Hydrochemical Characterisation of High-Fluoride Groundwater and Development of a Conceptual Groundwater Flow Model Using a Combined Hydrogeological and Hydrochemical Approach on an Active Volcano: Mount Meru, Northern Tanzania

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Abstract: This study characterises high-fluoride groundwater in the aquifer system on the flanks of Mount Meru, focusing on parts of the flanks that were only partially or not at all covered by previous research. Additionally, we analyse the impact of rainwater recharge on groundwater chemistry by monitoring spring discharges during water sampling. The results show that the main groundwater type in the study area is NaHCO₃ alkaline groundwater (average pH = 7.8). High F⁻ values were recorded: in 175 groundwater samples, the concentrations range from 0.15 to 301 mg/L (mean: 21.89 mg/L, median: 9.67 mg/L), with 91% of the samples containing F⁻ values above the WHO health-based guideline for drinking water (1.5 mg/L), whereas 39% of the samples have Na⁺ concentrations above the WHO taste-based guideline of 200 mg/L. The temporal variability in F⁻ concentrations between different seasons is due to the impact of the local groundwater recharge. We recommend that a detailed ecohydrological study should be carried out for the low-fluoride springs from the high-altitude recharge areas on the eastern and northwestern flanks of Mount Meru inside Arusha National Park. These springs are extracted for drinking purposes. An ecohydrological study is required for the management of these springs and their potential enhanced exploitation to ensure the sustainability of this water extraction practice. Another strategy for obtaining safe drinking water could be to use a large-scale filtering system to remove F⁻ from the groundwater.

Keywords: groundwater quality; groundwater resource management; alkaline groundwater; high fluoride concentration; volcanic aquifer; Mount Meru; Tanzania; East African Rift System
1. Introduction

In Tanzania, the availability of water is constricted by the increasing water needs due to a rapid population growth and ongoing climate change that is responsible for repeated drought episodes and the drying up of surface water bodies [1]. Groundwater is the main source of domestic water supply for both urban and rural areas in Tanzania, which consumes about 60% of total groundwater use whereas irrigation, mining and industrial use, livestock, and dry land fishing consume 40% [1]. The main challenges for groundwater quantity are depletion of shallow aquifers due to over-pumping, climate change, conflicting land uses, and uncontrolled urban development [1–3]. The main challenges for groundwater quality are high F\(^{−}\) concentration [3–7], contamination from domestic sewage from on-site sanitation, industrial effluents, leachates from solid waste dumpsites, leaking fuel filling and waste oils [2], and saltwater intrusion (saltwater pollution) in coastal areas due to over-pumping of the aquifer [2,8].

The East African Rift System contains some of the regions with the highest F\(^{−}\) concentrations in the world: Kenya, Tanzania, and Ethiopia [9]. High F\(^{−}\) concentrations exceeding the WHO health-based guideline for drinking water (1.5 mg/L) [10] have been reported in both the surface and groundwater in Tanzania [2–7,11], Ethiopia [12,13], and Kenya [14–16]. The regions are rich in highly weathered Na-K-rich volcanic rocks with low Ca-Mg content. The weathering and dissolution of these rocks in combination with other processes such as calcite precipitation produce NaHCO\(_3\) waters and alkaline groundwaters with pH > 7. These alkaline groundwaters with very low or absent Ca-Mg contents favor the dissolution of fluorite (CaF\(_2\)) or fluorapatite (Ca\(_5\)(PO\(_4\))\(_3\)F); hence, high F\(^{−}\) concentrations are observed [5,15]. However, this problematic is not only constrained to the East African Rift System: other African countries affected by the problem include Algeria, Ghana, Malawi, Nigeria, South Africa, Sudan, and Uganda [9,17].

In the Arusha volcanic region in northern Tanzania, within the eastern branch of the East African Rift System, several studies have been conducted on the water quality and hydrogeochemical characteristics of surface and groundwater around Mount Meru, with a focus on F\(^{−}\) concentration. The study by Kilham and Hecky [18] which covered the Ngarenanyuki river and the closed basin lakes (Momella lakes, Lake Tulusia and Lake Rishateni) on the slopes of Mount Meru identified that the chemical weathering of crystalline rocks is the primary hydrogeochemical process controlling water chemistry and F\(^{−}\) concentration in surface waters in the area. The study also identified that in the closed basin lakes, the evaporative concentration and carbonate precipitation are other processes playing a role. The study by Nanyaro et al. [11] on the eastern and southeastern flanks of Mount Meru identified that natural waters in some rivers, springs, alkaline ponds, and lakes are characterised by exceptionally high F\(^{−}\) values due to the weathering of F\(^{−}\)-rich nephelinitic and carbonatitic rocks and soil, whereas in the rivers draining the Mount Meru crater, gaseous emanations through mineral springs may also contribute to the high concentrations. Additionally, the study identified that the flushing of F\(^{−}\)-rich NaHCO\(_3\) evaporitic salt (locally called “magadi”) from the surface and top soil at the onset of the rainy season affects the F\(^{−}\) concentrations in shallow groundwater and in surface water bodies, due to the preceding continuous evaporative enrichment during the dry season. Furthermore, the study by Ghiglieri et al. [5] on the eastern and northern flanks of Mount Meru found that samples collected from springs, one borehole, and surface water showed that mineral dissolution, exchange processes, and precipitation of Ca\(^{2+}\) from supersaturated solutions, joined with local permeability and hydraulic gradients, control the distribution of F\(^{−}\) concentration in the area. Kitalika et al. [19] reported the variations of F\(^{−}\) concentrations in the four rivers (Temi, Nduruma, Tengeru, and Maji ya Chai) on the southern flank of Mount Meru. The study found that the F\(^{−}\) containing rocks exposed to pH above 7.6 display high leaching of F\(^{−}\) in solution, which gradually increased with the increase in pH, indicating that the dissolution of F\(^{−}\) in water is a function of pH. The study by Chacha et al. [6] on the southern flank of Mount Meru found that high F\(^{−}\) concentration and general groundwater chemistry (NaHCO\(_3\) water type) are more controlled by aquifer
lithology than by anthropogenic activities. This study identified two potential aquifers in the area, both containing significant concentration of F\textsuperscript{−}. Additionally, the study by Makoba and Muzuka [7] on the northern and southeastern flanks of Mount Meru found that surface and groundwater chemistry are controlled by geology, water–rock interaction time, and climatic conditions. This study found that the aquifer composed of fractured mafic volcanics, breccia, and tuffs shows low total dissolved solids (TDS) and F\textsuperscript{−} values compared to the aquifer composed of lahars, which are susceptible to weathering and hence lead to high TDS and F\textsuperscript{−} values. These lahars have been re-interpreted as debris avalanche for a main part by Delcamp et al. [20]. The study also recognised the contribution of anthropogenic pollution in few cases.

The present research investigates the hydrochemistry of high-fluoride groundwater on the eastern, northern, western, and southwestern flanks of Mount Meru. Parts of the western and southwestern flanks were partially covered by previous studies, whereas the far east of the eastern flank (i.e., on the northern flank of Ngurdoto crater) was not investigated before. The hydrochemical characterisation is presented in this paper. The detailed study of hydrochemical processes, resulting in the observed groundwater compositions, and the origin of fluoride in the groundwater, is the subject of a parallel paper (Bennett et al., in preparation). Moreover, the study analyses the impact of rainwater recharge on the groundwater chemistry by monitoring spring discharges during water sampling, which has not been previously characterised in the area.

2. Materials and Methods
2.1. Study Area
2.1.1. Location, Topography, and Climate

The study area covers the eastern, western, and northern flanks of Mount Meru volcano, and it occupies about 1000 km\textsuperscript{2} in the Arusha region, northern Tanzania (Figure 1). The relief map of Mount Meru in Figure 1 was derived from the Advanced Spaceborne Thermal Emission and Reflection Radiometer Global Digital Elevation Model Version 2 (ASTER GDEM 2), with 30-meter spatial resolution [21]. Mount Meru is situated in the Arusha National Park (ANAPA) just north of the city of Arusha. It is located 70 km west of Mount Kilimanjaro. The city of Arusha has a population of 416,442 inhabitants, while the Arusha district and Meru district have populations of 323,198 and 268,144 inhabitants, respectively [22] (p. 26). The study covers most parts of the Meru and Arusha districts.

The topography of the study area is dominated by Mount Meru, which is a steep stratovolcano with a summit culminating at 4565 m summit [23], but the highest elevation in the relief map in Figure 1 is 4532; this is due to the limitation of the ASTER GDEM 2 dataset. Our study area covers most of its slopes. The eastern flank of Mount Meru is incised by a deep valley formed by a catastrophic sector collapse that left a horseshoe-shaped valley now occupied by an ash cone that last erupted in 1910 [20]. Multiple parasitic cones are notable features in the vicinity [20,23,24].

Rainfall data from four existing rainfall stations—Agricultural Seed Agency (ASA) Farm at Ngaramtoni with 50 years data trend (1969–2018), Arusha Airport with 51 years data trend (1960–2010), Arusha Urban Water Supply and Sanitation Authority (AUWSA) with 27 years data trend (1992–2018), and Tengeru Livestock Institute with 29 years data trend (1990–2018)—were used to analyse long-term trends and the amount of rainfall in the study area. The stations cover the southern and southwestern flanks. The average monthly rainfall data show that the area experiences a bimodal rainfall pattern (Figure 2a). The long “masika” rains extend from late February to late May, and the short “vuli” rains extend from early November to early January. The dry “kiangazi” season is from June to October.
Figure 1. (a) Map of Africa showing the location of Tanzania (Source: CIA [25], the image is copyright free), (b) map of Tanzania showing the Arusha region (Source: Wikipedia [26], the image is under an open access Creative Commons CC BY 4.0 license; credit line: Sémhur/Wikimedia Commons/CC-BY-SA-3.0) and (c) map showing the spatial distribution of inventoried water points in the study area (water points with label were sampled for chemical analysis).
Figure 2. (a) Average monthly rainfall for the four existing rainfall stations and (b) average monthly rainfall for the four new installed rainfall stations.

The average annual rainfall at the two stations on the southwestern flank of Mount Meru; ASA Farm and Arusha Airport, is 800 mm and 822 mm, respectively. On the southern flank, the average annual rainfall at the two stations, AUWSA and Tengeru, is 942 mm and 981 mm, respectively. Four newly installed rainfall stations, each with 2 years of data trend (2019 and 2020), were used to analyse and compare the amount of rainfall on different flanks. Two stations are at Ngaramtoni (ASA Farm and Olmotonyi), one at Mamsa and one at Ngarenanyuki. The stations cover the southwestern, western, and northeastern flanks. Figure 2b shows the average monthly rainfall for the stations. The average annual rainfall at the two stations on the southwestern flank, ASA Farm and Olmotonyi, is 977 mm and 1232 mm, respectively, whereas on the western flank (at Mamsa), it is 905 mm and on the northeastern flank (at Ngarenanyuki), it is 638 mm. The southern and eastern flanks of Mount Meru (windward sides) receive more rainfall than the western and northern flanks. The areas in the windward sides (eastern and southern flanks) experience a subtropical highland climate, while areas in the leeward sides (northern flank) experience a semi-arid climate (steppe climate). The temperature typically ranges from 13 to 30 °C with an average annual temperature of about 25 °C [6].

2.1.2. Geological and Hydrogeological Setting

Mount Meru is considered as an active stratovolcano located within the Northern Tanzanian Divergence Zone of the eastern branch of the East African Rift. It is characterised by alkaline magmatic activity, which is typical within the East African Rift System [4,20,23]. A large sector of its east flank was lost in the early Holocene due to a major collapse associated with the formation of large-scale debris avalanche deposits (DADs) between the base of Mount Meru and Kilimanjaro [20]. Meru last erupted in 1910 AD when a small amount of ash was ejected for a few days from the ash cone located within the large valley formed by the collapse. Significant fumarolic activity was recorded at the ash cone area until 1954 [23].

Most rocks within the area are Pleistocene volcanic-sedimentary sequences, but older sequences date back to the Miocene-Pliocene [4,23,24,27]. The lithology in the study area is dominated by volcanic rocks lava flows, pyroclastic, and debris avalanche deposits from the Mount Meru, with some alluvium, alluvial fan, and lake deposits found around the volcano base (Figure 3). Lava flows are found mainly at higher elevations on the main Mount Meru cone and on the southern flank, while the DADs, ash deposits, alluvium, alluvial fan deposits, and lake deposits are found at lower elevations at the base of Mount Meru. Pyroclastic deposits are mainly found on the western flank, whereas DADs are dominant on eastern and northern flanks. No crystalline basement rocks are exposed in the area, but Wilkinson et al. [23] reported that pegmatite and gneiss were recorded in a water borehole log west of Ngarenanyuki (northeastern part of the study area) at a depth...
of about 15 m, implying that metamorphic rocks underlie the northern part of the study area at shallow depth.

Figure 3. Geological map of the study area (modified after Wilkinson et al. [23] and Delcamp et al. [20]), indicating different geological formations and spatial distribution of F⁻ concentrations of sampled water points. The geological descriptions are based on Wilkinson et al. [23] with updates from Delcamp et al. [20], who re-interpreted the deposits that had originally been mapped as lahar, as debris avalanche deposits (DADs). The deposits that had originally been mapped as tholoids by Wilkinson et al. [23] are now re-interpreted as lava domes in this study.
Existing borehole completion reports and field stratigraphic descriptions of subsurface sediments during the digging of new hand-dug wells were used to characterise the geology of the aquifers. On the northeastern flank, data from one borehole at Mkuru (depth of around 65 m) described by Ghiglieri et al. [4] and three hand-dug wells—one at Mkuru (depth of 23 m) and two at Uwiro (depth of 4 m and 10 m)—were used to characterise the geology of the aquifer, whereas on the northern flank of Ngurdoto crater, data from two hand-dug wells were used: one at Nkoasenga (depth of 8 m) and one at Leguruki (depth of 5 m). On the western flank, data from two hand-dug wells at Mamsa (depth of 39 m and 42 m) were used, whereas on the southwestern flank, data from two boreholes (depth of 115 m and 150 m) and eight hand-dug wells (depth range: 12–39 m) at Ngaramtoni were used. On the northeastern and southwestern flanks, there are two aquifers: a shallow and a deep aquifer. On the northeastern flank, the shallow aquifer in some area is unconfined and composed of debris avalanche deposits, while in another area, it is semi-confined and composed of weathered fractured lava with thickness more than 3 m, whereas the deep aquifer is confined and composed of weathered fractured lava with thickness more than 30 m. On the southwestern flank, the shallow aquifer is unconfined and composed of pyroclastic deposits with thickness more than 8 m, whereas the deep aquifer is semi-confined and composed of weathered fractured lava and weathered pyroclastic deposits with thickness varying from 65 to 100 m. On the western flank, the shallow aquifer is unconfined and composed of weathered fractured lava with thickness more than 3 m, whereas on the northern flank of Ngurdoto crater, the shallow aquifer is unconfined, and it is composed of debris avalanche deposits with thickness more than 7 m. The geomorphology of the landscape in the study area plays a great role in controlling the groundwater flow paths. The general groundwater flow system on each flank is involving a multidirectional flow from the higher elevation areas, including the parasitic cones, towards the lower areas.

2.2. Inventory of Water Points

Four field campaigns were conducted during July–September 2017, March–September 2018, February–August 2019, and April–December 2020. A total of 211 water points (205 groundwater and 6 surface water) were mapped and inventoried with the aim to quantify and characterise the groundwater resources on the flanks of Mount Meru (Figure 1). The 205 groundwater points consist of 104 hand-dug wells (depth range from 0.7 to 50 m), 68 springs, and 33 boreholes (depth range from 48 to 170 m). In this study, a well with depth greater than 50 m is considered as deep well; therefore, all hand-dug wells are classified as shallow wells, whereas one borehole is classified as a shallow well, and the rest are classified as deep wells. Shallow wells characterise the shallow aquifer, while deep wells characterise the deep aquifer. The 6 surface water points consist of 1 water pond, 1 stream (Njekukumia stream), 1 river (Ngarenanyuki river), and 3 lakes (Big Momella lake, Small Momella lake, and Lake Rishateni). For each water point, the following information was recorded: elevation, geographical coordinates (GPS), lithology, year of well/borehole construction, well/borehole depth and groundwater level (for the well/borehole), spring setting and spring discharge (for the spring), and uses of water. Each water point was identified by an alphanumeric code.

The distribution of water points is in six clusters located at Ngaramtoni and near Arusha town (southwestern flank), Mamsa (western flank), Oldonyo Sambu (northwestern flank), Mkuru, Uwiro, and Ngarenanyuki (north and northeastern flanks), eastern part of the Arusha National Park (eastern flank), and Nkoasenga and Leguruki (far east of the eastern flank). In Ngaramtoni and near Arusha town, the area is dry with scarce vegetation; there are many shallow hand-dug wells and boreholes but with few springs. In Mamsa, the area is dry with scarce vegetation, there are a few shallow hand-dug wells and only one spring on the slope of Mount Meru inside the Arusha National Park. In Oldonyo Sambu, the area is very dry with scarce vegetation, two boreholes with depths of 55 m and 150 m respectively are found, but both did not reach groundwater, nor was any shallow hand-dug well found; this is probably due to the presence of very thick porous pyroclastic
deposits, which led to deeper groundwater flow, and there is only one spring at the base of the Mount Meru with other springs located on the slope of the Mount Meru inside the Arusha National Park. In Mkuru, Uwiro, and Ngarenanyuki, the areas are very dry with few vegetation, there are few shallow hand-dug wells, boreholes, and springs with only one perennial river called “Ngarenanyuki River”. On the eastern part of Arusha National Park, the area is very densely vegetated and green; there are numerous springs with two hydrothermal springs (S42—Small Njekukumia and S43—Big Njekukumia) located just at the foot of the ash cone on the collapsed eastern flank of Mount Meru. In this study, the names ‘Small’ and ‘Big’ specified to the Njekukumia springs were ascribed to their discharge. Their discharges were qualitatively assessed; the Big Njekukumia has high flow discharge compared to the Small Njekukumia. The springs have been characterised as hydrothermal springs by Ghiglieri et al. [5] and Nanyaro et al. [11]; they join to form the Njekukumia stream, which discharges its water to the Ngarenanyuki river. At lower elevations, in the discharge area, three lakes are found (L1—Small Momella Lake, L2—Big Momella Lake, and L3—Lake Rishateni). In Nkoasenga and Leguruki, the areas are very densely vegetated and green; there are several shallow hand-dug wells and only two springs. The hydrogeology of these areas is mainly influenced by the Ngurdoto crater due to its proximity and not the main Mount Meru.

2.3. Sampling

Water samples were collected in high-density polyethylene bottles with a capacity of 250 ml and thoroughly pre-washed with water to be sampled. During sampling, an icebox cooler was used in the field to keep and transport samples before being stored under refrigeration. The samples were transported to Belgium and analysed for their chemical properties at the Laboratory for Applied Geology and Hydrogeology, Ghent University. A total of 181 water samples (175 groundwater and 6 surface water) from 128 water points were collected for chemical analysis from the four field campaigns. All 6 inventoried surface water points were sampled. It should be mentioned that the six surface water samples are not representative of all surface water in the study area, since they were sampled because of their known high F⁻ concentrations. Table 1 summarises the distribution of groundwater samples that were collected from the inventoried groundwater points. From the 205 inventoried groundwater points, 60% (n = 122) of the points were sampled. The sampling of the water points ensured a representative coverage of the whole study area. Few of the inventoried boreholes were sampled, because most of them are cased, as they are not in use, and others are connected into storage tanks that are inaccessible. Some of the hand-dug wells and springs were sampled more than once; this was done in order to study the variations with time in the F⁻ concentrations in the groundwater. The selection of water points to be studied more in detail was based on the sampling of water points so as to have a representative coverage of the whole study area. The springs found in the Arusha National Park were not easily accessed due to their remoteness; thus, they were sampled once. All sampled hand-dug wells (shallow wells) were characterised as shallow aquifers, whereas one sampled borehole is a shallow well was characterised as a shallow aquifer, and the other three sampled boreholes are deep wells are characterised as deep aquifers.
Table 1. Distribution of groundwater samples that were collected from the inventoried groundwater points.

| Type of Water Points | Number of Inventoried Points | Number of Sampled Points | % of Sampled Points | Number of Samples | Number of Samples per Water Point | Characteristic of Sampled Wells/Boreholes |
|----------------------|------------------------------|--------------------------|---------------------|------------------|-----------------------------------|------------------------------------------|
| Hand-dug wells       | 104                          | 66                       | 63                  | 86               | 3 points were sampled three times | Shallow wells                            |
|                      |                              |                          |                     |                  | 14 points were sampled twice     |                                          |
|                      |                              |                          |                     |                  | 49 points were sampled once      |                                          |
| Springs              | 68                           | 52                       | 68                  | 85               | 2 points were sampled five times |                                          |
|                      |                              |                          |                     |                  | 10 points were sampled three times|                                          |
|                      |                              |                          |                     |                  | 5 points were sampled twice      |                                          |
|                      |                              |                          |                     |                  | 35 points were sampled once      |                                          |
| Boreholes            | 33                           | 4                        | 12                  | 1                | Samples once                     | Shallow well                              |
|                      |                              |                          |                     |                  | 3                                 | Each point sampled once                  | Deep wells                                |

2.4. Field Measurements

During the four field campaigns conducted in the framework of this study, a portable Aquaread AP-700 device was employed in the field to measure in situ physicochemical properties of water samples including temperature, pH, oxidation-reduction potential (ORP), dissolved oxygen (DO), and electrical conductivity (EC). The device also records geographical coordinates (GPS), elevation, date, and time of measurement. Additionally, the device gives the calculated readings of resistivity (RES), total dissolved solids (TDS), salinity (SAL), and seawater specific gravity (SSG) based on the EC and temperature measurements. A total of 174 in situ measurements from 126 water points were recorded from the four field campaigns.

2.5. Laboratory Analysis

Chemical analyses were performed in the Laboratory for Applied Geology and Hydrogeology at Ghent University. Different analytical methods were applied to determine the concentration of various hydrochemical parameters. The pH was measured using a pH meter while the electrical conductivity was measured using an electronic EC meter. The samples that were used for cation analysis after filtration (0.45 µm) were brought to a pH of around 2 prior to analysis by adding ultra-pure nitric acid. The following cations were measured: sodium (Na⁺), potassium (K⁺), magnesium (Mg²⁺), iron (Fe²⁺/Fe³⁺), manganese (Mn²⁺), ammonium (NH₄⁺), and silicon (Si⁴⁺). Concentration of Na⁺, K⁺, Ca²⁺, Fe²⁺/Fe³⁺, Mg²⁺, Mn²⁺, and Si⁴⁺ were determined in a diluted solution using flame atomic absorption spectroscopy (AAS) using a Varian Zeeman Spectra AA 400. The concentration of NH₄⁺ was measured using the molecular absorption spectrophotometer UV-VIS Shimadzu UV mini 1240. Anions (chloride (Cl⁻), sulphate (SO₄²⁻), nitrate (NO₃⁻), and nitrite (NO₂⁻)) were measured using the molecular absorption spectrophotometer UV-VIS Shimadzu UV mini 1240. Carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) contents were obtained by titration with dilute HCl acid, but during the analysis, the tipping point between them at pH = 8.2 was not determined analytically with sufficient accuracy, suggesting that the distribution of HCO₃⁻ and CO₃²⁻ in the samples is strongly variable with pH; hence, it was impossible to measure it accurately using pH as the criterion. Therefore, in this study, the total alkalinity (TA), which is the sum of HCO₃⁻ and CO₃²⁻, is expressed as mg/L HCO₃⁻. The fluoride (F⁻) was measured using an ion selective electrode (ISE). Detailed descriptions of the different analytical methods are extensively explained in the laboratory manual and in standard methods for examination of water and wastewater [28].
2.6. Data Processing and Analysis

The hydrochemical characterisation of groundwater in the study area has been investigated based on the analysis of a Schoeller diagram, Piper diagram, bivariate diagrams, and statistical analyses.

The concentrations of $F^-$ determined in water samples were compared to the maximum permissible limits for drinking water set by the WHO (1.5 mg/L) and Tanzanian standards (4.0 mg/L).

Major physicochemical parameters were tested for normality using IBM SPSS Statistics 27 software. Considering that all were not normally distributed, the Spearman’s correlation was used for analysis. Since the IBM SPSS Statistics 27 reported all the significant $p$-values for this test as 0.000 (only in three decimal places), the calculation of $p$-values in more decimal places was done using Microsoft Excel 2019. A Mann–Whitney U Test was carried out to assess whether the $F^-$ concentrations in September 2017 and September 2018 (two different dry seasons) are significantly different.

3. Results and Discussion

Table 2 summarises descriptive statistics: minimum, maximum, mean, median, standard deviation, and coefficient of variation for the physicochemical parameters of the water samples analysed in this study. On average, the springs show low concentrations of the different hydrogeochemical parameters followed by the deep wells, shallow wells, and lastly the surface waters (river, water pond, stream, lakes) except for NH$_4^+$, NO$_3^-$, and NO$_2^-$, which are depleted in surface waters due to their uptake by aquatic organisms. All the physicochemical parameters show high variability as revealed by very high coefficients of variation; this may be due to the complexity of groundwater flow passing through different geological formations of variable weatherability [29] and variable residence times. Overall, the water samples contain concentrations in the order of Na$^+$ > K$^+$ > Ca$^{2+}$ > Mg$^{2+}$ > Fe$^{2+}$/Fe$^{3+}$ > Mn$^{2+}$ > NH$_4^+$ for cations and HCO$_3^-$ + CO$_3^{2-}$ > SO$_4^{2-}$ > Cl$^-$ > NO$_3^-$ > F$^-$ > NO$_2^-$ for anions. Figure 4 shows the concentrations of major ions for all analysed water samples in this study. Na$^+$ is the dominant cation in 99% ($n = 180$) of the analysed water samples ($n = 181$), whereas HCO$_3^-$ + CO$_3^{2-}$ is the dominant anion in all samples; therefore, the main water type for both surface water and groundwater in the area is NaHCO$_3$ (Figure 5) [30].
Table 2. Summary of descriptive statistics for major and minor physicochemical parameters of water samples (units are in mg/L for the ions, except for Mn\textsuperscript{2+}, NH\textsubscript{4}\textsuperscript{+}, and NO\textsubscript{2}\textsuperscript{−} which are in µg/L, the pH is unitless and EC is in µS/cm at 25°C. n: number of samples; SD: standard deviation; CV: coefficient of variation; * as mg/L HCO\textsubscript{3}−).

| Water Type          | pH | EC  | Na\textsuperscript{+} | K\textsuperscript{+} | Ca\textsuperscript{2+} | Mg\textsuperscript{2+} | Fe\textsuperscript{2+}/Fe\textsuperscript{3+} | Mn\textsuperscript{2+} | NH\textsubscript{4}\textsuperscript{+} | F\textsuperscript{−} | Cl\textsuperscript{−} | SO\textsubscript{4}2− | NO\textsubscript{3}− | NO\textsubscript{2}− | (HCO\textsubscript{3}− + CO\textsubscript{3}2−) | PO\textsubscript{4}3− | SiO\textsubscript{2} | TDS |
|---------------------|----|-----|-----------------------|----------------------|-----------------------|-----------------------|---------------------------------|------------------|----------------------|-----------------|----------------|----------------|-------------|-------------|---------------------|------|--------|-----|
| Eastern flank       |    |     |                       |                      |                       |                       |                                 |                  |                      |                 |                |                |             |             |                     |     |        |     |
| Springs (n = 16)    |    |     |                       |                      |                       |                       |                                 |                  |                      |                 |                |                |             |             |                     |     |        |     |
| Min                 | 7.1| 105 | 15.1                  | 3.5                  | 1.0                   | 0.2                   | 0.0                            | 0.0              | 0.1                  | 1.7             | 0.0            | 0.0             | 44.5        | 0.00        | 27.2              | 117  |
| Max                 | 8.6| 1183| 425                   | 58                   | 11.9                  | 0.9                   | 0.14                           | 7.0              | 10                   | 274             | 19             | 68              | 5.4         | 11          | 330                | 39.1 |
| Mean                | 7.7| 339 | 80                    | 19.6                 | 5.8                   | 0.4                   | 0.06                           | 2.0              | 2.0                  | 36.1            | 6.6            | 9.2             | 2.3         | 1.0         | 137                | 38.8 |
| Median              | 7.7| 231 | 28.4                  | 13.4                 | 5.8                   | 0.4                   | 0.05                           | 0.0              | 0.0                  | 1.4             | 5.0            | 0.4             | 2.2         | 0.0         | 114                | 37.5 |
| CV (%)              | 0.4| 327 | 131                   | 16.6                 | 3.6                   | 0.2                   | 0.03                           | 3.0              | 3.0                  | 89              | 4.8            | 23              | 1.3         | 3.0         | 82                 | 7.6  |
| Hydrothermal springs|    |     |                       |                      |                       |                       |                                 |                  |                      |                 |                |                |             |             |                     |     |        |     |
| Min                 | 8.2| 3650| 899                   | 179                  | 8.4                   | 1.6                   | 0.07                           | 0.0              | 0.0                  | 301             | 100            | 260             | 2.5         | 4.0         | 1287               | 3070 |
| Max                 | 8.5| 4590| 1123                  | 216                  | 3.8                   | 2.3                   | 0.04                           | 6.0              | 16                   | 95.2            | 148            | 418             | 0.9         | 0.0         | 2170               | 3421 |
| Mean                | 8.4| 4033| 1012                  | 203                  | 4.1                   | 2.4                   | 0.02                           | 2.0              | 2.0                  | 450             | 167            | 270             | 1.0         | 25.0        | 3067               | 5362 |
| Far east of the eastern flank (Northern flank of Ngurdoto crater) |    |     |                       |                      |                       |                       |                                 |                  |                      |                 |                |                |             |             |                     |     |        |     |
| Springs (n = 2)     |    |     |                       |                      |                       |                       |                                 |                  |                      |                 |                |                |             |             |                     |     |        |     |
| Min                 | 7.4| 481 | 72                    | 17.8                 | 5.0                   | 0.4                   | 0.00                           | 0.0              | 0.0                  | 1.0             | 3.6            | 3.4             | 0.0         | 0.0         | 186.0               | 506  |
| Mean                | 7.8| 788 | 134                   | 34.3                 | 11.5                  | 2.4                   | 7.26                           | 0.02             | 16                   | 18.8            | 10.4           | 25.7            | 3.7         | 1.0         | 355.9               | 737  |
| Median              | 8.1| 483 | 117                   | 30.4                 | 9.4                   | 1.8                   | 0.06                           | 60               | 0.0                  | 4.5             | 9.1            | 21.9            | 5.3         | 0.0         | 342.5               | 640  |
| CV (%)              | 0.5| 381 | 100.0                 | 14.0                 | 7.8                   | 1.8                   | 11.9                           | 96               | 23                   | 36.7            | 5.7            | 18.1            | 3.1         | 457        | 143                 | 294  |
| Shallow wells (n = 13) |   |     |                       |                      |                       |                       |                                 |                  |                      |                 |                |                |             |             |                     |     |        |     |
| Water pond (n = 1)  |    |     |                       |                      |                       |                       |                                 |                  |                      |                 |                |                |             |             |                     |     |        |     |
| Min                 | 6.9| 292 | 58.7                  | 8.1                  | 1.3                   | 0.4                   | 0.00                           | 0.0              | 0.0                  | 3.0             | 2.3            | 4.9             | 2.1         | 0.0         | 151                 | 276  |
| Max                 | 8.6| 3510| 1012                  | 124                  | 36.0                  | 11.2                  | 0.50                           | 400              | 345                  | 113             | 136           | 499             | 59.1        | 3731       | 1643                | 3560 |
| Mean                | 7.8| 1809| 393                   | 58.8                 | 13.8                  | 4.1                   | 0.08                           | 37               | 67                   | 30.0            | 44.7          | 169             | 15.9        | 280        | 820                 | 1616 |
| Median              | 7.8| 1205| 224                   | 49.4                 | 12.2                  | 3.5                   | 0.06                           | 3.0              | 11                   | 12.5            | 18.4          | 58.3            | 11.3        | 2.0         | 716                 | 1005 |
| CV (%)              | 0.5| 1162| 286                   | 33.7                 | 7.0                   | 2.4                   | 0.12                           | 92               | 95                   | 33.2            | 46.9          | 181             | 14.9        | 765        | 453                 | 1002 |
| North-eastern flank |    |     |                       |                      |                       |                       |                                 |                  |                      |                 |                |                |             |             |                     |     |        |     |
| Springs (n = 27)    |    |     |                       |                      |                       |                       |                                 |                  |                      |                 |                |                |             |             |                     |     |        |     |
| Min                 | 6.3| 417 | 74                    | 57                   | 51                    | 58                    | 142                            | 246              | 142                  | 111             | 105           | 107             | 274         | 55          | 117                 | 86   |
| Mean                | 7.6| 74  | 73                    | 57                   | 51                    | 58                    | 142                            | 246              | 142                  | 111             | 105           | 107             | 274         | 55          | 117                 | 86   |

Water Type
Table 2. Cont.

| Water Type | pH | EC | Na⁺ | K⁺ | Ca²⁺ | Mg²⁺ | Fe²⁺/Fe³⁺ | Mn²⁺ | NH₄⁺ | F⁻ | SO₄²⁻ | NO₃⁻ | NO₂⁻ | (HCO₃⁻ + CO₃²⁻) | PO₄³⁻ | SiO₂ | TDS |
|------------|----|----|-----|----|------|------|-----------|------|------|----|-------|------|------|------------------|------|------|-----|
| Shallow wells (n = 12) | 7.6 | 424 | 80.4 | 12.4 | 2.7 | 0.3 | 0.02 | 0.0 | 0.0 | 3.6 | 3.8 | 1.9 | 0.0 | 0.0 | 220 | 0.00 | 24.2 | 412 |
| Max | 8.5 | 2680 | 579 | 80.9 | 11.7 | 6.4 | 30.8 | 2480 | 80 | 121 | 78.3 | 204 | 36.5 | 633 | 1080 | 1.36 | 160 | 2322 |
| Mean | 8.0 | 1034 | 259 | 29.3 | 6.3 | 1.7 | 5.27 | 14 | 72 | 124 | 70 | 124 | 301 | 40 | 138 | 63 | 48 |
| Median | 8.1 | 890 | 205 | 26.3 | 5.7 | 1.1 | 1.61 | 59 | 28 | 14.7 | 21.8 | 27.1 | 4.3 | 4.0 | 485 | 0.18 | 65.5 | 869 |
| SD. | 0.4 | 53 | 53 | 60 | 44 | 99 | 184 | 162 | 93 | 126 | 70 | 124 | 301 | 40 | 138 | 63 | 48 |
| River (n = 1) | 8.8 | 1736 | 464 | 87.2 | 9.3 | 1.2 | 0.08 | 0.0 | 0.0 | 144 | 45.1 | 126 | 1.1 | 2.0 | 645 | 0.55 | 20.8 | 1544 |
| North-western flank | 7.5 | 441 | 86 | 20.7 | 2.2 | 0.4 | 0.06 | 1.0 | 1.0 | 17.8 | 4.2 | 9.0 | 2.5 | 2.0 | 196 | 0.12 | 43.0 | 400 |
| Median | 7.5 | 441 | 86 | 20.7 | 2.2 | 0.4 | 0.06 | 1.0 | 1.0 | 17.8 | 4.2 | 9.0 | 2.5 | 2.0 | 196 | 0.12 | 43.0 | 400 |
| South-western flank | 8.4 | 719 | 111 | 164 | 33.4 | 16.4 | 3.1 | 0.03 | 0.0 | 15 | 3.7 | 25.7 | 14.9 | 20.7 | 6178 | 0.07 | 50.6 | 51.0 |
| Median | 7.8 | 1152 | 180 | 39.9 | 39.7 | 6.1 | 0.53 | 16 | 60 | 3.7 | 25.7 | 75.1 | 36.7 | 2743 | 539 | 0.07 | 67.3 | 1017 |
| Spring (n = 1) | 8.4 | 719 | 111 | 164 | 33.4 | 16.4 | 3.1 | 0.03 | 0.0 | 15 | 3.7 | 25.7 | 14.9 | 20.7 | 6178 | 0.07 | 50.6 | 51.0 |
| South-western flank | 7.1 | 464 | 75.8 | 20.4 | 4.2 | 0.7 | 0.00 | 0.0 | 0.0 | 4.7 | 5.5 | 3.9 | 0.0 | 0.0 | 209 | 0.00 | 33.0 | 383 |
| Mean | 7.8 | 922 | 164 | 53.8 | 18.8 | 4.2 | 0.13 | 132 | 50 | 8.7 | 14.9 | 20.7 | 31.3 | 139 | 485 | 0.11 | 105 | 907 |
| SD. | 0.5 | 65.6 | 10.0 | 8.8 | 13.6 | 2.6 | 1.19 | 36 | 48 | 0.3 | 2.6 | 11.7 | 5.1 | 6718 | 529 | 0.06 | 47.1 | 1011 |
| CV (%) | 6 | 24 | 36 | 31 | 57 | 79 | 263 | 261 | 342 | 73 | 39 | 66 | 99 | 292 | 29 | 97 | 61 | 24 |
| Western flank | 7.8 | 1378 | 239 | 53.8 | 19.6 | 4.4 | 0.22 | 26 | 79 | 14.8 | 18.6 | 33.9 | 40.5 | 611 | 649 | 0.26 | 78.9 | 1153 |
| South-western flank | 7.1 | 715 | 88 | 26.5 | 5.3 | 1.1 | 0.00 | 0.0 | 0.0 | 2.0 | 6.3 | 8.7 | 3.1 | 0.0 | 347 | 0.00 | 2.4 | 610 |
| Mean | 8.5 | 2320 | 425 | 99.0 | 68.0 | 24.6 | 6.88 | 220 | 1309 | 122 | 67.0 | 88.7 | 258 | 6124 | 1114 | 1.66 | 209 | 1817 |
| SD. | 0.4 | 370 | 90 | 17.2 | 12.7 | 3.6 | 0.93 | 54 | 235 | 18.6 | 10.6 | 18.0 | 44.3 | 1360 | 203 | 0.36 | 61.7 | 319 |
| CV (%) | 6 | 29 | 38 | 32 | 65 | 82 | 420 | 208 | 297 | 126 | 87 | 53 | 109 | 223 | 31 | 140 | 78 | 28 |
Table 2. Cont.

| Water Type | pH  | EC  | Na⁺ | K⁺  | Ca²⁺ | Mg²⁺ | Fe²⁺/Fe³⁺ | Mn²⁺ | NH₄⁺ | F⁻  | Cl⁻  | SO₄²⁻ | NO₃⁻ | NO₂⁻ | (HCO₃⁻ + CO₃²⁻) * | PO₄³⁻ | SiO₂ | TDS |
|------------|-----|-----|-----|-----|------|------|-----------|------|-------|-----|------|-------|------|------|---------------------|-------|------|-----|
| Deep wells (n = 3) | | | | | | | | | | | | | | | | | | |
| Min        | 7.5 | 606 | 105 | 21.9| 7.9  | 1.6  | 0.03      | 0.0  | 0.0   | 3.8 | 5.7  | 7.3   | 0.0  | 1.0  | 310                 | 0.53  | 40.4 | 508 |
| Max        | 8.0 | 769 | 133 | 25.5| 25.5 | 6.9  | 0.05      | 6.0  | 7.8   | 8.8 | 21.8 | 9.1   | 54   | 457  | 0.65                | 51.9  | 742  |
| Mean       | 7.7 | 700 | 120 | 27.7| 27.7 | 2.0  | 0.05      | 4.0  | 5.4   | 7.5 | 16.2 | 5.4   | 20   | 400  | 0.58                | 46.8  | 653  |
| Median     | 7.6 | 726 | 121 | 27.7| 27.7 | 2.0  | 0.05      | 5.0  | 4.6   | 7.9 | 19.5 | 7.2   | 4.0  | 433  | 0.54                | 48.1  | 710  |
| SD         | 0.3 | 84.5| 14.0| 5.8 | 5.8  | 2.8  | 0.01      | 3.0  | 2.1   | 1.6 | 7.8  | 4.8   | 30   | 78.9 | 0.06                | 5.9   | 127  |
| CV (%)     | 4   | 12  | 12  | 21  | 51   | 58   | 35        | 88   | 39    | 21 | 48   | 88    | 153  | 20   | 11                  | 13    | 19   |

* TDS: Total Dissolved Solids
3.1. Physicochemical Characteristics and Conceptual Groundwater Flow Model

In 175 groundwater samples, pH values range from 6.7 to 8.6 with an average of 7.8 and a median of 7.8, indicating alkaline groundwater. In the six surface water samples, pH values range from 8.8 to 10.1 with an average of 9.4 and a median of 9.3, also, indicating alkaline water. Figure 6 shows the spatial distribution of TDS in the study area with a clear increasing trend from the higher elevations towards the lower elevations. On the eastern flank, below the ash cone, water samples from the springs show pH values between 7.1 and 8.6 with an average of 7.8 and a median of 7.8. Their EC values range from 105 $\mu$S/cm (at reference temperature of 25 $^\circ$C) to 4590 $\mu$S/cm (hydrothermal spring) with an average of 759 $\mu$S/cm and a median of 239 $\mu$S/cm, while their TDS values range from 117 to 4214 mg/L with an average of 703 mg/L and a median of 238 mg/L. Despite being at higher elevations in the recharge area, water samples from the two hydrothermal springs (S42—Small Njekukumia and S43—Big Njekukumia) near the ash cone are highly mineralised (average: 3642 mg/L) compared to the surrounding springs, which show low mineralisation (average: 203 mg/L; they are warmer (average temperature: 20.0 $^\circ$C) compared to the surrounding springs (average temperature: 13.3 $^\circ$C)), which indicates they are originating from a deep source. In addition, the water sample from the Njekukumia stream (at point STP9), which receives its water from the hydrothermal springs, shows high mineralisation and pH (pH = 9.1, EC = 4390 $\mu$S/cm, TDS = 3540 mg/L). The two springs (S44—Small Tululusia and S45—Big Tululusia) that lie on the same line below the hydrothermal springs show significant mineralisation (average: 1174 mg/L). This suggests that their mineralisation might be influenced by the infiltrated water from the hydrothermal springs or derived from the same source.
At lower elevations, in the discharge area, surface water samples from the three lakes (L1—Small Momella lake, L2—Big Momella lake, and L3—Lake Rishateni) show pH values ranging from 9.5 to 10.1 with an average of 9.8 and a median of 9.9, while their EC values range from 8630 to 19,820 µS/cm with an average of 15,340 µS/cm and a median of 17,570 µS/cm, and their TDS values range from 7438 to 17495 mg/L with an average of 13,541 mg/L and a median of 15,691 mg/L. The lakes are highly mineralised compared to other water samples. These lakes are closed basin lakes (no water in, no water out); therefore, a longer water residence time and evapoconcentration lead to high mineralisation of these waters.

Figure 7 shows a simplified groundwater flow conceptual model for the northeastern flank of Mount Meru showing different flow systems: local, intermediary, and regional [31,32]. The model was developed based on hydrogeochemical processes, ground-
On the far east of the eastern flank, on the northern flank of Ngurdoto crater, at Nkoasenga, water samples from the two springs found in the area show that spring S1 at elevation of 1560 m is less mineralised (pH = 7.2, EC = 632 µS/cm, TDS = 573 mg/L) compared to S2 at lower elevation of 1483 m (pH = 7.6, EC = 919 µS/cm, TDS = 789 mg/L), indicating that the groundwater mineral content progressively increases along the flow path with increasing residence time, long residence times favouring prolonged water–rock interaction. The trend is also observed in shallow wells where wells at high elevations (average: 1586 m) show low mineralisation (average values: pH = 7.7, EC = 621 µS/cm, TDS = 605 mg/L) compared to wells at low elevations (average: 1491 m), which show significant mineralisation (average values: pH = 8.2, EC = 1221 µS/cm, TDS = 1118 mg/L). The only surface water sample WP from a water pond which is at lower elevation of 1429 m is highly mineralised (pH = 9.2, EC = 4310 µS/cm, TDS = 3237 mg/L) compared to other samples; this is attributed to longer water residence time and evapoconcentration. In Leguruki, shallow wells at lower elevation of 1354 m show low mineralisation (average values: pH = 7.7, EC = 743 µS/cm, TDS = 666 mg/L), similar mineralisation as water samples from high elevations in Nkoasenga. The low mineralisation of these wells, despite being at lower elevations, suggests shorter water residence times. These shorter residence times suggest that there are different local flow systems in the area.

Table 3 shows the average values of pH, EC, and TDS in the water samples from different elevations and different well depths on the northeastern, northwestern, western, and southwestern flank of Mount Meru. On the northeastern flank, at Ngarenanyuki, Uwiro, and Mkuru, both springs and wells also show a similar trend of progressive
mineralisation of the groundwater along the flow paths. On average, on the northwestern flank, at Oldonyo Sambu, there is progressive mineralisation of the groundwater from elevation of 2567 m (average TDS: 242 mg/L) to 2084 m (average TDS: 410 mg/L); then, the mineralisation remains comparable towards the lower elevations (average TDS: 446 mg/L at 1838 m elevation). This suggests that the groundwater is flowing through fractures between 2084 and 1838 m elevations or is due to a local flow system in the area. On the western flank, at Mamsa, there is also clear progressive mineralisation of the groundwater along the flow path as the spring at higher elevation of 2240 m shows low mineralisation (TDS: 590 mg/L) compared to shallow wells at lower elevation of 1649 m (average TDS: 1017 mg/L). On the southwestern flank, at Ngaramtoni and near Arusha town, also the similar trend of progressive mineralisation of the groundwater from the upstream to the downstream is observed in both springs and wells but with some exceptions in some wells. Despite being at lower elevation of 1379 m, two shallow wells (W100 and W101) show low mineralisation (average TDS: 893 mg/L) compared to shallow wells at intermediate elevation of 1548 m (average TDS: 1188 mg/L), also, this suggests shorter water residence times, due to different local flow systems in the area. In addition, despite being at lower elevations, deep wells show low mineralisation (average TDS: 653 mg/L) compared to all shallow wells (range of average TDS: 744–1188 mg/L); this suggests that these are deep circulating waters that have undergone deep infiltration in the recharge area at higher elevations, possibly through fractures and faults. The low mineralisation in the deep circulating groundwater compared to the shallow one can be attributed to slow weathering and dissolution of aluminosilicate minerals in the weathered fractured lava composing the deep aquifer compared to the pyroclastic deposits that form the composition of the shallow aquifer.

Table 3. Average values of pH, EC, and TDS in the water samples from different elevations and different well depths on the northeastern, northwestern, western, and southwestern flank of Mount Meru.

| Region          | Water Source | Number of Samples | Average Elevation (m) | Average Well Depth (m) | Average pH | Average EC (µS/cm at 25°C) | Average TDS (mg/L) |
|-----------------|--------------|-------------------|-----------------------|------------------------|------------|---------------------------|-------------------|
| North-eastern   | Springs      | 2                 | 1705                  |                        | 6.9        | 307                       | 286               |
|                 |              | 13                | 1430                  |                        | 7.6        | 998                       | 916               |
|                 |              | 4                 | 1402                  |                        | 8.1        | 1915                      | 1819              |
|                 |              | 8                 | 1332                  |                        | 8.2        | 3449                      | 2984              |
|                 | Shallow wells | 1                 | 1551                  | 48                     | 7.7        | 424                       | 412               |
|                 |              | 10                | 1452                  | 8                      | 8.0        | 930                       | 891               |
|                 |              | 1                 | 1399                  | 27                     | 8.5        | 2680                      | 2322              |
|                 | River        | 1                 | 1443                  |                        | 8.8        | 1736                      | 1544              |
| North-western   | Springs      | 4                 | 2567                  |                        | 7.9        | 214                       | 242               |
|                 |              | 15                | 2084                  |                        | 7.6        | 444                       | 410               |
|                 |              | 6                 | 1838                  |                        | 7.1        | 496                       | 446               |
| Western flank   | Spring       | 1                 | 2240                  |                        | 8.4        | 719                       | 590               |
|                 | Shallow wells | 6                 | 1649                  | 44                     | 7.8        | 1152                      | 1017              |
|                 | Springs      | 2                 | 1921                  |                        | 7.9        | 465                       | 386               |
|                 |              | 10                | 1566                  |                        | 7.8        | 1014                      | 1012              |
|                 | Shallow wells | 3                 | 1631                  | 16                     | 7.3        | 833                       | 744               |
|                 |              | 51                | 1548                  | 19                     | 7.9        | 1310                      | 1188              |
|                 |              | 2                 | 1379                  | 6                      | 8.2        | 1068                      | 893               |
| South-western   | Deep wells   | 3                 | 1467                  | 151                    | 7.7        | 700                       | 653               |

3.2. Major and Minor Ions Origin

Table 4 shows the correlation matrix between the main hydrogeochemical parameters. The significant strong positive correlations are highlighted in green colour. The significant strong positive correlation between total alkalinity (HCO$_3^-$ + CO$_3^{2-}$), alkaline elements (Na$^+$ and K$^+$), SO$_4^{2-}$, and Cl$^-$ suggests that they are released in groundwater
by simultaneously occurring hydrogeochemical processes. The strong positive correlation of TDS with Na⁺, K⁺, HCO₃⁻ + CO₃²⁻, SO₄²⁻, and Cl⁻ indicates that the concentration of these elements progressively increases together with the mineralisation of the groundwater along the groundwater flow path in response to the main hydrogeochemical processes [29]. The strong positive correlation of Cl⁻ with Na⁺, K⁺, HCO₃⁻ + CO₃²⁻, and SO₄²⁻ suggests the evapoconcentration along the flow path, the localised dissolution of evaporitic salts such as halite (NaCl), sylvinite (KCl), gypsum (CaSO₄·2H₂O), anhydrite (CaSO₄), thenardite (Na₂SO₄), and mirabilite (Na₂SO₄·10H₂O) [29,36], and the admixture of volcanic gases (which are containing lots of CO₂, SO₂, HCl, HF) as Mount Meru is an active volcano [33–35]. The significant moderate positive correlations of F⁻ with Na⁺ and K⁺ indicate that the progressive increase of F⁻ goes parallel with the increase in alkaline elements (suggesting progressive rock–water interaction), whereas the significant weak negative correlations of F⁻ with Ca²⁺ and Mg²⁺ indicate that the progressive increase of F⁻ goes parallel with the decrease in alkaline earth elements along the groundwater flow paths, through precipitation of carbonate minerals: aragonite, calcite, and dolomite. The high concentrations of HCO₃⁻ + CO₃²⁻, SO₄²⁻, Cl⁻, and F⁻ in the two hydrothermal springs suggest that the volcanic emissions are responsible for their composition.

### Table 4. Correlation matrix for all water samples (n = 181). Strong correlations are highlighted in green colour.

|       | Na⁺   | K⁺    | Ca²⁺   | Mg²⁺   | HCO₃⁻ + CO₃²⁻ | SO₄²⁻ | Cl⁻   | F⁻    | NO₃⁻  | SiO₂  | TDS  |
|-------|-------|-------|--------|--------|---------------|--------|-------|-------|-------|-------|------|
| Na⁺   | 1     |       |        |        |               |        |       |       |       |       |      |
| K⁺    | 0.803 ** | 1     |        |        |               |        |       |       |       |       |      |
| Ca²⁺  | 0.335 ** | 0.464 ** | 1      |        |               |        |       |       |       |       |      |
| Mg²⁺  | 0.445 ** | 0.593 ** | 0.855 ** | 1      |               |        |       |       |       |       |      |
| HCO₃⁻ + CO₃²⁻ | 0.946 ** | 0.831 ** | 0.502 ** | 0.574 ** | 1              |        |       |       |       |       |      |
| SO₄²⁻ | 0.782 ** | 0.707 ** | 0.469 ** | 0.594 ** | 0.732 **       | 1      |       |       |       |       |      |
| Cl⁻   | 0.627 ** | 0.727 ** | 0.478 ** | 0.551 ** | 0.808 **       | 0.823 ** | 1      |       |       |       |      |
| F⁻    | 0.611 ** | 0.421 ** | -0.267 ** | -0.179 ** | 0.467 **       | 0.335 ** | 0.336 ** | 1      |       |       |      |
| NO₃⁻  | 0.393 ** | 0.479 ** | 0.345 ** | 0.550 ** | 0.442 **       | 0.463 ** | 0.428 ** | 0.011 | 1     |       |      |
| SiO₂  | -0.087 | 0.016 | 0.229 ** | 0.274 ** | -0.048        | -0.044 | -0.016 | -0.180 | -0.269 ** | 0.518 ** |      |
| TDS   | 0.969 ** | 0.870 ** | 0.472 ** | 0.563 ** | 0.964 **       | 0.795 ** | 0.853 ** | 0.518 ** | 0.473 ** | 0.024 | 1    |

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).

### 3.2.1. Eastern and Northeastern Flanks

The concentration of Na⁺ in groundwater varies between 15.1 mg/L (spring water from the recharge area) and 1123 mg/L (hydrothermal spring water). The spatial distribution of Na⁺ shows an increasing trend from the higher elevations where the springs from the recharge areas show lower concentrations (average: 29.7 mg/L) towards the lower elevations (flow-through and discharge areas), where water samples show higher concentrations (springs: average 393 mg/L; wells: average 230 mg/L), indicating a progressive increase along groundwater flow paths. The two hydrothermal springs show higher Na⁺ concentrations (average: 1011 mg/L); they may contribute high Na⁺ concentrations in the shallow aquifer on these flanks. In all 57 groundwater samples from these flanks, the average concentrations of Na⁺, K⁺, Ca²⁺, and Mg²⁺ in mg/L are 293, 46.4, 9.7, and 2.5 respectively, suggesting that the contribution of Na-K-bearing minerals in releasing cations in the groundwater is more important than that of Ca-Mg-bearing minerals.

The concentration of total alkalinity (HCO₃⁻ + CO₃²⁻) in groundwater varies between 44.5 mg/L (spring water from the recharge area) and 2170 mg/L (hydrothermal spring water). The total alkalinity increases from the recharge area where springs show lower concentrations (average: 103 mg/L) towards the discharge areas where water samples show higher concentrations (springs: average 820 mg/L; wells: average 507 mg/L). This indicates that the concentration of the total alkalinity progressively increases along the groundwater flow path with increasing residence time as the result of the dissolution of CO₂(g) in groundwater that forms H₂CO₃ that causes extensive aluminosilicate dissolution, raising HCO₃⁻ in the groundwater; at high pH, the HCO₃⁻ transforms to CO₃²⁻. The CO₂(g) comes from the admixture of volcanic gases [33–35], the atmosphere, the respiration of microorganisms in the soil zone, and the aerobic and anaerobic decomposition of organic matter in infiltrating water [29].
The two hydrothermal springs show the highest $\text{HCO}_3^- + \text{CO}_3^{2-}$ concentrations (average: 1728 mg/L $\text{HCO}_3^-$); this indicates that volcanic emissions are here contributing high $\text{CO}_2$(g) in the groundwater; also, they may contribute high $\text{HCO}_3^- + \text{CO}_3^{2-}$ concentrations in the shallow aquifer on these flanks.

$\text{SO}_4^{2-}$ concentration in groundwater varies between 0.0 mg/L (spring water from the recharge area) and 499 mg/L (spring water from the discharge area). In addition, the $\text{SO}_4^{2-}$ shows a similar increasing trend from the recharge area where springs show lower concentrations (average: 0.6 mg/L) towards the discharge areas where there are higher concentrations (springs: average 159 mg/L; wells: average 42.8 mg/L). The two hydrothermal springs show higher $\text{SO}_4^{2-}$ concentrations (average: 339 mg/L), again pointing to volcanic emissions, which may also contribute to high $\text{SO}_4^{2-}$ concentrations in the shallow aquifer on these flanks, resulting from the reaction between $\text{SO}_2$ and $\text{H}_2\text{O}$ in the volcanic gases [33–35].

The concentration of $\text{Cl}^-$ in groundwater varies between 1.7 mg/L (spring water from the recharge area) and 148 mg/L (hydrothermal spring water). In general, chloride behaves as a conservative element, but the spatial distribution of $\text{Cl}^-$ shows a similar increasing trend from the higher elevations where springs from the recharge area show lower concentrations (average 4.7 mg/L) towards the lower elevations where there are higher concentrations (springs: average 41.7 mg/L; wells: average 27.7 mg/L). The hydrothermal springs show the highest $\text{Cl}^-$ concentrations (average: 198 mg/L), providing another indication of volcanic emissions containing $\text{HCl}$ [33,34] at depth, which may also contribute to elevated $\text{Cl}^-$ concentrations in the shallow aquifer on these flanks.

$\text{F}^-$ concentration in groundwater varies between 0.15 mg/L (spring water from the recharge area) and 301 mg/L (hydrothermal spring water). Similarly to the major parameters, the spatial distribution of $\text{F}^-$ shows an increasing trend from the higher elevations where the springs from the recharge areas show lower concentrations (average: 2.7 mg/L) towards the lower elevations where there are higher concentrations (springs: average 45.1 mg/L; wells: average 24.6 mg/L). The hydrothermal springs have lower $\text{F}^-$ concentrations (average: 198 mg/L), providing another indication of volcanic emissions at depth [33], which may also contribute high $\text{F}^-$ concentrations in the shallow aquifer on these flanks. The Njekukumia stream, which receives its water from the two hydrothermal springs is known for contributing high $\text{F}^-$ water to the Ngarenanyuki river [11]. The water sample collected at the Njekukumia stream at point STP9 (2.5 km away from the hydrothermal springs) shows an extremely high $\text{F}^-$ value of 553 mg/L, whereas the water sample collected at the Ngarenanyuki river at point STP10 (10 km away from STP9) shows a high $\text{F}^-$ value of 144 mg/L.

$\text{NO}_3^-$ concentration in groundwater varies between 0.0 mg/L (one spring water sample from recharge area and one well water sample from the flow-through area) and 59.1 mg/L (spring water from the discharge area). The springs from the recharge areas show lower $\text{NO}_3^-$ concentrations (average: 2.4 mg/L) than water samples from the lower elevations (springs: average 14.5 mg/L; wells: average: 8.2 mg/L). The hydrothermal springs have lower $\text{NO}_3^-$ concentrations (average: 1.7 mg/L), showing that the hydrothermal springs are characterised by the volcanic gases, which are not containing $\text{NO}_3^-$, while the parameters that are high in the hydrothermal springs (total alkalinity, $\text{SO}_4^{2-}$, $\text{Cl}^-$, $\text{F}^-$) are derived from the volcanic emissions.

Overall, the concentration of $\text{NO}_2^-$ is characterised by relatively low concentrations in all water samples. $\text{NO}_2^-$ concentration in groundwater varies between 0.0 mg/L (spring and well waters) and 3.7 mg/L (spring water from the flow-through area). The springs from the recharge areas show lower $\text{NO}_2^-$ concentrations (average: 0.001 mg/L) than water samples from the lower elevations (springs: average 0.25 mg/L; wells: average 0.06 mg/L). The two hydrothermal springs have lower $\text{NO}_2^-$ concentrations (average: 0.002 mg/L).

At Ngarenanyuki, locally occurring evaporitic salt (trona ($\text{Na}_2\text{CO}_3\cdot\text{NaHCO}_3\cdot2\text{H}_2\text{O}$)), an evaporite mineral locally called “magadi”, is observed as an efflorescent crust during
the dry season (Figure 8). The primary source of the “magadi” in this area is the NaHCO$_3$–type groundwater: during the dry season, the NaHCO$_3$-type groundwater is concentrated at/near the surface by capillary rise and evapoconcentration, and it may precipitate to form the salt. As a result of the local presence of this salt, its dissolution during the rainy season will only have a local effect on groundwater chemistry [29]. Figure 9 shows the projection of the different water samples from these flanks in the Piper diagram.

Figure 8. Pictures showing evaporitic salt “magadi” on the soil surface at Ngarenanyuki on the northeastern flank.

Figure 9. Piper diagram showing different water samples taken from springs, shallow wells, stream, river, and lakes on the eastern and northeastern flanks.
3.2.2. Far East of the Eastern Flank (Northern Flank of Ngurdoto Crater)

The concentration of Na⁺ in groundwater ranges from 58 to 443 mg/L (both from well waters), whereas the concentration of HCO₃⁻ + CO₃²⁻ ranges from 186 to 756 mg/L HCO₃⁻ (both from well waters). The concentration of F⁻ ranges from 1.0 to 134 mg/L (both from well waters). In all 15 groundwater samples from this flank, the average concentrations of Na⁺, K⁺, Ca²⁺, and Mg²⁺ in mg/L are 135, 34.3, 11.0, and 2.3, respectively, again showing that the Na-K-bearing minerals are dominant in releasing cations in the groundwater. Table 5 shows that, on average, water samples from both springs and wells at Nkoasenga show a progressive increase of Na⁺, K⁺, HCO₃⁻ + CO₃²⁻, SO₄²⁻, F⁻, and NO₃⁻ from the upstream to the downstream, whereas Ca²⁺, Mg²⁺, and Cl⁻ decrease along the flow path. In Leguruki, all three water samples are from lower elevations, their low values are attributed to the local flow system in the area (see Section 3.1). Figure 10 shows the projection of the different water samples from this flank in the Piper diagram.

Table 5. Average values of major and minor ions in the water samples from different elevations on the northern flank of Ngurdoto crater (* as mg/L HCO₃⁻).

| Region       | Water Source | Number of Samples | Average Elevation (m) | Average Concentrations (mg/L) | Na⁺ | K⁺ | Ca²⁺ | Mg²⁺ | (HCO₃⁻ + CO₃²⁻) * | SO₄²⁻ | Cl⁻ | F⁻ | NO₃⁻ | NO₂⁻ |
|--------------|--------------|-------------------|-----------------------|--------------------------------|-----|----|------|------|-----------------|-------|-----|----|------|------|
| Nkoasenga    | Springs      | 1                 | 1560                  | 106                            | 26.2| 14.0| 2.4  | 0.4  | 334             | 19.8  | 13.4| 2.6 | 5.7   | 0.002|
|              | Shallow wells| 7                 | 1483                  | 171                            | 42.8| 12.4| 2.4  | 0.4  | 478             | 25.7  | 3.3 | 10.7| 23.5  | 0.078|
|              | Shallow wells| 3                 | 1491                  | 251                            | 50.8| 4.5 | 1.2  | 0.4  | 508             | 35.6  | 10.9| 3.5 | 11.6  | 0.347|
| Leguruki     | Shallow wells| 3                 | 1534                  | 111                            | 33.5| 16.2| 3.7  | 0.4  | 346             | 29.9  | 11.8| 4.6 | 26.0  | 0.002|

Figure 10. Piper diagram showing different water samples taken from springs, shallow wells, and water pond on the northern flank of Ngurdoto crater.

3.2.3. Northwestern and Western Flanks

On the northwestern flank, all water samples are from springs, the concentration of Na⁺ in groundwater ranges from 17.0 to 135 mg/L, whereas the concentration of HCO₃⁻ + CO₃²⁻ ranges from 59.0 to 292 mg/L HCO₃⁻. The concentration of F⁻ ranges from 0.4 to 61.7 mg/L. In all 15 groundwater samples from this flank, the average concentrations of Na⁺, K⁺, Ca²⁺, and Mg²⁺ in mg/L are 83.9, 19.4, 3.0, and 0.6, respectively. Again, this shows that the Na-K-bearing minerals are dominant in releasing cations in the groundwater. On the western flank, the concentration of Na⁺ ranges from 111 mg/L.
(spring water) to 187 mg/L (well water), whereas the concentration of HCO$_3^-$ + CO$_3^{2-}$ ranges from 365 mg/L HCO$_3^-$ (spring water) to 567 mg/L HCO$_3^-$ (well water). The concentration of F$^-$ ranges from 3.4 mg/L (spring water) to 4.0 mg/L (well water). In all seven groundwater samples from this flank, the average concentrations of Na$^+$, K$^+$, Ca$^{2+}$, and Mg$^{2+}$ in mg/L are 170, 37.6, 36.4, and 5.7, respectively, showing once more that the Na-K-bearing minerals are dominant in releasing cations; however, in this case, there is also an important contribution from Ca-bearing minerals. Table 6 shows that on average, water samples from the northwestern flank show a progressive increase of Na$^+$, K$^+$, HCO$_3^-$ + CO$_3^{2-}$, SO$_4^{2-}$, F$^-$, and NO$_3^-$ from elevation of 2567 m to 2084 m, while Ca$^{2+}$, Mg$^{2+}$, and Cl$^-$ remain constant; descending further, most ions remain comparable towards the lower elevations (average: 1838 m); this is attributed to shorter residence time as groundwater flows through fractures between 2084 and 1838 m elevations (see Section 3.1). On the western flank, on average, all ions except F$^-$ (which remains constant) increase from the upstream to the downstream. Figure 11 shows the projection of the different water samples from the northwestern and western flanks in the Piper diagram.

**Table 6.** Average values of major and minor ions in the water samples from different elevations on the northwestern and western flanks (* as mg/L HCO$_3^-$).

| Region       | Water Source | Number of Samples | Average Elevation (m) | Na$^+$ | K$^+$ | Ca$^{2+}$ | Mg$^{2+}$ | (HCO$_3^-$ + CO$_3^{2-}$) * | SO$_4^{2-}$ | Cl$^-$ | F$^-$ | NO$_3^-$ | NO$_2^-$ |
|--------------|--------------|-------------------|-----------------------|--------|-------|----------|----------|----------------------------|------------|-------|------|---------|---------|
| North-western flank | Springs        | 4                 | 2567                  | 32.2   | 11.0  | 3.3      | 0.6      | 111            | 0.3       | 4.7   | 0.8  | 0.9     | 0.001   |
|               |               | 15                | 2084                  | 91.5   | 19.6  | 2.9      | 0.6      | 185           | 8.8      | 4.1   | 24.4 | 8.4     | 0.328   |
|               |               | 6                 | 1838                  | 99.1   | 24.6  | 3.2      | 0.5      | 235           | 8.7      | 4.1   | 24.8 | 5.2     | 0.022   |
| Western flank | Spring         | 1                 | 2240                  | 111    | 23.4  | 16.4     | 3.1      | 365           | 14.0     | 7.7   | 3.7  | 6.0     | 0.004   |
|               | Shallow wells  | 6                 | 1649                  | 180    | 39.9  | 39.7     | 6.1      | 539           | 75.1     | 25.7  | 3.7  | 36.7    | 2.743   |

**Figure 11.** Piper diagrams showing different water samples taken from: (a) springs on the northwestern flank and (b) the spring and shallow wells on the western flank.
3.2.4. Southwestern Flank

The concentration of Na\(^+\) in groundwater ranges from 75.8 mg/L (spring water) to 425 mg/L (shallow well water), whereas the concentration of HCO\(_3\)\(^-\) + CO\(_3\)\(^2-\) ranges from 209 mg/L HCO\(_3\)\(^-\) (spring water) to 1114 mg/L HCO\(_3\)\(^-\) (shallow well water). The concentration of F\(^-\) ranges from 2.0 to 122 mg/L (both from shallow well waters). In all 71 groundwater samples from this flank, the average concentrations of Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\) in mg/L are 221, 52.7, 19.4, and 4.4 respectively, indicating that the Na-K-bearing minerals are dominant in releasing cations in the groundwater. Table 7 shows that on average, water samples from springs show a progressive increase of all ions except F\(^-\) (which decreases) from upstream to downstream, whereas water samples from shallow wells show a progressive increase of all ions from elevation of 1631 to 1548 m; the two shallower wells (average well depth: 6 m) at lower elevations (average: 1379 m) show increases in Na\(^+\), K\(^+\), HCO\(_3\)\(^-\) + CO\(_3\)\(^2-\) and F\(^-\) but increases in Ca\(^{2+}\), Mg\(^{2+}\), SO\(_4\)\(^2-\), Cl, and NO\(_3\)\(^-\), this is attributed to the local flow system in the area (see Section 3.1). In addition, deep wells at the downstream show lower concentrations for in all ions except Ca\(^{2+}\) and Mg\(^{2+}\) (which remain constant) compared to shallow wells at intermediate elevations (average: 1548 m); these are low mineralised deep circulating waters that have undergone deep infiltration in the recharge area at higher elevations through fractures and faults (see Section 3.1). Table 8 shows water samples containing unusually high concentration of NO\(_3\)\(^-\). Two shallow wells W36 and W69 at intermediate elevations (1561 and 1513 m, respectively) show unusually high concentrations of NO\(_3\)\(^-\) (129 mg/L and 258 mg/L, respectively), which largely exceed the average concentration of this anion (37.3 mg/L) at intermediate elevations (average: 1548 m), as indicated in Table 7. In addition, two shallow wells W100 and W101 at lower elevations (1385 and 1373 m, respectively) show unusually high concentrations of NO\(_3\)\(^-\) (134 mg/L and 167 mg/L, respectively) despite the fact that shorter water residence times are attributed to these wells. The unusually high NO\(_3\)\(^-\) values in these four wells are accompanied by high SO\(_4\)\(^2-\) and Cl\(^-\) values, which all together are indicative of local anthropogenic pollution [29], especially from domestic sewage. Figure 12 shows the projection of the different water samples from this flank in the Piper diagram.

Table 7. Average values of major and minor ions in the water samples from different elevations on the southwestern flank (* as mg/L HCO\(_3\)\(^-\)).

| Water Source | Number of Samples | Average Elevation (m) | Average Well Depth (m) | Na\(^+\) | K\(^+\) | Ca\(^{2+}\) | Mg\(^{2+}\) | (HCO\(_3\)\(^-\) + CO\(_3\)\(^2-\)) \(*\) | SO\(_4\)\(^2-\) | Cl\(^-\) | F\(^-\) | NO\(_3\)\(^-\) | NO\(_2\)\(^-\) |
|--------------|------------------|-----------------------|------------------------|---------|-------|---------|---------|-----------------|---------|-----|-----|--------|--------|
| Springs      | 2                | 1921                  | 76.4                   | 22.8    | 4.4   | 0.7     | 212     | 7.5             | 6.1     | 12.0| 3.0  | 0.02   |
|              | 10               | 1566                  | 182                    | 60.0    | 21.7  | 4.9     | 539     | 23.4            | 16.6    | 8.1 | 37.0 | 0.16   |
| Shallow wells| 3                | 1631                  | 160                    | 30.8    | 10.2  | 1.4     | 439     | 24.5            | 9.0     | 6.3 | 20.8 | 0.15   |
|              | 51               | 1548                  | 248                    | 55.9    | 18.5  | 4.0     | 672     | 34.0            | 18.3    | 15.8| 37.3 | 0.64   |
|              | 2                | 1379                  | 6                      | 109     | 61.1  | 20.8    | 367     | 47.3            | 40.9    | 2.3 | 151  | 0.67   |
| Deep wells   | 3                | 1467                  | 151                    | 120     | 27.7  | 19.3    | 400     | 16.2            | 7.5     | 5.4 | 5.4  | 0.02   |

Table 8. Water samples containing an unusually high concentration of NO\(_3\)\(^-\) on the southwestern flank.

| Town         | Water Point ID | Water Source | Elevation (m) | Well Depth (m) | SO\(_4\)\(^2-\) (mg/L) | Cl\(^-\) (mg/L) | NO\(_3\)\(^-\) (mg/L) |
|--------------|----------------|--------------|---------------|-------------------|----------------------|-----------------|---------------------|
| Ngaramtoni   | W36            | Shallow well  | 1561          | 19                | 59.2                 | 28.7            | 129                 |
|              | W69            | Shallow well  | 1513          | 19                | 88.7                 | 67.0            | 258                 |
| Arusha       | W100           | Shallow well  | 1385          | 9                 | 37.0                 | 34.6            | 134                 |
|              | W101           | Shallow well  | 1373          | 2                 | 57.6                 | 47.2            | 167                 |
In all the analysed water samples (n = 181) for this study, 39% (n = 71) of the samples have Na⁺ concentrations above the WHO taste-based guideline of 200 mg/L [10] (p. 227); 51 samples are from wells, 24 are from springs and all of the six surface waters, whereas 7% (n = 13) of samples have SO₄²⁻ concentrations above the WHO taste-based guideline of 250 mg/L [10] (p. 227); eight samples are from springs from the discharge area, two are from the hydrothermal springs, and three are from surface waters (one lake, one stream, one water pond). In addition, 2% (n = 3) of samples have Cl⁻ concentrations above the WHO taste-based guideline of 250 mg/L [10] (p. 227); two samples are from lakes and one is from a stream, whereas 10% (n = 19) of samples have NO₃⁻ concentrations above the WHO health-based guideline of 50 mg/L [10] (p. 196); 14 samples are from wells and five are from springs from the discharge areas. In 175 groundwater samples, 91% (n = 160) of the samples have F⁻ concentrations higher than the WHO limit (1.5 mg/L) recommended for drinking water [10] (p. 42). The 9% (n = 15) of the samples with F⁻ concentrations lower than the WHO limit are mainly from springs (n = 13) from the recharge areas on the eastern and northwestern flanks of Mount Meru inside the Arusha National Park. Based on the Tanzanian limit (4.0 mg/L) [37] (p. 26), 79% (n = 138) of the samples are above the limit. All of the six surface waters have F⁻ concentrations higher than both WHO and Tanzanian limits. Table 9 summarises the overview of the usable groundwater sources from the sampled inventoried groundwater points in reference to their F⁻ concentrations. From the 122 sampled inventoried groundwater points, 93% (n = 114) of the points provide usable groundwater sources for different purposes; drinking, other domestic use, irrigation, and livestock. From the 114 usable groundwater points, 59% (n = 67) of the points are used to provide drinking water to the local community despite their high F⁻ values, which exceed both WHO and Tanzanian limits, as most local people do not have any alternative for drinking water. Only 11% (n =13) of the usable points are not used for drinking purpose due to their high F⁻ values, which exceed the limits of the two standards. It appears that the only way of accessing safe drinking water in the study area is to tap groundwater from the springs from the recharge areas at higher elevations on the eastern and northwestern flanks of the Mount Meru, inside the Arusha National Park, in which F⁻ concentrations
are lower due to lower rock weatherability and short water residence times. This has been the current practice on the ground.

Table 9. Overview of the usable groundwater sources from the sampled inventoried groundwater points in reference to their F\(^-\) concentrations (F\(^-\) upper limits recommended for drinking water: WHO = 1.5 mg/L; Tanzanian = 4.0 mg/L).

| Region                                               | Water Source | Number of Water Points | Range of F\(^-\) Values (mg/L) | Within WHO or Tanzanian Standard | Drinking Purpose                                      |
|-------------------------------------------------------|--------------|------------------------|---------------------------------|----------------------------------|------------------------------------------------------|
| Eastern flank, inside the Arusha National Park         | Springs      | 10                     | 0.1–1.5                         | WHO standard                     | Yes                                                  |
|                                                       |              | 3                      | 1.7–3.9                         | Tanzanian standard               | Yes                                                  |
|                                                       |              | 2                      | 15–19                           | Above the standards              | Yes                                                  |
| Far east of the eastern flank (Northern flank of Ngurdoto crater) | Springs      | 1                      | 2.6                              | Tanzanian standard               | No, used for other purposes                           |
|                                                       |              | 1                      | 11                              | Above the standards              |                                                      |
|                                                       | Wells        | 2                      | 1.0–1.3                         | WHO standard                     | Yes                                                  |
|                                                       |              | 4                      | 1.6–3.5                         | Tanzanian standard               | Yes                                                  |
|                                                       |              | 4                      | 4.5–8.2                         | Above the standards              | Yes                                                  |
|                                                       |              | 3                      | 31–134                          | Above the standards              | Yes                                                  |
| North-eastern flank                                   | Springs      | 2                      | 4.2–4.3                         | Above the standards              | Yes                                                  |
|                                                       |              | 1                      | 4.3                             | Above the standards              | No, used for irrigation and livestock                 |
|                                                       |              | 4                      | 6–13                            | Above the standards              | Yes                                                  |
|                                                       |              | 5                      | 48–75                           | Above the standards              | No, used for irrigation and livestock                 |
|                                                       | Wells        | 1                      | 3.6                             | Tanzanian standard               | No, used for irrigation                              |
|                                                       |              | 1                      | 12                              | Above the standards              | No, used for domestic use and livestock               |
|                                                       |              | 2                      | 14–19                           | Above the standards              | Yes                                                  |
|                                                       |              | 2                      | 20–22                           | Above the standards              | No, used for domestic use and livestock               |
|                                                       |              | 1                      | 121                             | Above the standards              | Yes                                                  |
| North-western flank                                   | Springs      | 3                      | 0.4–0.8                         | WHO standard                     | Yes                                                  |
|                                                       |              | 1                      | 1.7                             | Tanzanian standard               | Yes                                                  |
|                                                       |              | 5                      | 18–27                           | Above the standards              | Yes                                                  |
|                                                       |              | 1                      | 28                              | Above the standards              | No, used for irrigation                              |
|                                                       |              | 1                      | 48                              | Above the standards              | Yes                                                  |
| Western flank                                          | Spring       | 1                      | 3.4                             | Tanzanian standard               | Yes                                                  |
|                                                       | Wells        | 3                      | 3.5–4.0                         | Tanzanian standard               | Yes                                                  |
|                                                       | Springs      | 8                      | 5.1–13.0                        | Above the standards              | Yes                                                  |
|                                                       |              | 5                      | 2.0–3.8                         | Above the standards              | Yes                                                  |
|                                                       |              | 5                      | 4.6–6.1                         | Above the standards              | Yes                                                  |
|                                                       |              | 1                      | 6.3                             | Above the standards              | No, used for irrigation                              |
|                                                       |              | 1                      | 6.3–8.5                         | Above the standards              | Yes                                                  |
|                                                       |              | 1                      | 9.3                             | Above the standards              | No, used for other domestic use and irrigation       |
|                                                       | Wells        | 15                     | 9.6–17.0                        | Above the standards              | Yes                                                  |
|                                                       |              | 6                      | 22.4–60.4                       | Above the standards              | Yes                                                  |
|                                                       |              | 1                      | 77.9                            | Above the standards              | No, used for other domestic use and irrigation       |

4. Temporal Variability of Fluoride Concentrations and Precipitation/Recharge Values

Figure 13 shows the temporal variability of F\(^-\) concentrations in the groundwater samples taken in September 2017 and September 2018. The time variability in F\(^-\) concentrations (sampled in two different dry seasons) is more pronounced in Ngarenanyuki and Oldonyo Sambu (the driest areas) than in Ngaramtoni and Mamsa. In 29 investigated groundwater points, 93% (n = 27) showed higher F\(^-\) concentrations in September 2018 than in September 2017. The F\(^-\) concentrations in September 2018 range from a minimum of 3.4 mg/L to a maximum of 122.4 mg/L with an average of 35.0 mg/L and a median of 15.8 mg/L, while in September 2017, the values range from a minimum of 3.9 mg/L to a maximum of 41.2 mg/L with an average of 15.9 mg/L and a median of 9.8 mg/L. The Mann–Whitney U test showed that at the significance level (\(\alpha\)) of 0.05, the F\(^-\) concentrations are not statistically significantly different. This is probably due to a small sample size (n = 29), the chosen level of significance, and the variability in the samples. Since this small sample size fails to detect the difference at \(\alpha = 0.05\), therefore, the significance level for this test was increased to 0.1. At the significance level of 0.1, the F\(^-\) concentrations in September 2018 (mean rank = 33.64) are statistically significantly higher than in September 2017 (mean rank = 31.24).
The pronounced elevated F⁻ concentrations in Ngarenanyuki and Oldonyo Sambu can be attributed to low groundwater recharge as the year 2018 was drier (annual rainfall: 680 mm) than 2017 (annual rainfall: 797 mm) as recorded at ASA Farm station in Ngaramtoni. Table 10 shows that the spring discharges (Q) during water sampling in April 2019 (at the end of an exceptionally dry rainy season) were slightly lower than in August 2019 (dry season), while their F⁻ values were slightly higher; this indicates that the low spring discharge resulting from slow groundwater flow favors long water–rock interactions and hence high mineralisation of the groundwater (high EC values) with high F⁻ concentrations.

Table 10. Spring discharges (Q), F⁻ concentrations, and EC for springs S3 and S5 (at Oldonyo Sambu) and S22 (at Ngaramtoni).

| Spring ID | Date       | Q (m³/hr) | F⁻ (mg/L) | EC (µS/cm at 25 °C) |
|-----------|------------|-----------|-----------|---------------------|
| S3        | April 2019 | 5.98      | 20.3      | 443                 |
|           | Aug. 2019  | 7.17      | 18.6      | 415                 |
| S5        | April 2019 | 34.23     | 15.0      | 436                 |
|           | Aug. 2019  | 46.62     | 13.7      | 407                 |
| S22       | April 2019 | 1.97      | 5.5       | 822                 |
|           | Aug. 2019  | 2.24      | 4.7       | 781                 |

Figure 14 shows that the spring discharges at Oldonyo Sambu (S3 and S5) start to rise after approximately a month time lag (mid-May) after the start of heavy rains at mid-April and continue to rise through the dry season until the next rainy season, indicating that the recharge area is situated at relatively large distance. The spring discharge at Ngaramtoni (S22) starts to rise immediately after the start of rainfall and declines immediately after the end of the rainy season, indicating that the spring receives local recharge. Thus, the lower F⁻ concentration for S22, both during the dry and the rainy season, is due to shorter water–rock interactions, as is clearly demonstrated by S22’s much faster response to rainfall, compared to S3 and S5. However, the high EC values of S22 compared to S3 and S5 are attributed to the influence of the mantling ash deposits. The S22 is located in the pyroclastics with subordinate nephelinitic and phonolitic lavas covered with mantling ash. Here, the area is surrounded by mantling ash deposits. Ash deposits are very loose and fine-grained; these characteristics make them highly weatherable and readily dissolve in water. The S3 and S5 are located in the Lemurge DAD, and their recharge area is located in pyroclastics with subordinate nephelinitic and phonolitic lavas. There are no ash deposits in these areas. Therefore, the lower EC values of S3 and S5 compared to S22 are attributed.
to the slow weathering of lavas. The lavas deposits are more compact and less weatherable as compared to the DADs and mantling ash deposits.

![Spring discharge fluctuation graphs for S3, S5, and S22](image)

**Figure 14.** Spring discharge fluctuation at Oldonyo Sambu (S3 and S5) and at Ngarenanyuki (S22), and rainfall (Mamsa rain station for S3 and S5, and ASA Farm rain station for S22). Red dots indicate discharge values during water sampling.

### 5. Conclusions and Recommendations

The groundwater chemistry in the study area shows that the main groundwater type in the study area is NaHCO₃ alkaline groundwater with an average pH = 7.8. The groundwater shows high variability in most of the physicochemical parameters, indicating complex hydrochemical conditions, due to the complexity of groundwater flow lines with different residence times, and passing through different geological formations of variable weatherability. Mineralisation generally increases with increasing residence times. In general, the higher springs show lower concentrations of the different hydrogeochemical parameters compared to lower springs, followed by the deep wells and lastly the shallow wells, indicating different groundwater flow systems. The two hydrothermal springs near the ash cone are highly mineralised compared to the surrounding springs; this indicates that they are originating from a deep source, suggesting the influence of volcanic emissions at depth.

Most groundwater sources analysed in this study are not suitable for human consumption due to their high F⁻ concentrations exceeding the WHO recommended limit for drinking water (1.5 mg/L). This represents a challenge, as most people do not have any alternative for drinking water. The range of F⁻ concentrations in springs, deep wells,
and shallow wells in mg/L are 0.15–301, 3.8–7.8, and 1.0–134, respectively. One of the hydrothermal springs shows the highest $F^-$ value of 301 mg/L. The temporal variability in $F^-$ concentrations between different seasons is due to the impact of local groundwater recharge.

As a result of the superior quality of the low-fluoride spring water from the high-altitude recharge areas on the eastern and northwestern flanks of Mount Meru inside Arusha National Park, the current practice is to extract their water for drinking purposes and pipe it to taps for the rural communities in the lower parts of the flanks. We recommend that a detailed ecohydrological study should be carried out to ensure the sustainability of this water extraction practice. Since the low-fluoride springs are in the upstream within the Arusha National Park, their extraction possibly affects the ecology of wildlife in the downstream inside the national park. Therefore, a long-term spring discharge monitoring together with biodiversity monitoring will help to establish a sustainable water management plan for these springs. Another strategy for obtaining safe drinking water could be to use a large-scale filtering system to remove $F^-$ from the groundwater.

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