Baseline for rainwater chemistry and quality as influenced by Nyiragongo volcano permanent plume, East Africa

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ABSTRACT

Single rainwater samples were collected in the city of Goma (~1,1 million inhabitants), eastern Democratic Republic of the Congo, from January to June 2013 to draw a baseline for rainwater chemical composition and quality as influenced by the permanent plume of Nyiragongo volcano. This was a better period for a baseline as the neighboring Nyamulagira volcano, only 15 km apart, had no important degassing from its central crater, and hence the recorded volcanic influence on the rainwater chemistry was solely from Nyiragongo's lava lake which has been active since May 2002. The baseline for the rainwater chemistry and quality is important for this highly populated region where rainwater is the unique potable water source for the inhabitants of many villages surrounding the volcanoes, and for some of the inhabitants of the city of Goma. Our results show that samples collected at the crater rim of Nyiragongo were more acidic with pH ranging from 3.70 to 3.82, while the majority of rainwater samples collected in downtown Goma city and to the northeastern zone of the volcano had pH close to 5.7; which represents the value for rainwater from unpolluted continental areas (Berner and Berner, 2012). However, the pH was as low as 3.93 to the west of Nyiragongo volcano because the volcanic plume is directed westward by the dominant local wind direction. The western part of the city of Goma as well as the small town of Sake and many villages (e.g. Rusayo, Mubambiro, Kingi, …) are located in this zone, and experience endemic fluorosis caused by high fluoride in the available water. The mean F^- in this zone was 0.38 mg/L, while the southern and northeastern zones had mean F^- concentrations on 0.44 and 0.01 mg/L respectively; even though concentrations higher than the WHO guidelines were found in few samples from the western zone (1.69 mg/L) and from the southern zone (3.44 mg/L). Compared to data from Cuoco et al. (2012) obtained during the Nyamulagira 2010 eruption, and from Balagizi et al.2017 and Liotta et al., 2017 obtained during the intense degassing of both Nyiragongo and Nyamulagira lava lakes; we have noted similarity in the spatial variation of the pH, but samples from the present study showed notable lower concentrations of major elements. This is the case for fluoride which is strictly of volcanic origin. For the other major elements, anthropogenic sources, mainly the traffic and wind-blown dust; or other non-volcanic natural sources influenced their concentrations. Thus, the anions (Cl^- and SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) from the present study are either lower compared to that previously reported in the literature for the Virunga, or are both comparable for the zones impacted by anthropogenic activities.

1.Introduction

Rain chemistry has been widely used for the assessment of the rainwater hazards in regions with volcanic emissions, ranging from short to long lasting volcanic eruptions nearby highly populated zones; e.g., Harding and Miller (1982); Nachbar et al., 1989; Baxter and Ancia (2002); Vasselli et al. (2008); Burgi et al. (2010); Madonia and Liotta (2010); Balagizi et al., (2017), 2018a. In fact, during their eruptive phase, volcanoes release thousands of tons of acidic gases mixed with scoria, Pele's hair and ash into the atmosphere. Particularly, open system volcanoes and mostly those with permanent lava lakes release huge amounts of gases and aerosols into the atmosphere daily; these emissions may last up to many decades (e.g, Allard et al., 2016; Sawyer et al., 2008; Head et al., 2011; Burgisser et al., 2012; Moor et al., 2013; Beirle et al., 2014; Arellano et al., 2016; Balagizi et al., 2016; Coppola et al., 2016; Bobrowski et al., 2016). Such strong degassing influences the chemistry of the surrounding atmosphere and hence lowers both the air and rainwater quality (e.g., Aiuppa et al., 2009; Le Cloarec and Marty, 1991; Halmer et al., 2002; Robock, 2000; Textor et al., 2004; Von Glasow et al., 2009, Cuoco et al., 2012a,b). The rainwater chemistry around open system volcanoes has thus been found to be affected by volcanic gases (Liotta et al., 2006; Calabrese et al., 2011; Madonia and Liotta, 2010; Balagizi et al., 2017) and metal-bearing particles (Mather et al., 2003; Oppenheimer, 2003, Cuoco et al., 2012a,b; Liotta et al., 2017). Within the Virunga Volcanic Province (VVP), the release of volcanogenic products from the two highly active volcanoes, Mounts Nyamulagira and Nyiragongo, into the atmosphere of the densely populated city of Goma (1.1 million habitants; Mairie de Goma, 2019) and of many other small cities and villages (Fig. 1) presents important hazards. One of these hazards is related to the volcanic plume-derived chemical elements in the rainwater, in a region where rain is the unique water source for many villages, and an intermittent water source for some others, including part of the city of Goma (Balagizi et al., 2015, 2017, 2018a, b). In the VVP, rainwater composition has been used for the understanding of the impacts of Nyiragongo and Nyamulagira volcanic plumes on rain chemistry (e.g., Cuoco et al., 2012a, b; Liotta et al., 2017; Balagizi et al., 2017), on the environment, and on the moisture source and dynamics (Liotta et al., 2017; Balagizi and Liotta, 2019). The VVP represents a rare natural laboratory for the study of hazards caused by volcano emissions on both human health and the environment, because of its peculiarity of holding two of the world most active volcanoes, i.e., Nyiragongo and Nyamulagira only 14 km apart, and which are located less than 20 km from highly populated zones. Furthermore, while Nyiragongo holds the world largest and permanent lava lake which has been active since May 2002, Nyamulagira has erupted at least 44 times since ~1880 and has shown an intermittent lava lake since mid-2013 (see compilation in Balagizi and al, 2018a). Thus, any observed significant changes in the air quality and the rainwater chemistry in the region of Goma is directly linked to the volcanic activity because there are no major anthropogenic activities that might yield such significant impacts. In fact, in the VVP there are no S, Cl, N, F, C, … (e.g., H_2S, SO_2, NH_3, NOx, HCl, Cl_2, carbonyl sulfide, …) gases emitting industries, with the exception of very little amounts from farming activities and traffic. The farming activities mainly generate wind-blown dust, which is higher during the dry season periods, i.e., during the long dry season spanning from mid-June to August and a very short one of mid-January to late-February. In contrast, during the rainy season, the higher precipitation rate of up to 357.3 mm/month (Balagizi et al., 2018b; Balagizi and Liotta, 2019) yield soil water saturation and hence prevent the production of wind-blown dust. Therefore, the rainwater chemistry around the city of Goma varies widely, both spatially and temporally, in relation to Nyiragongo and Nyamulagira eruptive activities, and with the season. The present study was devoted to the understanding of the rainwater chemistry in and

around the city of Goma during a non-eruptive episode of Nyamulagira volcano. The obtained dataset is used to draw a rainwater chemistry and quality baseline for the city of Goma, as Nyiragongo is an open system volcano that has had a permanent active lava lake since May 2002. Nyiragongo has huge degassing rates with values up to t/day 5356.8 t/ daytons per day (t/d) for SO2, ~200 t/d for Cl, and 102 t/d for BrO (see Arellano et al., 2016; Balagizi et al., 2016 and Bobrowski et al., 2016), and has not shown any important decrease in its activity. This rainwater baseline is both important for volcano monitoring planning, for rainwater and air quality monitoring and the management of the resulting human health impacts.

2.Materials and methods

Single rainwater samples were collected from 15 sites located in the city of Goma, in the villages around, and on the top of Nyiragongo volcano (Fig. 1). Of these 15 sampling sites, one was located at the summit crater of Nyiragongo volcano, one in the village of Rusayo to the south-west of Nyiragongo, seven in the city of Goma (three to the western-southwestern side where the Nyiragongo volcanic plume is regularly directed by the local dominant wind direction, two to the center of the city, one to the south and one more to the north of the city), and the remaining six others in villages located to the west, east and northeast of Nyiragongo volcano (Fig. 1). Rainwater at each site was collected in a 5-Liter plastic container placed on the roof of a house at the beginning of a rain event between January and June 2013. The containers were washed with distilled water between sampling events. After each rain, an aliquot of water sample was taken from the container, filtered through a 0.45 µm polysulfone filter attached to a syringe. The filtered water was used to fill in a 50 ml polyethylene plastic bottle with a double cap, and stored at room temperature until laboratory analysis. No fixers were added to the samples. The pH and specific conductivity of the rain were measured in the field using an ORION STAR A325 probe, of which the electrodes were calibrated before the sampling campaigns using pH 4 and pH 7 (25 ◦C) and a 1413 µS/cm standard buffers, with an accuracy of 0.01 pH unit 1 µS/cm conductivity. The concentrations of major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and major anions (F^-, Cl^-, NO_3^-, SO_4^{2-}, $H_2PO_4^-$) were measured by ion Chromatograph (IC) mean (Dionex-120) at the University of Naples 2 in Italy. Four calibration levels were used for each of the major elements, while a “BURTAP-05” (Environment Canada) certified analytical reference material was used to control the accuracy of the IC analyses. The analytical precision and accuracy for the major cations and anions were better than 5%. The Total Dissolved Substances (TDS) was estimated from the rainwater specific conductivity using the Lloyd and Heathcote (1985) equation (TDS =Ke EC), where the correction factor Ke was 0.67 for diluted water (Atekwana et al., 2004).

3.Results and discussion

3.1. General variabilities in the chemistry of rainwaters

The results of the chemical analysis of the rainwater collected in the Goma region are given in Table 1. A diversity of pH values is observed among the samples, varying between 3.70 and 7.73, where the Nyiragongo Summit (3.70–3.82) and some Kingi sites (3.93–5.74) show the lowest pH values (Table 1 and Fig. 2A). The latter is both the result of the proximity of the sampling site at Nyiragongo summit to the source of the plume loading acidic gases such as HCl, HF, SO_2, NOx; and the fact that Kingi is located to the western part of the study area where the plume is directed by the wind (Fig. 1). These volcanic gases are highly soluble in water (Stumm and Morgan, 1995; Aiuppa et al., 2001; Madonia and Liotta,

2010), and thus quickly dissolved in the falling rain drops to yield the measured lower pH values at these sites. The specific conductivity span in a large range, varying from 8 µS/cm (at Rugari site, to the northeastern of the volcano) to 270 µS/cm (at Kasika site in the city of Goma); at the summit of the volcano, the value was 86 µS/cm with an average of 82 µS/cm (Table 1). The TDS values followed the same trend as that of the specific conductivity (Fig. 2A) as the former was estimated from the latter by applying the Lloyd and Heathcote (1985) equation. The F^- and Cl^- concentrations were higher at the crater of Nyiragongo volcano (Fig. 2B), with mean values of 0.98 mg/L (varied from 0.00 to 4.18 mg/L) and 4.85 mg/L (varied from 0.33 to 19.16 mg/L) respectively; as a result of the influence of the Nyiragongo plume and other non-volcanic activities. On the other hand, a higher concentration of SO_4^{2-} was found at Rusayo site (26.5 mg/L), while the majority of elevated values were found in sites located in the southern zone of the study area (Table 1) because of the anthropological prevalence of sulfur in the atmosphere of the city of Goma. The NO_3^- and $H_2PO_4^-$ concentrations were the lowest among the anions with mean values of 2.75 mg/L (ranged between 0.00 and 16.46 mg/L) and 0.20 mg/L (range from 0.00 to 1.84 mg/L) respectively, as a consequence of their absence in volcanic products, i.e., gases, ash, soil with volcanic origin. The alkaline cations Na^+ and K^+ had their single higher values to the southern side of the volcano (12.16 mg/L at Goma/ Ngangi for Na^+ and 12.21 mg/L at Rusayo for K^+), but their higher mean values were found to the western side of the volcano and at the summit. The high Mg^{2+} values were found in rainwaters from the southern zone of the volcano and, to the western zone for Ca^{2+} (Table 1). As a general trend, the following dominance was observed for major anions $Cl^->SO_4^{2-}>F^->NO_3^->H_2PO_4^-$ and $K^+>Na^+>Ca^{2+}>Mg^{2+}$ for major cations; Cl^-, accounting for up to 20.29% of the total ionic concentrations in some samples.

3.2. Spatial variations in the rainwater chemical composition

In order to understand the influence of Nyiragongo's permanent plume in the study area, we have subdivided the area into four zones based on their relative position to the Nyiragongo summit. These four zones include the summit of Nyiragongo volcano, the western zone where the plume is directed, the southern zone where the city of Goma is located and the north-eastern zone (Fig. 1). The variation of the rainwater chemistry in these zones are presented in Table 2, where the chemistry of the rainwaters around Nyiragongo volcano (from this study and from published literature) is further compared to that from other world's open systems volcanoes. As mentioned in section 3.1, the pH of rainwater depends on the amounts of acidic gases that dissolve in the rain and release of H^+ ions, and hence the summit of Nyiragongo measured the most acidic rains because of being closest to the plume vent. Also, the sites located to the western zone had the second most acidic rains, with lower pH because they are located in the zone where the plume is directed by the main wind direction (Fig. 1). All the samples from the summit had pH values that varied very little, while in sites from the other zones, especially those to the south (e.g. Goma and Sake), the pH showed important variations (Fig. 2A). This is because sometimes rain events may have taken place while the plume is in a different direction from the sites, which causes the increase in the pH in the resulting samples. Most samples from the other zones, principally those from the northeastern and southern zones have pH values close to 5.7, which is the pH value for rainwater in unpolluted continental areas (Langmuir, 1997; Berner and Berner, 2012). For the pH with values above 5.7 that were recorded in some samples from these sites, the high values are due to the fact that the dust load in rainwater and in the humid atmosphere reacts with the H^+ ions and causes both pH and TDS increases (Fig. 2A). This generally takes place when the rainwater amounts decreases and/or when the amount of dust in the atmosphere increases (Balagizi et al., 2017). The dissolution of volcanic plume and ash and of wind-blown dust loaded elements determined the chemistry of the rainwater allows one to distinguish the influence from the volcano (dissolution of volcanic plume and ash) from the direct and indirect human activities (e.g. dissolution of wind-blown dust in city and farms, traffic). The sites

impacted by the volcano showed the higher concentrations of elements contained in volcanic plume and ash, e.g., F^- and in some cases SO_4^{2-} (2 B and 2C). The summit and the western zone (e.g. Rusayo, Kingi and Sake, Fig. 1) have the most elevated F^- concentrations (Fig. 2B and C). While SO_4^{2-} was higher only at Rusayo and was mostly dominant at sites with impacts from anthropogenic activities such as traffic (Fig. 2C). The higher SO_4^{2-} value at Rusayo is due to the fact that this site is potentially affected both by anthropogenic and volcanic activities. This is similarly the case for Cl^- at most sites where anthropogenic influence or Cl^- originating from other natural sources predominates. This dual origin of elements caused the shift from the 1:1 line, with values which are in opposition to ratios found in the plume. As an example, in Nyiragongo plume, plume molar amount of SO_2, HCl and HF are 4.6%, 0.26%, and 0.11% respectively (Sawyer et al., 2008), ratios which are not in line with their respective concentrations observed in rainwaters. In fact, in the rainwaters, the Cl/F ratios average 4.8, but range between 0 and 25; the higher values being in samples with limited influence from the volcanoes (Fig. 2B), mainly to the south and northeastern side of Nyiragongo. Similar trends of disturbance of molar ratios in the plume were observed for SO_4/F (averaging 4.9, range 0.1 and 31.7; Fig. 2C) and for SO_4/Cl that averages 1.3 and varies from 1.2 to 9.9. This shifting from the plume composition is the result of anthropogenic and other non-volcanic natural inputs, as well as the dissolution of chemical elements that may be included in the ash (Cuoco et al., 2012a, b; Balagizi et al., 2017). The dissolution of the elements included in ash (e.g., Spilliaert et al., 2006) may have caused F to being enriched in rain-waters at the summit of Nyiragongo (Fig. 2A). Major cations originate from the dissolution of volcanic ash and wind-blown dust, with K^+ and Ca^{2+} being higher in samples from the sites influenced by volcanic products (i.e., summit, Rusayo, and Kingi), while on the other hand Na^+ and Mg^{2+} are dominant at sites with limited influence from the volcano (Rumangabo, Rugari and Kibumba; Fig. 2E and F). The latter further highlights the fact that the summit and the western zones of Nyiragongo are the most impacted by the volcanic plume, while the southern zone is partially impacted; and the north-eastern zone is almost not impacted by the plume. Of course, the dissolution of wind-blown dust of soil from volcanic parental material may yield major cations composition close to that volcanic ash. The presentation of both major cations and anions in a single chart (Fig. 3A) clearly shows that the summit of Nyiragongo and the western zone are the most impacted by the volcanic impacts with halogen (F^- and Cl^-) and alkaline cations (Na^+ and K^+) being dominant, followed by the southern zone where SO_4^{2-}, Mg^{2+}, and Ca^{2+} are dominant.

3.3. Comparison with previous studies in the Virunga: baseline for rainwater chemistry as impacted by Nyiragongo's permanent plume

When comparing the pH values measured in rainwater samples of the present study with those reported in the literature for the Virunga, it is noted that the mean pH values from each of the zones are comparable (Fig. 3B; Table 2). This is because the pH is the principal parameter that is directly linked to volcanic gases dissolution, and is continuously consumed during the interactions between the H^+ ions and the ash and dust that are also available. As noted by Balagizi et al. (2017), the availability of the H^+ ions in the rainwater and time are the limiting parameters to ash and dust dissolution, and hence in each zone it is quite reasonable to have comparable pH values. In some zones, the pH values from the present study are slightly higher compared to that from the literature (Fig. 3B and Table 2), implying the absence of any contribution from the neighbouring Nyamulagira that was also emitting a plume when the other studies were conducted (Fig. 1). The latter trend is confirmed by the prevalence of the high concentrations of major elements reported by Cuoco et al. (2012a), b; Liotta et al. (2017) and Balagizi et al. (2017), such as fluorine (Fig. 3C) and the total dissolved substances (Fig. 3D). The data reported by Cuoco et al. (2012a) are from single rainwaters collected during Nyamulagira 2010 eruption, those in Balagizi et al. (2018a) include single rainwaters from both Nyamulagira 2010 and 2011/2012 eruptions, those in Liotta

et al. (2017) (single rainwaters) and Balagizi et al. (2017) (monthly samples from rain gauges) are collected while both Nyiragongo and Nyamulagira had a lave lake in their main craters (the image of Fig. 1 was captured during this period). In all the studies, the fluorine concentrations at the summit of the Nyiragongo exceed the World Health Organization (WHO) limit for drinking water fixed at 1.5 mg/L (Tables 1 and 2; WHO, 2011). In the other zones, particularly the western of the volcano and of the city of Goma, the fluorine concentrations vary in a large range, with some values exceeding the WHO guidelines. Vaselli et al., 2009 have even reported fluoride concentrations as high as 1000 mg/L in rainwater during the Nyiragongo 2002 eruption, while Balagizi et al. (2015), 2018a reported values up to 6.9 mg/L in rivers of the Virunga. The high fluorine concentrations in waters (surface, rain and groundwater) have yielded the endemic fluorosis that is visible on the teeth of the population in the Virunga (see compilation in Balagizi et al., 2018a).

3.4. Comparison with others open system volcanoes with continuous degassing

In the Virunga, the rainwater is more acidic at the Nyiragongo crater and gradually decreases as one moves away from the summit towards the western zone where the wind carries the volcanic plume (Figs. 1 and 2A and Table 2). Similar behaviour is observed at others volcanoes, e.g., Kilauea volcano, Hawaii and Vulcano volcano, Italy. In fact, the pH at the summit of Nyiragongo averages 3.75 (Table 2), which is close to that reported at the Halemaumau crater (Kilauea) 3.6, (Harding and Miller, 1982), but is still slightly higher than that obtained in rainwater at la Fossa crater (Vulcano Island) (2.0–3.5), (Madonia and Liotta, 2010). While the average pH of rainwater on Hawaii Island is between 4 and 5 Harding and Miller (1982); Nachbar et al. (1989), in the Virunga we obtained an average of 5.6. These data are perfectly comparable since they are obtained from studies conducted on open systems volcanoes (i. e., presence of a lava lake, or persistent degassing), with non-classic eruption accompanied by lava flows formation. No unique trend of dominance of given major cations was observed: Stromboli volcano, Italy, has higher mean Na^+ values (0.46 mmol/L; Liotta et al., 2006) with its highest recorded value being 6.6 times higher than that found in Nyiragongo rainwaters (Table 2). Etna showed a higher K^+ value (1,02 mmol/L; Calabrese et al., 2011) which is 3.2 times higher than the one we report for Nyiragongo; while on the other hand, Stromboli has a higher Mg^{2+} value (Table 2). Similarly, Vulcano has higher Ca^{2+} mean concentrations (0.1 mmol/L; Madonian and Liotta, 2010) which is 1.25 times higher than we found in Nyiragongo rainwaters. This general tendency of higher major cations and some anions at Italian volcanoes (Table 2) is because of the higher precipitation in the tropical region of the Virunga (up to 2332 mm/year; Balagizi et Liotta, 2019) compared to the Mediterranean area (up to 1100 mm/year, Liotta et al., 2006). This high precipitation in the Virunga dilutes and reduces concentrations of elements in rainwaters.

3.5. Comparison with other studies conducted in cities with non volcanic activities

Atmospheric pollutants, gases and solid particles, are removed from the atmosphere during rain washout; the dissolved pollutants are then deposited on the ground where they may reach groundwater or accumulate in the soil. Hence, rainfall is one of the most effective ways of removing atmospheric pollutants (Hameed et al., 2006), while the chemical composition of the resulting rains is a useful index for the assessment of the atmosphere chemistry in a given area. The latter provides a better understanding of the relative contribution of different sources of atmospheric pollutants (Zhang et al., 2012; Xiao, 2016). Several studies have thus used the chemical composition of the rainwater to evaluate air pollution (see Table 3), in which major and trace elements as well as the pH of rainwater are the dominant key tracers. As expected, from Table 3, Nyiragongo summit has the most acidic rainwaters (pH averaging 3.75), along with other elements which are simultaneously with H^+ in the rainwater. Hence, the

concentrations of these elements, e.g., Cl, F, SO_4, are also at high concentrations at the crater and in most cases in Goma city (southern zone) as compared to concentrations in most cities reported in Table 3. In these cities, the major source of air pollution is anthropogenic activities (traffic, agriculture, industrial activities). Even though the pH values in these cities are close to that of unpolluted air (5,7; Berner and Berner, 2012), some however, have mean pH values below 5 (e.g. 4.6 in Ya'an, China, 4.5 in Hwasung, Korea, and 4.9 in Eastern France). These cities have their air either influenced by strong industrialization, or are semi-rural and semi-urban areas with less industry but pollutants (air masses) are transported from more polluted regions both near and far (Sanusi et al., 1996; Yobou´e et al., 2005; Zhao et al., 2013; Park et al., 2015). Some cities with high pH values compared to that of the Virunga are regions limited industrialization (7.7 in Xi'an, China; 7.03 in Roorke, India); (Hameed et al., 2006; Xiao, 2016), but their pH is also the result of the neutralization of industrial products in rainwater that yield high pH, similar to the wind-blown dust that consumes H^+ ions and higher the pH in the Virunga. The major cations in downtown Goma city (western and southern zones) are at higher concentrations compared to other cities reported in Table 3, while on the other hand; the northeastern zone that is less impacted by Nyiragongo plume has concentrations that are comparable to that found in other world cities. Hence, Na^+, K^+, Ca^{2+}, Mg^{2+} in the southern and eastern zones have concentrations up to 130, 100, 160 and 160 µeq/L, respectively (Table 3); which is generally about 2–20 times higher than the concentrations found in rainwaters of world cities listed in Table 3; except Xi'an and Ya'an in China and Ma'an in Jordan that have either comparable or higher concentrations to that in the Virunga.

4.Conclusions

•The pH at the crater and west of the Nyiragongo was more acidic than other groups due to the influence of the gas plume in these areas and which is carried by the wind whose preferential direction in the region remains from East to West.

•The dominance of F^- and Cl^- anions at the crater of the volcano and SO_4^{2-} anions in the south was noted due to the dissolution of HF, HCl and H_2SO_4 acids in water. Cl^- anion was the most dominant of the all ions and contributed to 20,29% of the total ionic concentration. Na^+ and K^+ were the most dominant of cations and were of volcanic origin.

•Volcanic emissions are the primary sources of dissolved solutes, and their impact decreases with distance. The Virunga region is not industrialized, hence vehicle traffic and soil dust from roads and farms remain the unique anthropogenic sources of pollution.

•Comparing the results of this work with published investigations (Balagizi et al., 2017; Cuoco et al., 2012a,b and Liotta et al., 2017), we remarked that the atmosphere of the region is less polluted when there is no contribution of the plume of the Nyamulagira volcano from eruption or presence of a lava lake. On the other hand, compared to others non volcanic areas the Virunga region maintains a high concentration of ions of volcanic origin. The mean pH value (3.75) of Nyiragongo volcano is comparable to that obtained at a site located 0.8 km from the Halemaumau crater of Kilauea volcano (3.6) but is high compared to that of La fossa crater in range of (2–3.5) at Vulcano Island. The Virunga region generally could be considered to be an unpolluted area with its mean pH of 5.6 compared to Hawaii Island with mean pH ranged between 4 and 5 which similarly is proximal to an open system volcano like Nyiragongo.

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Figure Captions

Fig. 1. Locations of sampling sites in Goma city, surrounding villages and around Nyiragongo volcanoes situated within the western branch of the East African Rift System, East Africa. In the Southern zone, the numbers correspond to the sites as follows: 1 for Kituku, 2 for Ndosho, 3 for Ngangi, 4 for Kibwe, 5 for Kasika and 6 for OVG.

Fig. 2. Relationship between total dissolved substances (TDS) and pH (A), F^- and Cl^-(B), SO_4^{2-} and F^- (C), Cl^- and SO_4^{2-} (D), Na^+ and K^+ (E), Mg^{2+} and Ca^{2+} (F) in rainwater collected on a daily basis in the Nyiragongo and Nyamulagira volcanic fields, situated within the western branch of the East African Rift System, East Africa; between January and June 2013.

Fig. 3. Mean major ion concentrations in different zones (A), comparison of pH (B), F^- concentration (C) and total dissolved substances (TDS) (D) means of this study and the previous studies in the Virunga and Nyamulagira volcanic fields, located within the western branch of the East African Rift System, East Africa; between January and June 2013.

Table Captions

Table 1 Sampling sites, physico-chemical parameters and major ions concentrations of single rainwater collected in Goma city, on and around Nyiragongo volcano, between January and June 2013.

Table 2 Comparison of physico-chemical parameters and major ions concentrations of single rainwater collected in Goma city, on and around Nyiragongo volcano, with literature data on rainwater chemistry at Nyiragongo and Nyamulagira volcanoes, as well as some Italian long lasting open system volcanoes.

Table 3 Comparison of physico-chemical parameters and major ions concentrations of single rainwater collected in Goma city, on and around Nyiragongo volcano, with literature data on rainwater chemistry from some world major cities without volcanic activities.

Figures

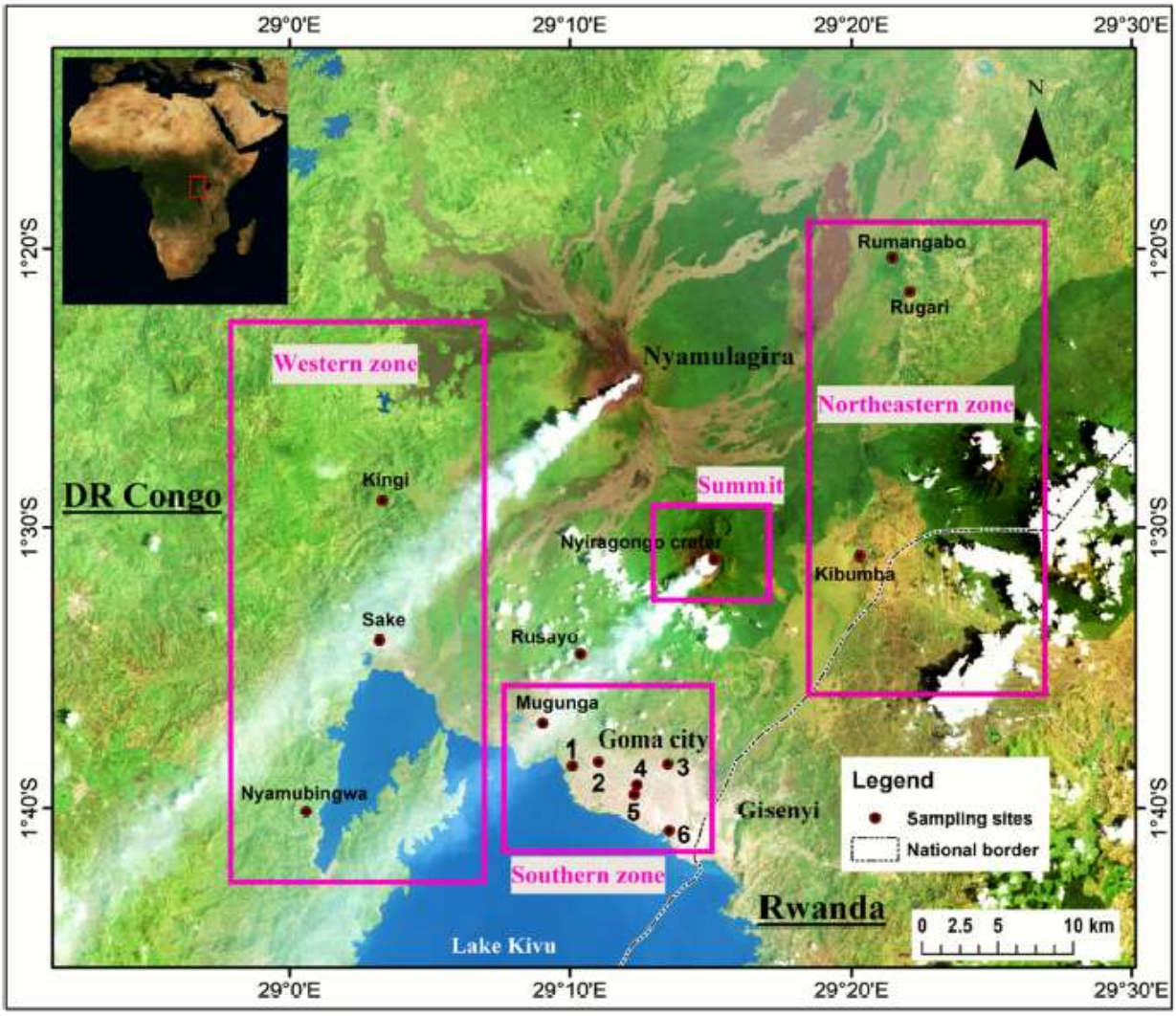

Fig.1

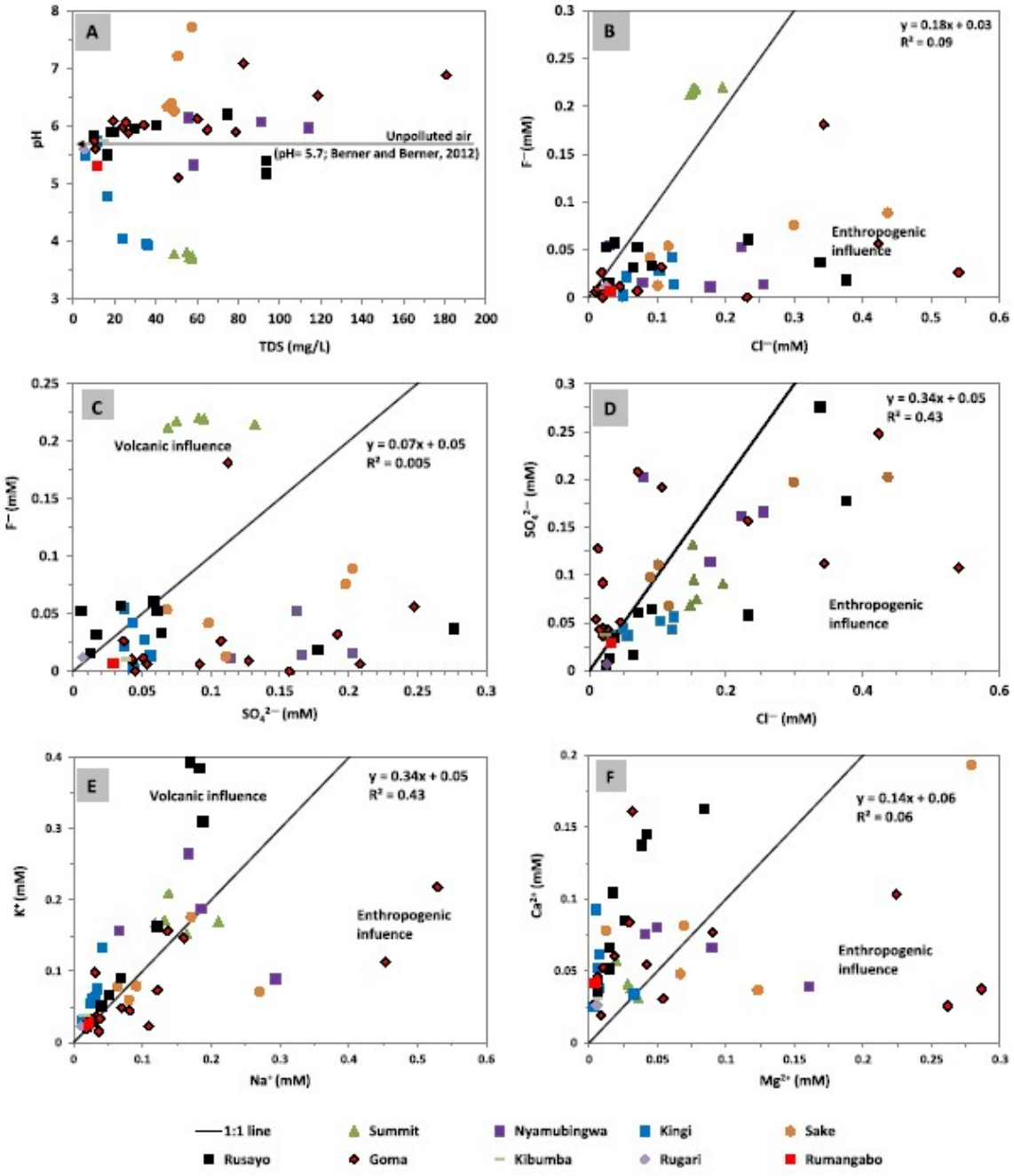
A
pH
TDS (mg/L)
Unpolluted air
(pH= 5.7; Berner and Berner, 2012)
B
y = 0.18x + 0.03
R² = 0.09
F⁻ (mM)
Cl⁻ (mM)
Enthropogenic influence
C
Volcanic influence
y = 0.07x + 0.05
R² = 0.005
F⁻ (mM)
SO4²⁻ (mM)
D
y = 0.34x + 0.05
R² = 0.43
SO4²⁻ (mM)
Cl⁻ (mM)
Enthropogenic influence
E
Volcanic influence
y = 0.34x + 0.05
R² = 0.43
K⁺ (mM)
Na⁺ (mM)
Enthropogenic influence
F
y = 0.14x + 0.06
R² = 0.06
Ca²⁺ (mM)
Mg²⁺ (mM)
Enthropogenic influence
1:1 line
Summit
Nyamubingwa
Kingi
Sake
Rusayo
Goma
Kibumba
Rugari
Rumangabo

Fig.2

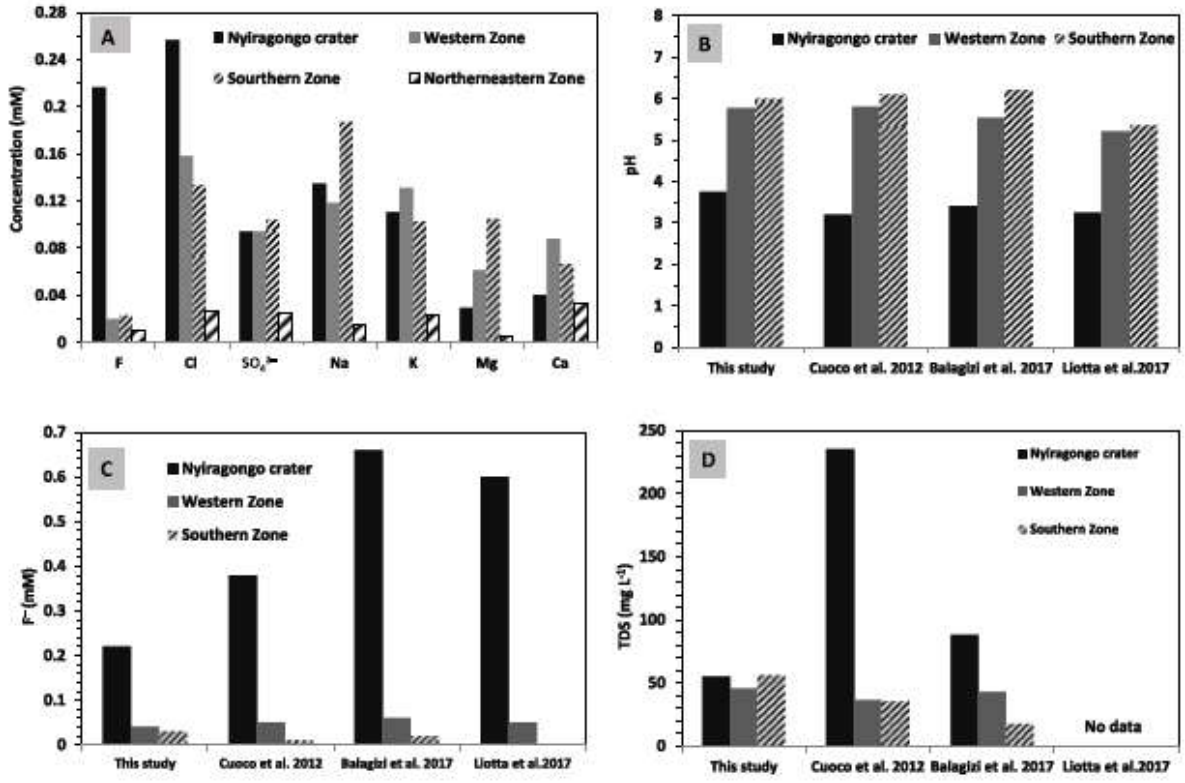
A
Nyiragongo crater
Western Zone
Sourthern Zone
Northerneastern Zone
Concentration (mM)
F
Cl
Na
K
Mg
Ca
B
Nyiragongo crater
Western Zone
Southern Zone
pH
This study
Cuoco et al. 2012
Balagizi et al. 2017
Liotta et al.2017
C
Nyiragongo crater
Western Zone
Southern Zone
F- (mM)
This study
Cuoco et al. 2012
Balagizi et al. 2017
Liotta et al.2017
D
Nyiragongo crater
Western Zone
Southern Zone
TDS (mg L-1)
No data
This study
Cuoco et al. 2012
Balagizi et al. 2017
Liotta et al.2017

Fig.3

TABLES

Site Name	Latitude (°)	Longitude (°)	Altitude (m a.s.l.)	Location zone with respect to summit	Sampling Date	E.C. (µS/cm)	pH	F^- (mg L^{-1})	Cl^- (mg L^{-1})	NO_3^- (mg L^{-1})	SO_4^{2-} (mg L^{-1})	$H_2PO_4^-$ (mg L^{-1})	Na^+ (mg L^{-1})	K^+ (mg L^{-1})	Mg^{2+} (mg L^{-1})	Ca^{2+} (mg L^{-1})	TDS (mg L^{-1})	Charge balance
Nyiragongo crater	−1.51833	29.2525	3429	Nyiragongo Summit	May 20, 2013	82.00	3.82	4.07	5.36	0.00	12.67	0.00	4.83	5.28	0.47	2.30	54.94	4.27
Nyiragongo crater	−1.51833	29.2525	3429	Nyiragongo Summit	June 8, 2013	73.00	3.78	4.02	5.23	0.00	6.60	0.00	2.73	5.24	0.68	1.63	56.28	9.21
Nyiragongo crater	−1.51833	29.2525	3429	Nyiragongo Summit	June 17, 2013	86.00	3.70	4.13	5.56	0.00	7.20	0.00	3.03	5.33	0.80	1.36	48.91	9.68
Nyiragongo crater	−1.51833	29.2525	3429	Nyiragongo Summit	June 13, 2013	86.00	3.74	4.16	6.94	0.00	8.72	0.00	3.18	6.51	0.74	1.53	57.62	9.81
Nyiragongo crater	−1.51833	29.2525	3429	Nyiragongo Summit	June 1, 2013	84.00	3.72	4.17	5.43	0.00	9.14	0.00	3.77	4.73	0.87	1.25	57.62	9.96
Nyamubingwa	−1.66883	29.00963	1473	Western zone	April 26, 2013	136.00	6.07	0.27	9.05	4.17	15.94	1.57	6.74	2.77	3.89	1.56	58.29	−5.64
Nyamubingwa	−1.66883	29.00963	1473	Western zone	April 20, 2013	87.00	5.38	0.21	6.27	12.79	10.96	0.00	3.85	8.25	0.98	3.02	91.12	−3.78
Nyamubingwa	−1.66883	29.00963	1473	Western zone	May 2, 2013	83.00	6.15	0.29	2.79	1.73	19.44	0.00	1.51	4.91	1.21	3.20	55.61	−4.23
Nyamubingwa	−1.66883	29.00963	1473	Western zone	May 9, 2013	170.00	5.97	1.00	7.89	0.49	15.56	1.84	4.26	5.84	2.17	2.65	113.90	−6.47
Kingi/Kunene	−1.48366	29.05516	2011	Western zone	April 19, 2013	53.00	3.97	0.79	4.30	0.86	4.11	0.00	0.94	4.17	0.08	1.01	36.18	3.79
Kingi/Kunene	−1.48366	29.05516	2011	Western zone	March 19, 2013	17.00	5.74	1.04	1.09	0.74	3.56	0.00	0.57	1.71	0.19	1.53	11.39	3.31
Kingi/Kunene	−1.48366	29.05516	2011	Western zone	May 2, 2013	25.00	4.78	0.41	1.97	0.63	3.56	0.00	0.60	1.94	0.80	1.36	24.12	−9.72
Kingi/Kunene	−1.48366	29.05516	2011	Western zone	April 25, 2013	9.00	5.48	0.05	1.76	0.37	4.19	0.00	0.31	0.95	0.19	2.45	35.51	−5.17
Kingi/Kunene	−1.48366	29.05516	2011	Western zone	March 16, 2013	54.00	3.93	0.26	4.38	1.05	5.39	0.00	0.79	2.35	0.12	3.71	6.03	0.72
Kingi/Kunene	−1.48366	29.05516	2011	Western zone	April 4, 2013	36.00	4.04	0.52	3.66	0.00	4.95	0.00	0.74	2.03	0.15	2.09	16.75	7.65
Sake	−1.56683	29.05333	1511	Western zone	April 24, 2013	73.00	6.26	1.02	4.12	0.05	6.54	0.00	2.09	2.48	1.62	1.92	47.57	−8.82
Sake	−1.56683	29.05333	1511	Western zone	May 25, 2013	68.00	6.33	0.24	3.57	2.90	10.65	0.00	1.84	1.88	0.30	3.14	57.42	7.95
Sake	−1.56683	29.05333	1511	Western zone	April 20, 2013	85.70	7.73	1.69	15.49	0.52	19.46	0.00	6.21	2.21	6.79	7.75	48.91	−4.97
Sake	−1.56683	29.05333	1511	Western zone	May 10, 2013	75.50	7.22	1.44	10.60	0.81	18.97	0.00	3.93	5.48	2.99	1.47	50.59	7.16
Sake	−1.56683	29.05333	1511	Western zone	April 24, 2013	71.00	6.39	0.80	3.16	2.00	9.40	0.00	1.45	2.45	1.69	3.27	45.56	−5.76
Rusayo	−1.57500	29.17316	1671	Western zone	April 8, 2013	140.00	5.39	0.70	11.98	16.46	26.50	0.89	4.21	11.96	2.03	6.52	74.37	6.41
Rusayo	−1.57500	29.17316	1671	Western zone	January 26, 2013	111.00	6.21	1.15	8.24	13.46	5.59	1.01	4.32	9.64	0.93	5.50	40.20	−7.56
Rusayo	−1.57500	29.17316	1671	Western zone	May 1, 2013	44.00	5.95	1.00	2.53	1.79	5.84	1.00	1.56	2.83	0.63	3.40	18.09	−9.16
Rusayo	−1.57500	29.17316	1671	Western zone	May 12, 2013	25.00	5.50	0.61	2.28	0.77	1.61	0.00	0.66	0.92	0.14	1.75	93.80	7.51
Rusayo	−1.57500	29.17316	1671	Western zone	March 26, 2013	27.00	5.90	1.08	1.34	2.53	3.32	0.00	1.20	2.09	0.37	2.66	93.80	−8.23
Rusayo	−1.57500	29.17316	1671	Western zone	March 21, 2013	60.00	6.02	0.63	3.26	9.97	6.12	0.00	2.79	5.07	0.43	4.19	19.43	−7.53

(continued on next page)

Tab.1

Table 1 (*continued*)

Site Name	Latitude (°)	Longitude (°)	Altitude (m a.s.l.)	Location zone with respect to summit	Sampling Date	E.C. (µS/cm)	pH	F^- (mg L^{-1})	Cl^- (mg L^{-1})	NO_3^- (mg L^{-1})	SO_4^{2-} (mg L^{-1})	$H_2PO_4^-$ (mg L^{-1})	Na^+ (mg L^{-1})	K^+ (mg L^{-1})	Mg^{2+} (mg L^{-1})	Ca^{2+} (mg L^{-1})	TDS (mg L^{-1})	Charge balance
Rusayo	−1.57500	29.17316	1671	Western zone	May 20, 2013	15.00	5.85	0.30	1.04	1.29	1.22	0.00	0.45	0.71	0.16	1.41	29.48	−3.24
Rusayo	−1.57500	29.17316	1671	Western zone	April 5, 2013	140.00	5.18	0.35	13.34	3.46	17.07	0.91	3.89	12.21	1.02	5.79	16.75	−8.01
Rusayo	−1.57500	29.17316	1671	Western zone	April 14, 2013	29.00	5.91	1.00	0.88	2.54	0.56	0.50	0.92	1.60	0.36	2.07	10.05	−9.91
Goma/OVG	−1.68001	29.22583	1501	Southern zone	April 27, 2013	123.00	7.09	0.61	3.77	2.55	18.45	0.00	2.50	0.73	6.36	1.03	10.05	−6.07
Goma/OVG	−1.68001	29.22583	1501	Southern zone	March 26, 2013	15.00	5.74	0.50	0.67	0.80	3.51	0.00	0.84	0.49	0.15	1.84	82.41	−4.74
Goma/OVG	−1.68001	29.22583	1501	Southern zone	May 9, 2013	36.00	5.98	0.17	0.96	1.57	4.13	0.00	0.74	1.15	0.15	1.84	10.72	−7.55
Goma/OVG	−1.68001	29.22583	1501	Southern zone	May 11, 2013	38.00	6.06	0.12	0.70	1.38	8.82	0.00	0.59	1.05	1.02	2.18	24.12	−5.35
Goma/OVG	−1.68001	29.22583	1501	Southern zone	May 10, 2013	40.00	5.88	0.00	0.69	5.67	4.31	0.20	1.88	1.40	0.25	2.10	26.80	−9.07
Goma/OVG	−1.68001	29.22583	1501	Southern zone	May 12, 2013	29.00	6.09	0.20	0.55	1.46	4.10	0.00	0.88	1.04	0.21	0.78	25.46	−3.88
Goma/OVG	−1.68001	29.22583	1501	Southern zone	April 30, 2013	16.00	5.61	0.11	0.33	0.57	5.15	0.00	0.41	0.59	0.10	1.13	19.43	5.76
Goma/OVG	−1.68001	29.22583	1501	Southern zone	May 23, 2013	118.00	5.90	0.00	8.21	13.66	15.07	0.00	3.67	4.56	0.77	6.45	79.06	9.96
Goma/Kituku	−1.64133	29.16833	1479	Southern zone	April 10, 2013	51.00	6.02	0.17	0.45	0.97	12.26	0.20	1.60	1.51	1.31	1.23	34.17	−9.57
Goma/Ndosho	−1.63880	29.18366	1524	Southern zone	April 10, 2013	90.00	6.13	0.12	2.52	1.92	20.00	0.00	2.79	2.29	2.20	3.08	60.30	−6.66
Goma/ Mungunga	−1.61666	29.1505	1511	Southern zone	April 12, 2013	97.00	5.94	3.44	12.19	0.48	10.78	0.00	3.14	4.87	5.45	4.14	64.99	1.90
Goma/Ngangi	−1.64016	29.225	1568	Southern zone	April 17, 2013	177.00	6.53	0.50	19.16	0.50	10.32	0.00	12.16	6.78	0.45	2.42	118.59	−9.51
Goma/Kasika	−1.65850	29.205	1522	Southern zone	April 11, 2013	270.00	6.89	1.07	15.01	3.00	23.79	0.30	10.43	3.51	6.96	1.50	180.90	−6.65
Goma/Kibwe	−1.65250	29.20666	1547	Southern zone	April 16, 2013	76.00	5.11	0.22	1.62	8.87	4.87	0.60	0.72	3.07	0.72	3.35	50.92	2.85
Kibumba	−1.51666	29.33016	2026	Northeastern zone	April 13, 2013	22.00	5.75	0.20	0.83	0.22	3.65	0.00	0.35	1.18	0.15	1.26	14.74	−9.40
Rugari	−1.35916	29.368	1565	Northeastern zone	April 14, 2013	8.00	5.60	0.23	0.91	0.57	0.67	0.20	0.25	0.73	0.14	1.05	5.36	−8.37
Rumangabo	−1.33666	29.35766	1602	Northeastern zone	April 11, 2013	17.00	5.31	0.14	1.11	0.73	2.76	0.10	0.51	0.82	0.11	1.66	11.39	−8.10

TDS values calculated from measured specific conductivity after (Atekwana et al., 2004).
Charge balances were calculated using values expressed in mmol/L.

Tab.1

	Zone	pH	E.C. (μS/cm)	F^- (mmol L^{-1})	Cl^- (mmol L^{-1})	SO_4^{2-} (mmol L^{-1})	Na^+ (mmol L^{-1})	K^+ (mmol L^{-1})	Mg^{2+} (mmol L^{-1})	Ca^{2+} (mmol L^{-1})
This study	Nyiragongo crater	3.75 (3.70–3.82)	82.2 (73.00–86.00)	0.22 (0.21–0.22)	0.17 (0.15–0.21)	0.09 (0.07–0.13)	0.17 (0.14–0.21)	0.15 (0.13–0.18)	0.03 (0.02–0.04)	0.04 (0.03–0.06)
	Western zone	5.77 (3.93–7.73)	68.09 (9.00–170)	0.04 (0.00–0.09)	0.15 (0.02–0.44)	0.10 (0.01–0.28)	0.10 (0.01–0.29)	0.10 (0.02–0.32)	0.05 (0.00–0.28)	0.08 (0.03–0.19)
	Southern zone	6.00 (5.11–7.09)	84.00 (15.00–270)	0.03 (0.00–0.18)	0.13 (0.01–0.54)	0.11 (0.04–0.25)	0.13 (0.02–0.53)	0.06 (0.01–0.17)	0.08 (0.00–0.29)	0.06 (0.02–0.16)
	Northeastern zone	5.55 (5.31–5.75)	15.66 (8.00–22.00)	0.01 (0.01–0.01)	0.03 (0.02–0.03)	0.02 (0.01–0.04)	0.02 (0.01–0.02)	0.02 (0.02–0.03)	0.01 (0.00–0.01)	0.03 (0.03–0.04)
Cuoco et al. (2012a), b	Nyiragongo crater	3.20 (2.30–5.60)	256.0 (28–1828)	0.38 (bdl-10.21)	0.41 (0.01–7.59)	0.41 (0.01–3.53)	0.16 (0.01–1.17)	0.13 (0.01–0.65)	0.03 (0.00–0.54)	0.10 (0.01–0.71)
	Western zone	5.8 (4.0–7.0)	44 (11–115)	0.05 (0.01–0.74)	0.07 (0.01–1.55)	0.06 (0.01–0.20)	0.07 (0.02–0.29)	0.04 (0.02–0.30)	0.01 (0.00–0.15)	0.07 (0.01–0.39)
	Southern zone	6.10 (4.90–8.10)	40.0 (5.0–178)	0.01 (bdl-0.08)	0.03 (0.00–0.22)	0.03 (0.00–0.37)	0.04 (0.00–0.57)	0.03 (0.00–0.23)	0.02 (bdl-0.26)	0.04 (0.00–0.35)
Balagizi et al. (2017)	Nyiragongo crater	3.41 (3.10–3.17)	131 (85–172)	0.66 (0.10–2.64)	0.41 (0.04–1.07)	0.14 (0.05–0.36)	0.33 (0.04–1.16)	0.22 (0.04–0.57)	0.11 (0.01–0.46)	0.13 (0.02–0.50)
	Western zone	5.53 (4.06–6.77)	64 (26.33–95.33)	0.06 (0.02–0.17)	0.15 (0.04–0.54)	0.06 (0.03–0.15)	0.04 (0.02–0.18)	0.05 (0.03–0.57)	0.05 (0.01–0.40)	0.10 (0.03–0.91)
	Southern zone	6.22 (4.74–7.48)	41 (10–81.5)	0.02 (0.00–0.07)	0.09 (0.02–0.29)	0.04 (0.02–0.09)	0.05 (0.01–0.14)	0.10 (0.02–0.51)	0.03 (0.01–0.06)	0.05 (0.02–0.12)
Liotta et al. (2017)	Nyiragongo crater	3.25 (3.11–3.49)	No data	0.60 (0.46–0.63)	0.28 (0.15–0.36)	0.19 (0.14–0.25)	0.08 (0.07–0.10)	0.09 (0.06–0.17)	0.16 (0.01–0.03)	0.03 (0.02–0.05)
	Western zone	5.21 (3.4–6.41)	No data	0.05 (0.00–0.28)	0.12 (0.00–0.42)	0.05 (0.00–0.12)	0.03 (0.01–0.12)	0.04 (0.00–0.16)	0.01 (0.00–0.02)	0.03 (0.00–0.11)
	Southern zone	5.36 (4.96–5.85)	No data	0.00 (0.00–0.00)	0.02 (0.01–0.03)	0.02 (0.01–0.02)	0.03 (0.02–0.04)	0.03 (0.01–0.05)	0.01 (0.00–0.01)	0.03 (0.02–0.04)
Etna[a]		5.3 (2.0–8.2)	49 (7–2890)	0.01 (bdl-3.42)	0.12 (0.01–11.68)	0.06 (0.01–0.05)	0.08 (0.00–3.13)	0.01 (0.00–1.02)	0.02 (0.00–0.90)	0.05 (0.01–1.50)
Stromboli[b]		5.6 (3.2–7.6)	No data	0.06 (0.01–5.86)	0.65 (0.16–7.56)	0.09 (bdl-7.10)	0.46 (0.13–3.52)	0.07 (0.01–0.82)	0.47 (0.05–6.75)	0.06 (0.02–1.43)
Vesuvio et Vulcano[c]		3.6 (1.8–6.9)	No data	0.03 (bdl-1.20)	1.14 (bdl-23.72)	0.38 (bdl-11.09)	0.23 (0.00–1.60)	0.01 (bdl-0.53)	0.07 (0.00–0.70)	0.10 (0.00–0.98)

bdl: below detection limit.

[a] Calabrese et al. (2011).

[b] Liotta et al. (2006).

[c] Madonia and Liotta (2010).

Tab.2

Area	pH	Spec. Cond. (μS/cm)	F^- (μeq L^{-1})	Cl^- (μeq L^{-1})	NO_3^- (μeq L^{-1})	SO_4^{2-} (μeq L^{-1})	Na^+ (μeq L^{-1})	NH_4^+ (μeq L^{-1})	K (μeq L^{-1})	Ca^{2+} (μeq L^{-1})	Mg^{2+} (μeq L^{-1})	Reference
DRC, Nyiragongo (crater)	3.75	82.20	220.00	170.00	0.00	180.00	170.00	Ndt	150.00	80.00	60.00	This Study
DRC, Nyiragongo (Western zone)	5.77	68.09	40.00	150.00	50.00	200.00	100.00	Ndt	100.00	160.00	100.00	
DRC, Nyiragongo (Southern zone)	6.00	84.00	30.00	130.00	50.00	220.00	130.00	Ndt	60.00	120.00	160.00	
DRC, Nyiragongo (Nothereastern zone)	5.55	15.66	10.00	30.00	10.00	40.00	20.00	Ndt	20.00	60.00	20.00	
Eastern France	4.90	20.00	–	17.00	26.00	30.00	15.00	38.00	4.00	5.00	3.00	Sanuni et al. (1996)
Avignon, France	–	–	–	60.20	45.70	77.00	49.80	29.20	13.30	117.80	16.70	Celle-Jeanton et al. (2009)
Ma'an, Jordan	6.85	160.60	–	80.60	35.70	53.20	75.60	–	18.40	163.10	62.30	Al-Khashman et al. (2009)
Roorke, India	7.03	22.33	–	59.38	33.36	22.59	38.50	–	14.72	145.13	23.28	Hameed et al. (2006)
Korea, Hwasung	4.50	–	–	45.00	68.00	127.00	33.00	117.00	9.00	57.00	15.00	Park et al. (2015)
Ya'an, Chine	4.61	110.69	–	69.89	180.54	419.85	47.48	330.06	50.75	233.75	37.40	Zhao et al. (2013)
Xi'an, Chine	7.70	161.50	–	136.50	162.50	612.30	101.50	363.30	79.20	662.50	86.90	Xiao (2016)
Lamto, Ivory Coast,	5.16	–	–	7.10	7.70	6.50	6.30	17.60	2.40	9.50	2.70	Yoboué et al. (2005)
Southeastern Brazil	5.77	11.30	–	17.30	16.20	14.20	25.00	20.80	7.12	39.60	24.10	Cerqueira et al. (2014)
Acegua, Brazil	5.43	7.51	–	14.70	2.15	11.70	15.20	31.40	2.42	7.79	5.41	Textor et al. (2008)
Argentina Salta City	5.72	9.91	–	26.60	28.20	16.40	6.80	–	3.40	22.10	1.80	Romero Oruê et al. (2019)

Tab.3