and/or biochemical processes controlling water chemistry (i.e., water-rock interactions, bacterial activity) that is not homogeneously distributed all over the entire lake [8, 18, 19]. Furthermore, Hategekimana et al. [16] studied the chemistry of Nyamyumba hot springs located
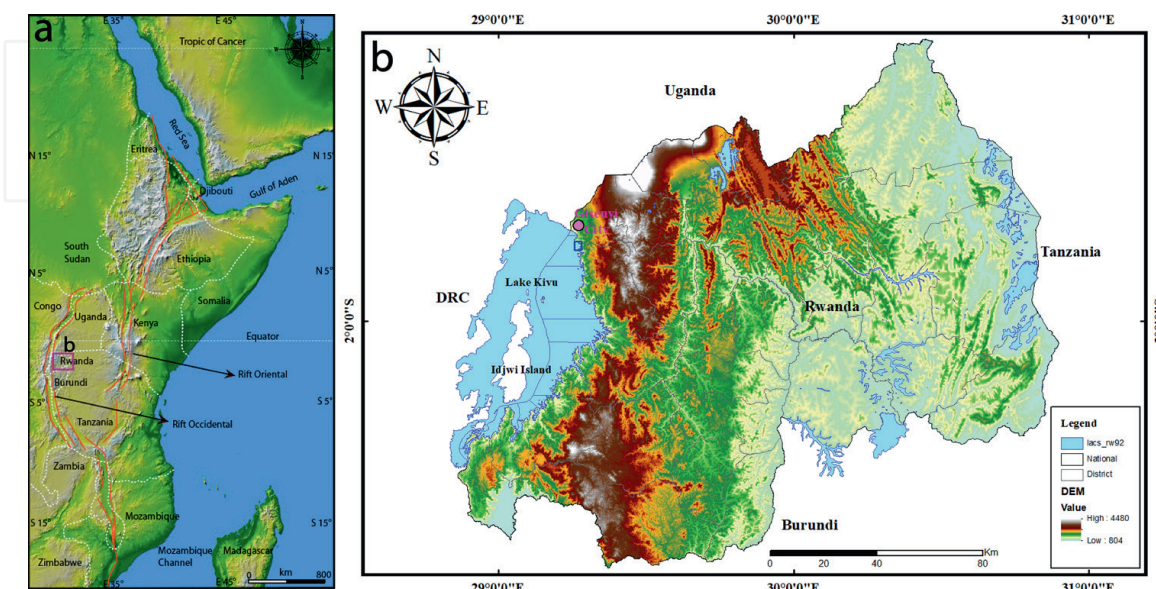

Figure 1.
Location map of Rwanda: (a) a map of Africa for Rwanda localization; (b) an elevation map of Rwanda in meters. The study area is shown by a blue rectangle. DRC stands for the Democratic Republic of Congo.

along the shores of Lake Kivu and interpreted that there is a contribution of these hot springs to the chemistry of Lake Kivu water.

In this chapter, we reviewed earlier research findings from Lake Kivu to identify the causes of its water chemistry while considering vertical chemistry variations and their corresponding environmental issues, particularly for aquatic and human life.

2. Geological, geochemical, and hydrogeological background of Lake Kivu

The lake's surface area is 2370 km^2, and its drainage basin is 4940 km^2 excluding the lake [20]. The majority of the drainage basin is made up of a river-active region (4255 km^2) that is dominated by humic ferralsols in the southwest, humic acrisols in the east, and haplic acrisols in the northwest and southeast [21].

Lake Kivu is one of the rift lakes located in the western branch of the East African Rift System. Different geodynamic processes, such as faulting and magmatism, influenced and contributed to the formation of the lake and various structures along Lake Kivu's margin (**Figure 1**).

The East African Rift System resulted from two mantle plumes beneath the Afar and Kenyan Plateau [22–24]. The tectonic uplift and an extension led to the creation of the East African Rift (EAR) [25], the best example of an active rift system. The plateaus are dynamically supported by the convective activity under the asthenosphere [26], providing heat transfer for partial melting of the lithospheric mantle. All of these parameters make the East Africa Rift System (EARS) a very good potential area for geothermal resources [27]. The western branch of the East African Rift System has a limited and localized volcanic product with a more diverse chemistry than the eastern branch.

The Kivu rift valley is composed of deep lacustrine basins and structural heights which are overlain by volcanic rocks [28] indicating the presence of a mantle plume beneath the lithosphere. The northern basin of Lake Kivu contains about 0.5 km of sediments which overlie a basement believed to be of crystalline rocks of Precambrian age [9].

Lake Kivu's deep waters are known to have high concentrations of carbon dioxide and methane. A trace amount of nitrogen is present at all depths, and the amount of dissolved oxygen decreases with depth. The pH of oxygenated waters is around 9, while that of anoxic waters is below 7.

Furthermore, the distribution of principal cations shows that salt content increases with water depth, and they are at a relatively uniform concentration level at a given depth in an independent geographical location [9].

3. Material and methods

Seven water samples were collected from the surface to a depth of 390 meters, with at depths of (0 m, 40 m, 90 m, 240 m, 290 m, 340 m, 390 m) using Niskin bottles suspended on a calibrated cord in Lake Kivu near Gisenyi city (**Figure 1**), with the assistance of a Kilindi boat. Other 14 samples were collected at different locations from Hot spring sources to Lake Kivu for the comparison of the chemistry of Hot springs and Lake Kivu waters.

Conductivity, temperature, and depth (CTD) sonde data were also gathered. Utilizing Hatch kits, water samples were examined in the lab of the Lake Kivu Monitoring Program.

With increasing salinity, conductivity—a metric of water's capacity to conduct electricity—increases [18]. Using a CTD Sonde, the conductivity of water samples was assessed in seven different locations. Comparing the dissolved ions and factors facilitating the dissolution at various locations is made easier by measuring the conductivity at each location.

Using Hach test kits and procedures, the concentrations of sulfate, iron, ammonia, silica, and phosphate as well as the alkalinity of the water were determined in water samples.

The silico-molybdate method (silica, high range [0–75.0 mg/L]) was used to determine the silica content. The samples were warmed to room temperature before being analyzed to determine the silica concentration. The silica standard solution contained 50 mg/L of SiO_2. Under acidic conditions, the sample's silica and phosphate reacted with the molybdate ion to form yellow silico-molybdic acid complexes and phosphormolybdic acid complexes. In order to dissolve the phosphate complexes, citric acid was added. The remaining yellow complex was measured to obtain the silica content.

Furthermore, a digital titrator was used to measure the alkalinity, or the water's ability to resist acidification. The sample bottles for phosphate analysis, in contrast to other chemicals, were first cleaned with a 1:1 hydrochloric acid solution and rinsed with deionized water. The mixing bottle was filled with the sample. One pillow of phenolphthalein indicator powder was added, then blended. Drops of a standard solution of sulfuric acid, 0.035 N, were added. After each drop, the solution was thoroughly blended to achieve colorlessness from pink. The alkalinity of phenolphthalein was calculated as $CaCO_3$ by multiplying the number of drops until the color changed by 20. One pillow of bromocresol green-methyl red powder was added, and the mixture was stirred. Drops of a standard solution of sulfuric acid, 0.035 N, were added. After every drop, the solution was thoroughly mixed once more, and drops continued to be added until the color changed from green to pink. The total number of drops for the whole procedure was calculated and multiplied by 20 to obtain the total alkalinity (methyl orange) as $CaCO_3$.

Using the method described above, a standard solution containing 500 mg/L of $CaCO_3$ was used. Water samples were collected and stored in plastic containers that had been acid-cleaned before the iron concentration was measured. No acid was added because the water samples were analyzed right away. The analysis made use of the Ferro Ver method for iron (0–3.00 mg/L). By adding 100 mg/L of Fe to 100 mL of deionized water and diluting 1.00 mL of iron standard solution, 1.0 mg/L of iron standard solution was prepared. The test was then conducted using the AccuVac Ampuls method.

Phosphorus concentration was determined by adding 25 mL of sample to a 25 mL sample cell. A 1 mL calibrated dropper was used to add the molybdate reagent. The addition of 1 mL of the amino acid reagent solution came next. The reaction took 10 minutes to complete and the sample was thoroughly mixed. The sample was added to the sample cell in a volume of 25 mL. The timer beeped, and mg/L PO_4 was shown. The cell holder was filled with the blank. The instrument cap was placed over the sample cell, and after pressing "zero," the cursor moved to the right and the reading of 0.0 mg/L PO_4 appeared. The prepared sample was put into the cell holder, then the instrument cap was put on top of it. After selecting "read," the cursor shifted to the right and the sample's final concentration was shown. To determine the concentration of each sample, this was finished. Reactive (0–30.0 mg/L PO_4 3) method was used for phosphorus analysis. A 50 mg/L as PO_4 3 phosphate standard solution was pipetted into a 50 mL volumetric flask to create a 10.0 mg/L phosphate standard. Deionized

water was used to dilute the sample to the desired volume. The procedure was carried out as described above, and a concentration of 10 mg/L was obtained.

By adding 5 mL of the sample to two tubes, the concentration of ammonia was also calculated. The left opening of the color comparator box received one tube, and the second tube received the ammonia salicylate reagent powder pillow. The powder was shaken out of the tube completely. An ammonia cyanurate reagent powder pillow was added after a short while, shaken, and after 15 minutes, a green color appeared. In the color comparator box, which was held up in front of the light source, the second tube was placed. By rotating the color disc, color matching was discovered, and the outcome was displayed in the scale window. Ammonium ions (NH_4^+) and unionized ammonia (NH_3) are the two different forms of ammonia that are found in water.

So, this method measures both NH_4^+ and NH_3 as ammonia nitrogen (NH_3–N). One mg/L NH_3–N of nitrogen ammonia standard solution was used. The mg/L NH_3 in the sample was calculated as follows: • mg/L NH_3 = ((mg/L NH_3–N × percent NH_3 of water sample at a given temperature and pH) ÷ 100) × 1.2 [29].

To calculate the salinity of the water samples, a CDC401 conductivity probe was employed. The probe was then dried with a lint-free cloth after being rinsed with deionized water. The shroud was put in place. The sensor was fully inserted into the sample when the probe was inserted. Shaking the probe removed air bubbles. It was shaken, then stirred while the salinity was measured.

Furthermore, the Sulfa-Ver 4 method for sulfate (0–70 mg/L) was used to complete the sulfate analysis. The method was initially calibrated using a 50 mg/L sulfate standard solution. Pipetting 1 mL of a Pour Rite ampule standard for sulfate (2500 mg/L) into a 50 mL volumetric flask produced the standard solution. Deionized water was used to dilute the sample. In this procedure, barium sulfate precipitate is created when sulfate ions react with the metal in Sulfa-Ver 4, a sulfate reagent. The stabilizing agent in Sulfa-Ver 4 holds the suspended precipitates, and the turbidity formed is proportional to the sulfate concentration.

4. Results and discussion

4.1 Lake Kivu water chemistry variation with depth

Hategekimana et al. [8] concluded that Lake Kivu water chemistry varies significantly along the depth profile. Lake Kivu exhibits a unique vertical density stratification that is driven by dissolved gasses and the influx of saline groundwater. Except for anaerobic microbial processes, biologic activity only occurs in the mixoliminion (upper 60–65 m of the lake) [8, 17].

According to Hategekimana et al. [8], Lake Kivu water chemistry varies significantly along the depth profile.

Phosphorus concentration range from 0 to 3 mg/L in Lake Kivu. It shows an abrupt change at around the depth of 45 m (**Figure 2a**). This concentration also changes at 240 m deep to the constant value of 3 mg/L. According to ref. [30], phosphate concentration between 40 and 120 mg/L can lead to environmental pollution. The concentrations recorded in this study are below that range indicating that Lake Kivu water is less prone to pollution.

Like other chemicals, silica concentration also shows a constant value up to 45 m deep. In the deeper part, silica content increased downward up to the depth of 390 m
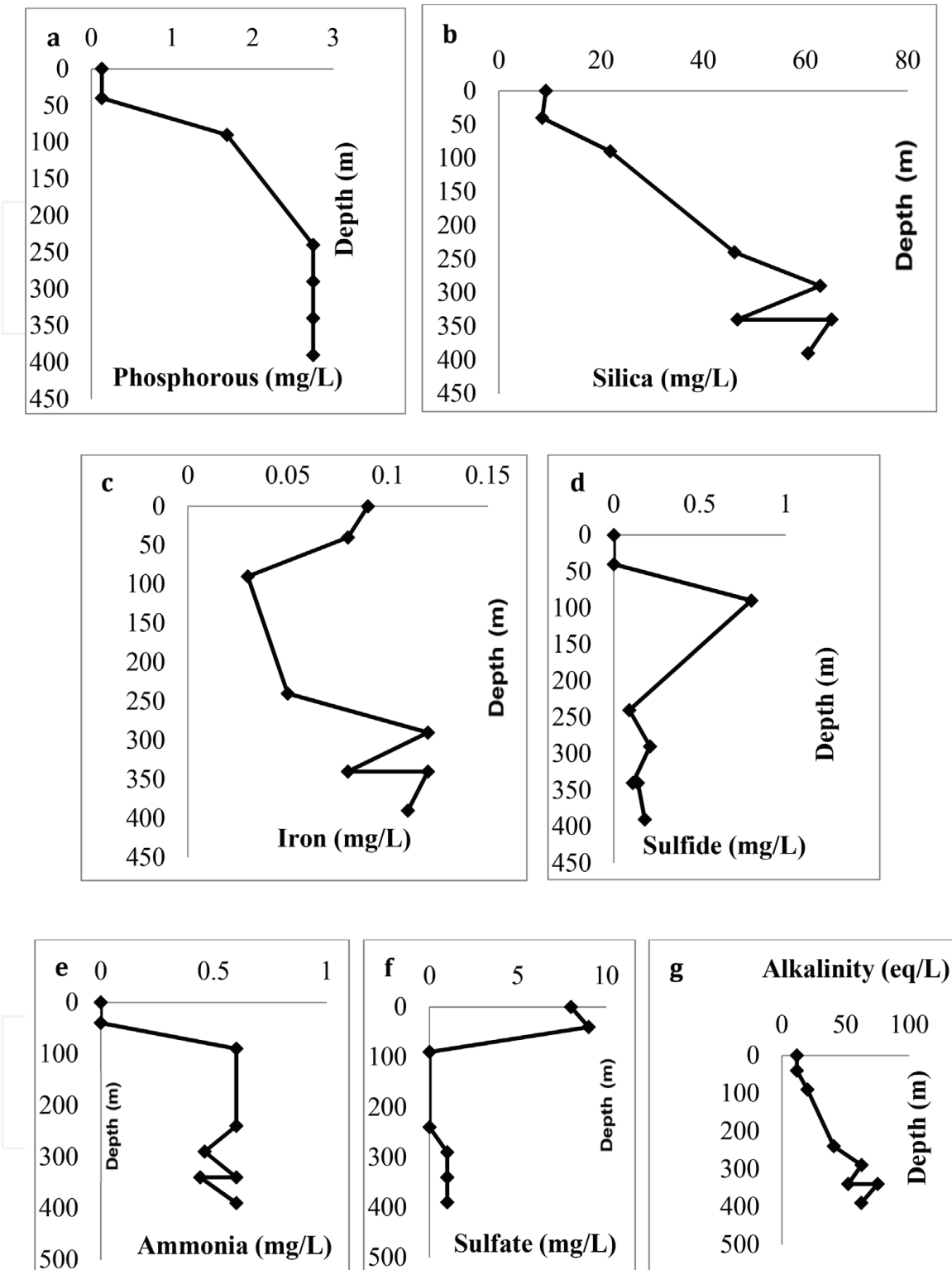
Figure 2.
The variation of Lake Kivu water chemistry with depth (modified from [8]).

(**Figure 2b**). The increase in silica concentration could be probably related to the sinking of dead diatoms [31].

Iron concentration in Lake Kivu water decreases with depth up to 90 m deep as shown in **Figure 2**. The concentration then increased downward up to the depth of 390 m (**Figure 2c**).

Sulfide and sulfate concentrations showed a decrease and increase respectively in the range from 0 to 45 m deep. This increase in sulfate concentration can be explained as the result of sulfide oxidation in an oxic environment. In contrast, the concentration of sulfate decreases in the region below 100 m. This reduction of sulfate increases the concentration of sulfide in Lake water (**Figure 2d** and **f**]. This change in concentrations can be used to determine the boundary between oxic and anoxic zones in Lake Kivu which is estimated at 45 m deep also consistent with the boundary set by Roland et al. [32].

Up to 45 m from the water surface, the ammonia concentration is 0 mg/L. The concentration suddenly increased with depth up to 100 m. Ammonia concentration is constant up to 390 m deep (**Figure 2e**). The increase in ammonia could be probably related to the deposition of organic matter in the deeper part.

The alkalinity increases with depth (**Figure 2g**) indicating the ability of Lake Kivu water to withstand the acidity. The alkalinity in Lake Kivu is in the range recommended by WHO [16, 33].

The concentration of dissolved oxygen reduces with depth but is still above the critical level of 3 mg/L for fish (**Figure 3a**); [34]. The decrease in dissolved oxygen is the result of bacterial oxygen consumption during the decomposition of organic substances including from public sewage and agricultural farms [10, 34].
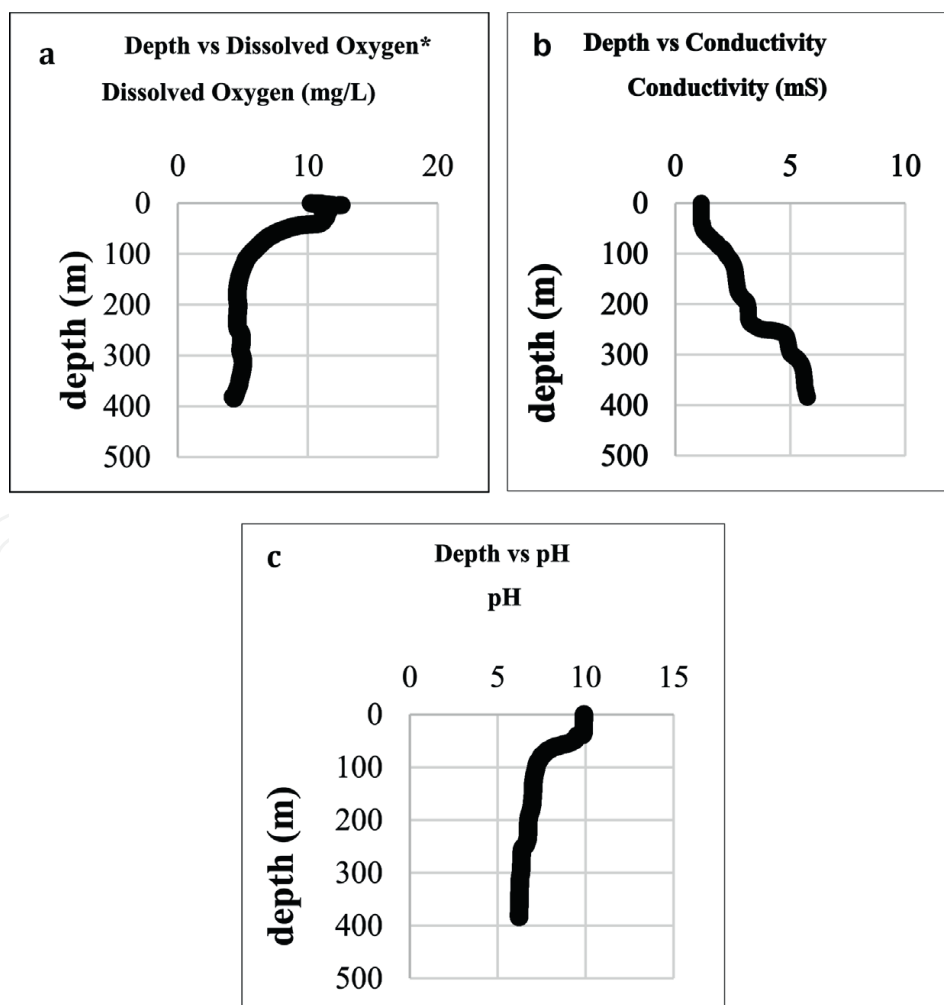

Figure 3.
The variation of Lake Kivu water chemistry with depth (modified from [8]).

Conductivity also increases with depth (**Figure 3b**). The increase in conductivity in Lake Kivu is probably related to the increased salinity [16]. The pH in **Figure 3c** indicated a decrease from 10 at the surface and tends to be neutral which is better for swimming.

4.2 The source of Lake Kivu water chemistry

This research disclosed that Lake Kivu water chemistry is mostly derived from sewage water from resident houses, hospitals, runoff from farming activities, and water-rock interaction through the dissolution process [8, 16].

In fact, Lake Kivu is located in the vicinity of two densely populated cities; Gisenyi (Rwanda) and Goma (DRC). Therefore, the chemistry of Lake Kivu water could be associated with the urbanization in those two cities.

A significant amount of wastewater is disposed of without proper treatment as a result of urbanization. To increase agricultural yields, farming activities also need more fertilizers. In addition, rivers carry domestic sewage and rainwater from agricultural fields to Lake Kivu. As a result, chemicals like nitrogen and phosphorus are present in higher concentrations in water. According to Ref. [35], higher concentrations worsen the aquatic environment and impair lakes' functionality, causing eutrophication.

Additionally, it was discovered that because the water from Nyamyumba Hot Springs is directly discharged into Lake Kivu, it affects the chemistry of the Lake (**Figure 4**) [16].

The higher concentration of silica (9.2 mg/L) found closer to the shoreline is probably the result of an influx of sediment from weathered bedrock (**Figure 2b**), especially close to stream and river outlets. Due to the dissolution of diatoms below the photic zone and the precipitation of calcite after it has been dissolved in water, deeper waters have higher concentrations of silica than surface waters [16].

Dissolved oxygen levels show a decrease near the water's surface that may be caused by photosynthetic processes (**Figure 3a**).
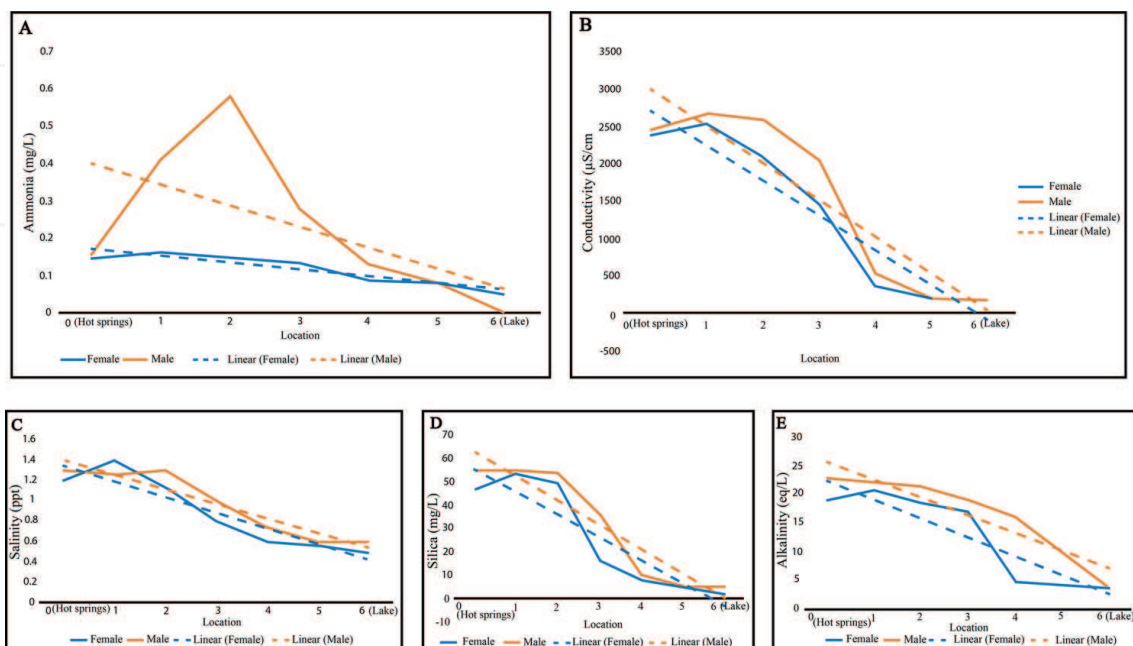

Figure 4.
The comparison of chemical concentrations in water from Lake Kivu and hot springs was adapted from [16].

With the inflow of saline groundwater, the conductivity, which reflects the salinity of the water, is increasing downward (**Figure 3b**). Saline groundwater is most likely alkaline, and alkalinity rises in the monimolimnion most likely because of calcium carbonate precipitation in the upper levels of the water column and mixolimnion dissolution (**Figure 3b**). Due to phytoplankton deposition in deep waters, the concentration of phosphorus typically rises with depth as depicted in **Figure 1**.

Figure 3 shows that as the age of deep waters increases, iron concentrations at a depth of about 100 m decrease. Due to the remineralization of iron, the concentration rises in the intermediate zone. After that, iron is taken out of the water and added to the sediments, where it cannot mix back in and cause replenishment. The main factor contributing to the increase in ammonia in the lake water may be the use of fertilizers, which cause runoff into waterways from farmlands (**Figure 2e**). Alkalinity was used to calculate the partial pressure of CO_2, but it is currently difficult to evaluate how accurate this calculation was.

The CO_2 flux calculation indicates that CO_2 moves upward in the water column, with the exception of the deepest measurements where it is more likely to move downward from 340 to 390 m.

The data collected by Schmidt in February 2004 and June 2018 differ from one another. At greater depths, the change is typically significant.

The pH level of lake water rises as a result of higher algal and plant growth that is influenced by rising temperatures or excess nutrients from farmland runoff and wastewater streams. The pH drops downward as the temperature rises, and the presence of carbon dioxide increases acidity, which in turn causes the pH to drop.

The sulfide concentration suggests that phytoplankton numbers are declining, temperatures are rising [36], there is an increase in organic matter in the sediment [37], the sediments are iron-poor [38], and the water is deeper and has less oxygen. Due to the implementation of control measures, the concentration of sulfide decreased between 2004 and 2018 and was a result of the slower organic matter sedimentation rate.

Over time, the phosphate concentration is lowering. This is because of the managed runoff, measures taken to keep livestock out of water sources, and a manure management plan.

When a significant amount of wastewater from homes and hospitals is dumped directly into a lake, it adds chemicals to the lake's water body, like phosphate and nitrates. Additionally, the use of fertilizers causes agricultural runoff, which raises the phosphate concentration in water. According to ref. [39], phosphorus increases the productivity of plankton and aquatic plants, which in turn feed larger organisms like zooplankton, fish, humans, and other mammals. The aquatic life that consumes phytoplankton and zooplankton will be greatly impacted by the gradual decrease in phosphate concentration. Some organisms will vanish at a later time.

4.3 Environmental impacts

According to this study, the concentration of the majority of chemicals in Lake Kivu water rises with depth. Aquatic life is impacted by the increased chemicals [8]. The increased pollutants in the water cause an overabundance of phytoplankton, which causes eutrophication. According to Ref. [8], when nitrogen and phosphorus levels rise in water, algae and other microorganisms grow erratically, which reduces the amount of oxygen in the water. This buildup of nutrients is essential for the eutrophication of Lake water. In order to prevent eutrophication in Lake Kivu, consistent monitoring should be considered.

The chemical concentration levels in Lake Kivu are lower than those in hot springs [16]. Because the chemical concentrations were below the WHO-recommended

ranges, they concluded that swimming in hot springs water was safe. As a result, swimming is also safe in Lake Kivu.

5. Conclusions

In Lake Kivu, where water chemistry varies greatly with depth, the mixolimnion and monolimnion boundary was found at a depth of about 40 meters, which is 20 meters closer compared to the previous researches. Hospitals and residential wastewater both add nitrates and sulfates to Lake Kivu's water supply. Additionally, farmlands contribute to an increase in the concentration of phosphates in water through water runoff. Increased chemical concentrations encourage the growth of plankton and other marine organisms, which can cause eutrophication, the depletion of available oxygen, and adverse effects on aquatic life. In order to safeguard Lake Kivu's aquatic ecosystem, we advise the relevant organizations to continue monitoring the lake's chemical state.

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Conflict of interest

The authors declare no conflict of interest.

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