Scientific Research Publishing

Major Ions in Atmospheric Deposition in Lake Kivu Basin

Mashimango Bagalwa[1,2,3]*, Jackson Gilbert Mwanjalolo Majaliwa[4], Katcho Karume[3,5], Sarah Akello[1], Frank Kansiime[1]

[1]College of Agricultural and Environmental Sciences, Makerere University, Kampala, Uganda
[2]Department of Biology, Centre de Recherche en Sciences Naturelles (CRSN/Lwiro), Bukavu, Democratic Republic of Congo
[3]Faculté des Sciences Agronomique et Environnement, Université Evangélique en Afrique, Bukavu, Democratic Republic of Congo
[4]Regional University Forum for Capacity Building in Agriculture (RUFORUM), Kampala, Uganda
[5]Centre de Recherche en Géothermie, Bukavu, Democratic Republic of Congo
Email: *mashibagalwa@gmail.com

Abstract

This study investigated the major ion composition and sources in wet and dry deposition samples collected over 15 months (December 2017 to February 2019) at four stations representing four different land use/cover types on the western side of Lake Kivu basin in D.R. Congo. The samples were collected every 13 days for dry deposition and two to three times per month for wet deposition. Samples were analyzed for major ionic components (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Ca^{2+}, CO_3^{2-}, HCO_3^- and Mg^{2+}). Electrical conductivity and pH were analyzed immediately in the field while major ion measurements were in the laboratory. Results showed the pH of both the dry and the wet depositions were higher than what would have been expected based on equilibration with atmospheric CO_2 (pH > 5.6) at all four sites, with conductivity less than 50 μS/cm. The neutralization process in dry and wet atmospheric deposition is due to Ca^{2+}, NH_4^+, HCO_3^- and CO_3^{2-}. The anion: cation ratio in dry deposition was close to 1 for Iko and Bukavu, and it was greater than 1.0 (1.1 - 1.2) for Lwiro and Goma in wet deposition. The dominant anions in wet deposition were SO_4^{2-} and NO_3^- found around the rural area near cement factory and the urban area near active volcanoes, respectively. The most abundant cation was Na^+ followed by K^+. The enrichment factors and correlation analysis suggest that the main sources of Ca^{2+}, Na^+ and Mg^{2+} were disintegration of soil processes, aeolian suspension of soil and volcanic ash, biomass burning and the cement/lime factory around the Lake Kivu basin.

Keywords

Dry and Wet Deposition, Major Ions, Lake Kivu

1. Introduction

Measurements of dry and wet atmospheric deposition of major ions are vital to enhancing the understanding of surface water quality since atmospheric deposition is a significant source of major ions loading to aquatic systems [1]. Measurements of atmospheric deposition are key in determining ion mass balances and understanding aquatic biogeochemical cycles of major ions and other chemical components that interact with these ions [2]. Wet deposition removes substances from the troposphere and boundary layer by precipitation, while dry deposition directly transports gases and particulates onto land and water surfaces. These air-surface exchanges depend strongly on meteorological conditions and local emissions [3].

The study of major ions in wet and dry atmospheric deposition has increased in the past decades because of their adverse environmental and human health effects [3]. The potentially harmful effects of acid deposition on ecosystems have remained the main reason behind environmental problems and have received extensive research recently [4]. Base cations are known to neutralize acids because they can react with oxidized forms of sulphur (S) and nitrogen (N) to reduce the acidity caused by these elements [3].

Several studies on atmospheric chemistry in Africa have been conducted in the region [2] [4] [5] [6] [7]. However, much of the research on atmospheric deposition and its biogeochemical impacts have focused on nutrient elements such as nitrogen, phosphorus and iron [8], with less attention given to major ions, especially in the African Great Lakes region. These ions affect water quality directly (e.g., by affecting pH and total dissolved solids) and indirectly by interacting with the cycling of other elements, including N and P. Major ions can be useful as indicators of processes affecting atmospheric and aquatic chemistry, such as biomass burning, industrial emissions, active volcanoes and accelerated land use change such as deforestation for creating arable land [9].

Atmospheric deposition of nutrients to Lake Kivu is high, similar to that in other African Lakes [4] [5]. The study of major ions deposition may help determine the possible sources of those nutrients and the development of nutrient management plans. The overall objective of this study was to provide insight into the atmospheric deposition and potential sources of major ions in the Lake Kivu region.

2. Materials and Methods

2.1. Description of the Study Area and Localization of Sampling Stations

This study was carried out in the Lake Kivu basin on the Democratic Republic of Congo side. Lake Kivu is located at 1463 m above the sea level, between 1˚34.5'S and 2˚30'S and 28˚50'E and 29˚23'E. Its basin is dominated by steep (<3%) mountainous topography underlain by sedimentary sandstone and siltstone soils [10]. The climate is tropical with bimodal rainfall distribution. Annual rainfall is

about 1500 mm in the Lake Kivu basin [11]. This study considered four sampling stations: Goma in the north, Iko Island within the Lake, Lwiro in the west, and Bukavu in the south all of which are located on the DRC side of the Lake (**Figure 1**).

The Goma and Bukavu regions are located within urban areas in the northern and southern parts of the lake at 1˚41.58'S, 29˚22.690'E and 2˚29.817'S, 28˚51.558'E respectively. These areas are densely populated with high transport activities. Goma is also located near the active Virunga volcanoes. The Lwiro and Iko stations are situated at 2˚14.228'S, 28˚48.441'E and 2˚14.064'S, 28˚53.555'E respectively in rural areas. The dominant land use/cover in these areas is agriculture. Lwiro area is located near the Kahuzi Biega National Park Forest. These areas (Lwiro and Iko) are not densely populated.

2.2. Samples Collection

For wet deposition, rainwater samples were collected monthly during rain events over fifteen months period (December 2017-February 2019) using polyethylene buckets (750 cm^2 collection area), each in four different locations in the stations
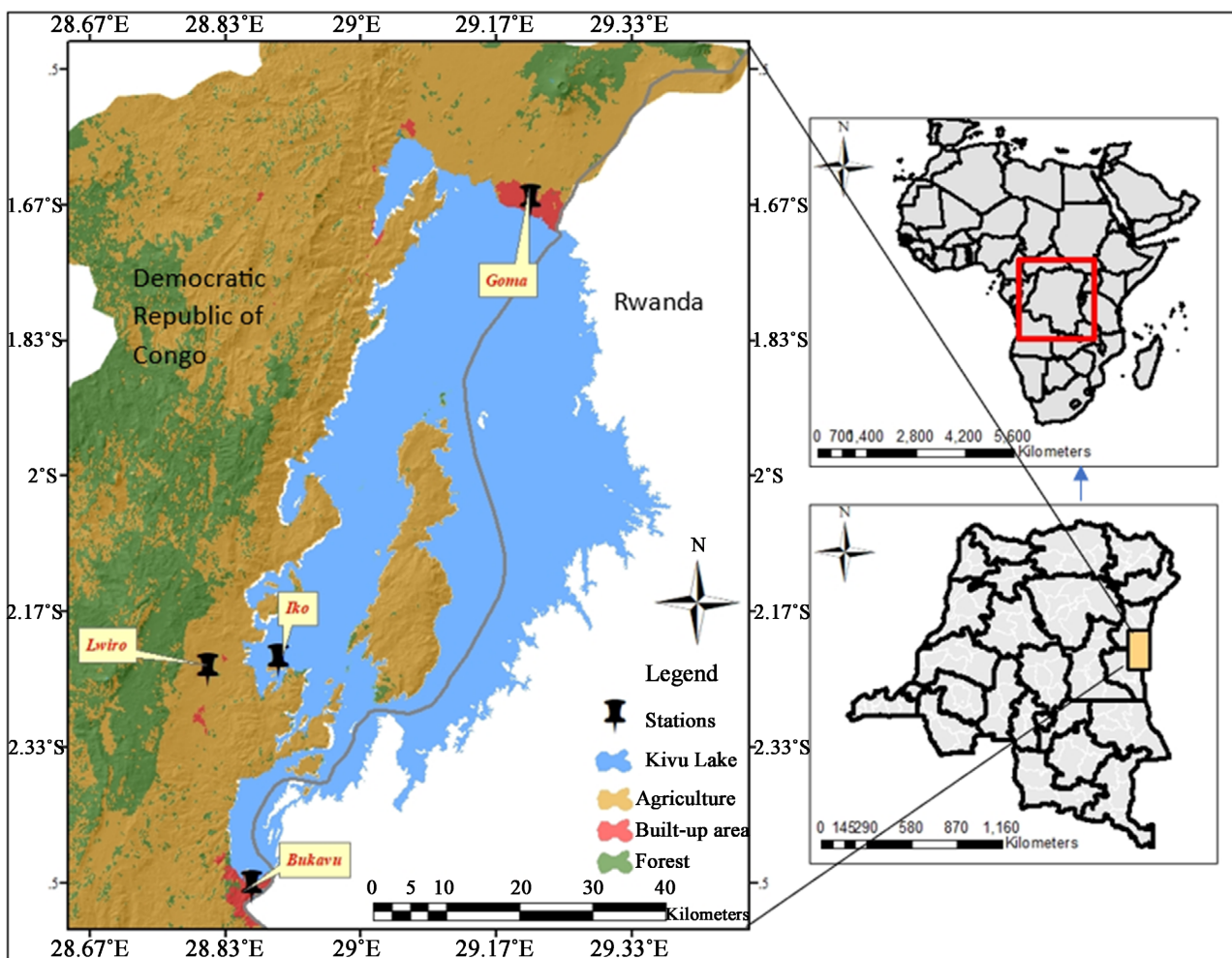

Figure 1. Location of sampling stations within the Lake Kivu basin.

of Goma, Lwiro, Iko and Bukavu. The rain collectors were situated 1.5 m above ground level to avoid contamination with soil [12]. The start and end times of each rain event and the volume of water collected was recorded. The pH, electrical conductivity (EC) and volume measurements were conducted immediately after each sample was collected. Water samples were transported to the Laboratory of Malacology at the Centre de Recherche en Sciences Naturelles (CRSN) of Lwiro and stored at 4°C where samples were not analysed immediately. For dry deposition, buckets containing 2 L of deionized water were exposed for 24 hours. Samples were collected at each station after 13 days (two or three times in the month). Buckets were placed on an elevated surface of 1.5 m to avoid contamination [12]. They were rinsed with several aliquots of deionized water before use. Sample water was analysed in the same manner as wet deposition samples. Before collecting samples, bird droppings that could contaminate the samples were checked, and if present, the samples were not considered for analysis. After collection, sample volume was recorded, and samples were transferred to the laboratory, where one sub-sample was filtered through a Whatman GF/F glass fiber filter (nominal pore size = 0.7 μm). The filtrate and the remaining samples were stored at 4°C awaiting analysis. At each station (Lwiro, Goma, Iko and Bukavu), four sites were identified as representative of the land use in that area, and the result was taken as the mean for the station.

2.3. Analytical Methods

The analytical procedures used to measure major ions and other physico-chemical parameters in dry and wet deposition samples were similar to those described by other authors [13] [14] [15]. Briefly, the methods were as follows: Sodium and potassium were analysed by atomic absorption spectrophotometer (Perkin Elmer-A Analyst 400) with an air acetylene flame in the Soil Science Laboratory at Makerere University. Calcium and magnesium were determined by the Eriochrome Black T titration method using the buffer solution suggested by Golterman *et al.* [13]. Ammonium and nitrate (after passing through a zinc column to reduce NO_3^- to NH_4^+) were analysed by spectrophotometric indophenol blue method [14]. Chloride was analysed by the argentometric titration method, and sulphate was analysed by the gravimetric method using barium chloride [13]. Carbonate (CO_3^{2-}) and bicarbonate were determined by standard acid titration methods [13] [15]. The pH was measured with a digital Hanna multi-parameter probe calibrated with pH 4.0 and 10.0 buffers, and electrical conductibility (EC) was calibrated against a reference KCl solution.

2.4. Neutralizing Capacity and Enrichment Factors Analysis

Precipitation acidity originates primarily from sulfuric acid and nitric acid and neutralization by Ca²⁺ and Mg²⁺, the ratios of SO_4^{2-} + $2NO_3^-$/Ca²⁺ + Mg²⁺ can be considered as indicators for acidity. The ratio less than one indicates the alkaline nature of rainwater, and the ratios greater than unity indicate the presence

of free anions, which are responsible for precipitation acidity [16].

An enrichment factor (EF) ratio for some ion species was calculated for samples as the ratio of the ions of interest to an ion expected to have only a soil/water origin [17]. Na^+ is commonly taken as the best reference element for marine sources [18]. Al^{3+} and Ca^{2+} are two typical lithophilic elements normally used as reference elements for the continental crust [19]. Since there was no measurement of Al^{3+} element in dry and wet atmospheric deposition samples, Ca^{2+} was chosen as a reference element for continental origin [20].

Enrichment factors (EF) were computed as in equations 1:

$$\text{EF for soil} = [X/Ca^{2+}]_{\text{wet and dry deposition}}/[X/Ca^{2+}]_{\text{soil}} \quad (1)$$

where: X was the concentration of the desired ion, X/Ca^{2+} ratio was from crust composition of soil in the region [21]. According to Enrichment Factors (EF), the source of major ions in atmospheric deposition can be summarized in **Table 1**:

To capture better the temporal variability in rates and sources of atmospheric deposition to the Lake Kivu basin, concentrations of major ions were measured two to three times a month in all four stations around the Lake Kivu, and the average was recorded.

2.5. Statistical Analysis and Other Computations

Statistical analysis was performed using one-way analysis of variance (ANOVA), and the station means were compared using the Least Significant Difference (LSD) for the critical value $p \leq 0.05$. Pearson correlation (r) test was conducted to examine potential relationships among pair-wise comparisons at each station.

3. Results

3.1. Major Ions Composition of Dry and Wet Atmospheric Deposition

The major ion dry volume weight concentration for the different stations during the study period from December 2017 to February 2019 is presented in **Table 2**. No significant differences were observed between stations ($p = 0.98$) when all the parameters were considered together, however significant differences were observed between difference dry deposition rates ($p < 0.05$). All the major ions

Table 1. Sources of some major ions by enrichment factors analysis.

Ions	Main sources
Na^+	Biomass burning
Ca^{2+}	Lake, soil
Mg^{2+}	Lake, soil
Cl^-	Soil, volcanic, biomass burning
SO_4^{2-}	Soil, volcanic, cement and lime industry
NO_3^-	Soil, volcanic

were significantly different between stations except for CO_3^{2-} (p > 0.05). Major ions deposition rates varied in dry atmospheric deposition form one station to other (Table 2).

Highest Cl^-, HCO_3^-, Mg^{2+}, Na^+ deposition rates and EC were recorded at Goma, highest values of Ca^{2+} and SO_4^{2-} were recorded at Iko whereas the pH and PO_4^{3-} were highest at Bukavu and high values of CO_3^{2-}, NH_4^+, NO_3^- and K^+ were recorded at Lwiro. The means of the ions were significantly different (P < 0.05) between the stations except for CO_3^{2-}, where no significant difference was recorded (p > 0.05). The coefficient of variation was greater between all the stations except for pH which was 0.7 or less different.

The highest EC was recorded at Goma (47.4 ± 54 µS/cm) and the lowest at Lwiro (36.9 ± 52.8 µS/cm). The coefficient of variation varied between 1.1 and 1.4 in the stations. The highest pH was recorded at Bukavu (5.8 ± 0.4) and the lowest at Goma (5.6 ± 0.5). Total alkalinity calculated based on the [HCO_3^-] + 2[CO_3^{2-}]− [H^+] + [OH^-] ratio, indicated that high alkalinity was recorded at Goma (126.9 mg/L) in dry atmospheric deposition and Bukavu in wet atmospheric deposition (258.5 mg/L). There is a statistically significant difference between Goma and Lwiro and Bukavu and Goma (p < 0.05). The mean pH showed that deposition was slightly acidic (pH < 6) at all four stations.

Wet atmospheric deposition results are presented in Table 3. The atmospheric deposition rate of major ions in wet atmospheric deposition varied slightly from station to station.

In the wet atmospheric deposition, the highest VWM concentration of Cl^-,

Table 2. Mean dry deposition rate (µmol/m²/day) of major ions at four stations around Lake Kivu (± represent standard deviation).

	Mean Dry Goma	Mean Dry Iko	Mean Dry Bukavu	Mean Dry Lwiro
Cl^-	95.5 ± 112.0	72.8 ± 64.2	66.3 ± 57.9	66.3 ± 46
CO_3^{2-}	5 ± 1.8	2 ± 80.1	2.6 ± 10.2	3.5 ± 13.4
HCO_3^-	491.2 ± 438.9	634.4 ± 647.7	528.5 ± 548.2	471.8 ± 453.6
Ca^{2+}	56 ± 5.2	91 ± 6.1	76 ± 7.1	67 ± 5.7
Mg^{2+}	95 ± 8.5	88 ± 6	55 ± 3.8	77 ± 4.7
SO_4^{2-}	137.3 ± 281.7	109.2 ± 93.2	159.0 ± 89.2	178.4 ± 54.9
PO_4^{3-}	16.7 ± 21.6	12.5 ± 8.8	14.2 ± 11.6	11.2 ± 6.5
NH_4^+	63.4 ± 42.9	66.1 ± 50.3	80.3 ± 65.1	99.5 ± 53.5
NO_3^-	66.5 ± 57.9	71.1 ± 62.9	105.5 ± 71.9	109.4 ± 79.3
Na^+	340 ± 22.8	206 ± 12.5	287 ± 9.4	267 ± 12.6
K^+	22.6 ± 6.8	26.9 ± 12.3	223 ± 9.6	36.6 ± 12.8
pH	5.6 ± 0.5	5.6 ± 0.7	5.8 ± 0.4	5.7 ± 0.7
EC (µS/cm)	47.4 ± 54	38.2 ± 53.2	46.12 ± 51.7	36.9 ± 52.8

Table 3. Mean wet atmospheric deposition of major ions (μeq/L) around Lake Kivu basin in four stations (± represent standard deviation).

	Mean Wet Goma	Mean Wet Iko	Mean Wet Bukavu	Mean Wet Lwiro
Cl^-	18.5 ± 19.3	15.7 ± 15.5	15.6 ± 15.2	24.3 ± 22.5
CO_3^{2-}	13.3 ± 11.6	10.6 ± 7.6	16 ± 13.3	37 ± 22.5
HCO_3^-	98.6 ± 85.2	105.3 ± 90	135.6 ± 122.8	124.5 ± 93.6
Ca^{2+}	15 ± 1.3	35.5 ± 1.5	19 ± 1.9	32 ± 1.4
Mg^{2+}	19 ± 1.3	17 ± 1.6	13 ± 0.8	19 ± 0.8
SO_4^{2-}	45.9 ± 25.4	55.3 ± 43.4	45.5 ± 22.4	60.5 ± 24.3
PO_4^{3-}	6.3 ± 13.8	6.7 ± 12.5	4.7 ± 8.2	7.1 ± 15
NH_4^+	28.1 ± 13.3	39.6 ± 37.2	28.3 ± 15.5	33.8 ± 10.9
NO_3^-	27.2 ± 11.1	36.3 ± 35.6	27.3 ± 16.2	33.3 ± 13
Na^+	84 ± 3.5	74 ± 5.5	86 ± 6.5	62 ± 4.4
K^+	103 ± 5.1	57 ± 3.2	69 ± 4.1	85 ± 2.6
pH	5.19 ± 0.5	5.3 ± 0.5	5.6 ± 0.5	5.3 ± 0.4
EC (μS/cm)	28.7 ± 13	17.4 ± 21.1	20.8 ± 17.3	24.2 ± 21.8

CO_3^{2-}, Ca^{2+}, SO_4^{2-} and PO_4^{3-} were recorded at Lwiro. The mean was significantly different ($P < 0.05$) between the stations except for K^+ ($p > 0.05$) and CO_3^- ($p > 0.05$). The coefficient of variation was greater between stations for ions VWM except for pH which was between 0.4 and 0.5.

High wet atmospheric deposition VWM concentration of the anion (Cl^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-}) and cation (Ca^{2+}) were recorded at Lwiro. High CO_3^{2-} and Na^+ was recorded at Bukavu, highest Mg^{2+}, K^+ and EC was recorded at Goma, while high NH_4^+ and NO_3^- occurred at Iko and high HCO_3^- and Na^+ were recorded at Bukavu. High EC was recorded at Goma 28.66 ± 13.0 μS/cm) and the lowest at Iko (17.4 ± 21.1 μS/cm). The pH was slightly acidic in all wet atmospheric deposition samples collected around the Lake Kivu basin (pH < 6). The total cation anion (TA/TC) ratios in wet atmospheric deposition revealed persistent free anions responsible for acidic precipitation in the region.

3.2. Origin of Major Ions as Inferred from Enrichment Factors

Enrichment factor (EF) was used to detect the source of major ions in dry and wet atmospheric deposition. The major ions ratios for dry and wet atmospheric deposition in different sites are given in Table 4.

Enrichment factors (EF) in the dry atmospheric deposition were generally low for the ratio of Na^+ than in wet atmospheric deposition. However, high ratio was recorded except for K+, whose high values were recorded at Lwiro. Furthermore, EF factors of SO_4^{2-} and Cl^- have high standard deviations in all the stations. Whereas the high EF factor of Ca^{2+} was different according to the ions taken,

Table 4. Major ions ratio for dry and wet atmospheric deposition in four stations around the Lake Kivu watershed, DR Congo side (± represent standard deviation).

	Lwiro	Iko	Goma	Bukavu
Dry				
Cl^-/Ca^{2+}	0.5 ± 87.6	0.5 ± 69.1	0.8 ± 64.4	0.5 ± 72.7
Mg^{2+}/Ca^{2+}	0.5 ± 0.5	0.5 ± 0.5	0.9 ± 0.5	0.4 ± 0.5
SO_4^{2-}/Ca^{2+}	2.9 ± 31.4	2.5 ± 36.1	3.8 ± 29.4	2.6 ± 23.7
Na^+/Ca^{2+}	5.4 ± 2.6	5.3 ± 3.6	12.8 ± 2.1	5.1 ± 3.6
K^+/Ca^{2+}	3.8 ± 14.4	0.4 ± 10.4	0.9 ± 8.2	0.9 ± 8.2
Wet				
Cl^-/Ca^{2+}	0.4 ± 78.4	0.5 ± 68.6	0.5 ± 70.1	0.5 ± 57.7
Mg^{2+}/Ca^{2+}	0.5 ± 0.5	0.7 ± 0.5	0.6 ± 0.5	0.4 ± 0.5
SO_4^{2-}/Ca^{2+}	2.6 ± 50.5	3.4 ± 23.7	2.3 ± 26.3	2.5 ± 29.4
Na^+/Ca^{2+}	2.4 ± 2.6	5.0 ± 2.6	3.9 ± 2.6	3.9 ± 2.1
K^+/Ca^{2+}	1.7 ± 5.7	3.3 ± 6.2	4.6 ± 5.7	3.6 ± 3.1

relatively high EF factor values of Cl^- were recorded in samples at Goma, high Mg^{2+} occurred at Iko, high SO_4^{2-} occurred at Lwiro, and high K^+ was recorded at Bukavu.

For wet atmospheric deposition, EF calculated for the ions showed no significant difference ($p > 0.05$). Relatively high EF values of Na^+ were recorded at Iko for Cl^-, Mg^{2+}, and SO_4^{2-} ions and at Bukavu for Ca^{2+} and K^+. While the EF ratios of Ca^{2+} were relatively high as recorded at Lwiro for Mg^{2+} and SO_4^{2-} and at Goma for Cl^- and K^+ ions.

3.3. Correlations between Major Ions In Atmospheric Deposition around Lake Kivu Basin

A Pearson correlation analysis was performed to distinguish the possible common sources of ionic constituents. Table 5 shows the matrix of Pearson correlation coefficients ($p < 0.05$) among the major ions analysed in dry and wet atmospheric deposition

The ions in the dry atmospheric deposition that are strongly correlated include; CO_3^{2-}, HCO_3^-, Mg^{2+}, SO_4^{2-}, PO_4^{3-} and K^+ while the others which are not correlated include NH_4^+, NO_3^- and Na^+. These correlations are positive or negative between the parameters in dry atmospheric deposition. Correlations between ions in wet atmospheric deposition are presented in Table 6.

The ions in the dry atmospheric deposition that are strongly correlated include; HCO_3^-, Mg^{2+}, NH_4^+, NO_3^-, SO_4^{2-}, PO_4^{3-}, Na^+ and K^+ while the others which are not correlated include CO_3^{2-} and Ca^{2+}. These correlations are positive or negative between the parameters in wet atmospheric deposition.

Table 5. Correlation matrix of dry atmospheric deposition of major ions in atmospheric deposition in Lake Kivu watershed. Legend: [c]: Correlated; [b]: Moderate correlated; [a]: Strongly correlated at $p < 0.05$.

	Cl^-	CO_3^{2-}	HCO_3^-	Ca^{2+}	Mg^{2+}	SO_4^{2-}	PO_4^{3-}	NH_4^+	NO_3^-	Na^+	K^+	pH	EC
Cl^-	1	0.73[c]	0.07	−0.12	0.12	0.95[c]	0.82[c]	0.94[c]	−0.98[c]	0.01	−0.57[a]	−0.48	0.31
CO_3^{2-}		1	−0.91[c]	−0.36	0.82[c]	−0.36	0.56[a]	0.94[c]	0.76[c]	0.85[c]	0.41	0.59[a]	0.69[b]
HCO_3^-			1	−0.35	0.21	0.80[c]	0.87[c]	−0.92[c]	−0.95[c]	0.04	−0.29	−0.39	0.33
Ca^{2+}				1	−0.14	0.93[c]	−0.87[c]	−0.71[c]	−0.90[c]	−0.17	−0.95[c]	0.63[b]	−0.50[a]
Mg^{2+}					1	0.57[a]	−0.72[c]	0.49	0.55[a]	0.10	−0.83[c]	−0.21	0.73[c]
SO_4^{2-}						1	−0.07	0.29	0.13	0.83[c]	−0.88[c]	−0.12	−0.42
PO_4^{3-}							1	−0.14	−0.03	0.91[c]	−0.75[c]	0.29	0.18
NH_4^+								1	0.04	0.90[c]	0.46	−0.36	−0.33
NO_3^-									1	0.95[c]	0.65[b]	−0.26	−0.26
Na^+										1	−0.51[a]	−0.39	0.37
K^+											1	0.70[b]	−0.42
EC												1	0.83[c]
pH													1

Table 6. Correlation matrix of wet atmospheric deposition of major ions in atmospheric deposition in Lake Kivu watershed. Legend: [c]: Correlated; [b]: Moderate correlated; [a]: Strongly correlated at $p < 0.05$.

	Cl^-	CO_3^{2-}	HCO_3^-	Ca^{2+}	Mg^{2+}	SO_4^{2-}	PO_4^{3-}	NH_4^+	NO_3^-	Na^+	K^+	pH	EC
Cl^-	1	0.49	0.21	0.12	0.57[a]	−0.70[b]	0.28	−0.55[a]	−0.30	0.33	0.07	0.99[c]	0.30
CO_3^{2-}		1	0.77[c]	0.72[c]	−0.63[b]	−0.54[a]	0.11	−0.00	−0.05	0.41	0.50[a]	0.20	−0.80[c]
HCO_3^-			1	0.50[a]	0.18	0.66[b]	0.75[c]	−0.83[c]	−0.70[b]	0.14	0.06	−0.60[a]	0.47
Ca^{2+}				1	0.73[c]	−0.43	0.34	−0.78[c]	−0.45	0.77[c]	0.34	−0.98[c]	0.13
Mg^{2+}					1	0.37	−0.69[b]	0.57[a]	0.71[c]	0.51[a]	0.41	−0.14	0.42
SO_4^{2-}						1	−0.26	0.54[a]	0.38	0.69[b]	0.97[c]	−0.34	−0.76[c]
PO_4^{3-}							1	−0.14	−0.02	0.59[a]	0.44	0.31	0.78[c]
NH_4^+								1	0.07	−0.45	−0.56[a]	−0.17	0.74[c]
NO_3^-									1	−0.47	−0.40	−0.28	−0.91[c]
Na^+										1	0.12	0.99[c]	0.92[c]
K^+											1	−0.90[c]	0.47
pH												1	−0.51[a]
EC													1

3.4. Temporal Variation in Atmospheric Deposition of Major Ions

Although major ions in atmospheric deposition are essential for assessing sources

of chemical influence, temporal trends in deposition are confounded by natural variability in wet and dry deposition. Temporal mean concentration (µeq/L) of some major ions in different sites of the Lake Kivu basin is depicted in Figure 2 for ions (Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, PO_4^{3-}, NO_3^-, Na^+ and K^+) in dry atmospheric deposition.

The high deposition concentration of major ions was recorded principally in January 2019 except for Ca^{2+} (December 2017) and NO_3^- (December 2018). But for all the major ions concentration, the trend remained similar in dry atmospheric deposition. Na^+, Ca^{2+}, K^+ and SO_4^{2-} were the dominant elements in the atmosphere around Lake Kivu basin in dry atmospheric deposition.

In the wet atmospheric deposition, the temporal mean concentration of some major ions in different sites in the Lake Kivu basin is presented in Figure 3.

High deposition concentrations of major ions were recorded principally in the rainy season. A high mean concentration of Cl^- was registered in January 2019, while high Ca^{2+} in June and SO_4^{2-} and NO_3^- was recorded in April. A high rate of Mg^{2+} deposition was recorded in September. High concentration of Na^+ (December), PO_4^{3-} (April) and K^+ (April) were recorded in these months respectively. This period corresponded with the period of rain in the area.

High mean concentrations of major ions in dry atmospheric deposition were recorded mainly in Goma for Cl^- and SO_4^{2-} and Iko for Ca^{2+}, Mg^{2+}, PO_4^{3-}, NO_3^-, Na^+ and K^+. This occurred in December to February and May to June for Goma. High rates of Cl^- were recorded in December and May, while those of; Ca^{2+} and SO_4^{2-} were recorded in January 2018 and October, respectively. Those of PO_4^{3-} and NO_3^- were recorded in January 2018 at Iko. Wet atmospheric deposition was high in the rainy season. High concentration of major ions such as (Cl^-, Ca^{2+}, Mg^{2+}, PO_4^{3-}, NO_3^-, Na^+ and K^+) were recorded at Lwiro, while high concentration for SO_4^{2-} were recorded at Iko and for K^+ at Bukavu. High concentration of major ions in the wet were recorded at Lwiro (Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-} and NO_3^-) and Iko (PO_4^{3-} and Na^+).

4. Discussion

4.1. Major Ions Composition of Dry and Wet Atmospheric Deposition

Major ions that characterized atmospheric deposition were recorded in dry and wet atmospheric deposition. The relative dominance of NO_3^-, SO_4^{2-} and Cl^- can potentially increase the acidity of the deposition although the dissolution of CO_2 in the samples would have already reacted with distilled water. The ratios of SO_4^{2-} + $2NO_3^-$/Ca^{2+} + Mg^{2+} showed alkaline water recorded in dry and wet atmospheric deposition respectively. The presence of Ca^{2+}, NH_4^+, HCO_3^- and CO_3^{2-} contributed to the neutralization process of acid in atmospheric deposition [22]. Whereas the presence of NO_3^-, SO_4^{2-} and Cl^- increased the acidity in atmospheric deposition. The results revealed that wet and dry atmospheric deposition samples were acidic at all the four stations with mean pH values varied
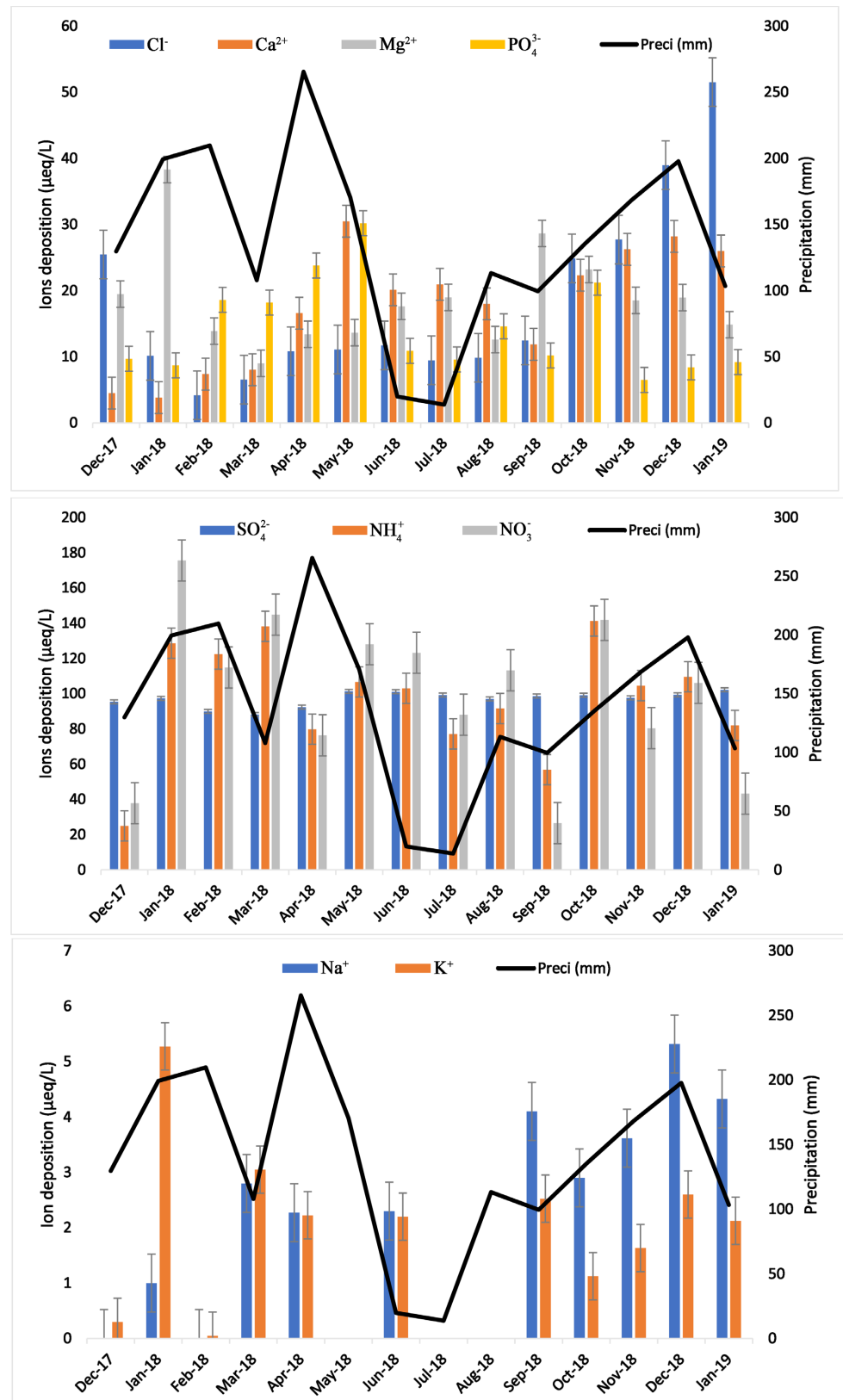
Figure 2. Monthly mean deposition rates of some major ions (μeq/L) in dry atmospheric deposition around the Lake Kivu basin. Values are the means of all four stations. Bars represent standard error.
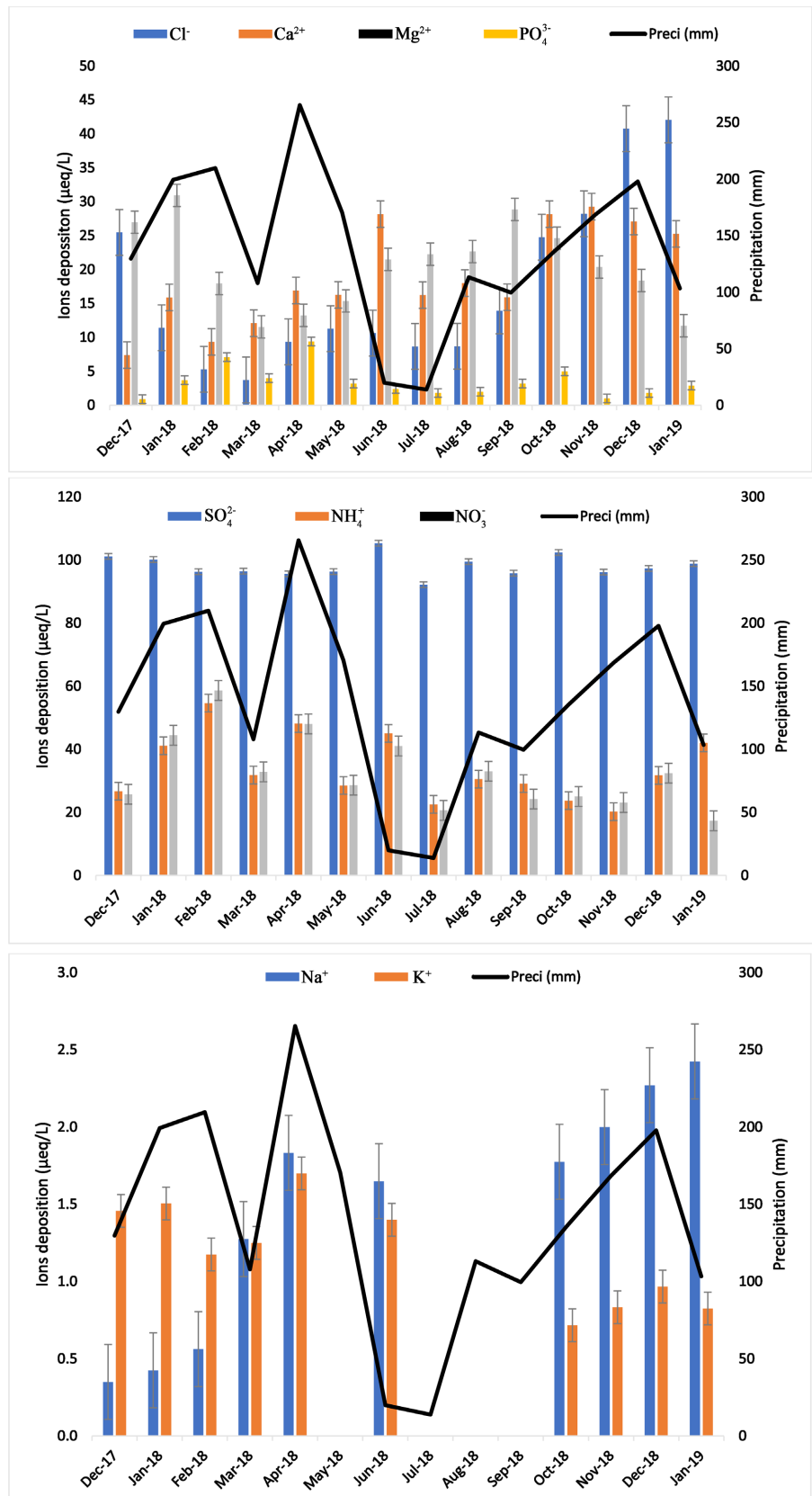
Figure 3. Temporal mean rates of some major ions (μeq/L) in wet atmospheric deposition around the Lake Kivu basin (bar represent the standard error).

between 5.19 and 5.57 in wet atmospheric deposition, and 5.56 and 5.82 in dry atmospheric deposition. I dry atmospheric deposition alkalinity varied from location as follows; Goma (126.7 ± 3.1 mg/L) > Iko (105.9 ± 2.1 mg/L) > Bukavu (105.8 ± 4.5 mg/L) > Bukavu (99.6 ± 3.1 mg/L) respectively; while in wet atmospheric deposition, it decreased as follows; Bukavu (258.5 ± 4.5 mg/L) > Goma (199.1 ± 3.1 mg/L) > Iko (152.2 ± 2.1 mg/L) > Lwiro (90.3 ± 3.1 mg/L) respectively.

Low mean pH wet deposition values were recorded at Goma station (5.19) compared to other stations. Bicarbonate ion rate is important for these values of pH obtained in the samples. This was a result of the acid-base balance of all chemical species in the rain. In a poorly buffered atmosphere, acid deposition leads to acidification and has a negative impact on the ecosystem as found by Wang *et al.*, [23] and Akimoto *et al.*, [24] in China and Japan respectively.

Except for Ca^{2+} and SO_4^{2-} dissolved major ions were close to those reported for other areas worldwide [25]. The most abundant anions in the dry and wet atmospheric deposition were SO_4^{2-}, similar to the finding by Derry and Chadwick [26]. The most abundant cation was Na^+ followed by K^+, contrary to the results observed by Bootsma *et al.* [27] in the Lake Malawi basin where Ca^{2+} was the abundant cation.

Stefánsson *et al.* [28] found that major ions were present for regions with active volcanoes which compared well with the results of this study. Volcanoes are considered the most important natural sources of emissions of major ions. In contrast, the most important anthropogenic sources are fossil fuel combustion for energy production, transportation, factories activities in big cities and their surroundings in the basin. However, biomass burning from deforestation, land clearing and bush fires are also potential sources of major ions in the atmosphere [29] [30]. In the Lake Kivu basin, the presence of active volcanoes of Virunga contributes to SO_4^{2-} and NO_3^- in dry and wet atmospheric deposition. Moreover, the presence of the cement factory of Katana (CIMENKI/Katana) and different lime production enterprises located near the lake are also potential sources of atmospheric SO_4^{2-}, HCO_3^- and CO_3^{2-} in the atmosphere of the Lake Kivu basin, which increase the concentrations in the atmosphere.

The factory releases dust in the atmosphere containing different chemical constituents such as SO_4^{2-} with a longer lifetime that, when deposited, can lead to being spread over greater distances [31]. This high atmospheric deposition of SO_4^{2-} can be explained in the region by the mineralogy of the soil material. The presence of calcite ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$) in the soil confirm the high atmospheric deposition of major ions in the atmosphere. The dissolution of these minerals' accounts for the high VWM of Ca^{2+} and SO_4^{2-}. These minerals were found in dust material in other regions and are used in the cement factory in CIMENKI/Kakondo and lime production enterprises in the basin. The high atmospheric deposition VWM of SO_4^{2-} and moderate Ca^{2+} at Iko station was probably due to the influence of the cement factory located near the site at Kakondo.

The atmospheric deposition rate of these ions (Ca^{2+}, SO_4^{2-} and Mg^{2+}) are associated with wind direction and transport mechanisms in the basin. During rain events, generally high atmospheric deposition rates of Ca^{2+} and SO_4^{2-} were recorded in the Lake Kivu basin similar to the observation of other authors in different regions [2]. The high rate may be due to the process of scavenging during the precipitation. For the station of Goma, major sources of ions are expected to be volcanic ash in the atmosphere but also an uncompleted road network where dust is usually blown when traffic is high. In the dry atmospheric deposition, high rates of major ions of SO_4^{2-} and CO_3^{2-} were recorded at the station of Goma. The occurrence of relatively high levels of anthropogenic activities and the volcanoes are the factors of high species of NO_3^-, SO_4^{2-} observed in this station. This was also observed in active volcanic areas like Indonesia, Costa Rica, and Nicaragua [32].

However, studies in central Africa and South America (e.g., [8] [33] [34]), found that the principal source of atmospheric deposition was the emission from burning forests, savannas and agricultural fields as observed in this study. As Wang *et al.* [25] reported, it is worthwhile to note that the proportion of Ca^{2+} in mineral dust varied from one site to another. Bootsma and Hecky [35] found that soil dust resulting from deforestation and agriculture was responsible for increased P deposition in Uganda.

4.2. Temporal Variation in Atmospheric Deposition of Major Ions

In general, temporal variability was recorded in the VWM of major ions for dry and wet atmospheric deposition in the four stations. High atmospheric deposition VWM was recorded in the rain season. Such temporal variation was also observed at Mt Etna in Italy [36]. At Bukavu, the dust blown from road traffic spreads out in the area, contributing to the ions into the atmosphere returning as dry and wet deposition. Other sources of pollutants in the atmosphere are anthropogenic activities such as burning waste and emissions from waste disposal sites. The same trend was observed at Goma station because the two stations are urbanized and characterized by high population and high traffic on the road. In addition, the Goma station is located in an active volcanic area. Emission of volcanoes in this region increases major ions in dry and wet atmospheric deposition. However, volcanic ash known as an aerosol contains major ions such as SO_4^{2-}, NO_3^-, Na^+, K^+, Ca^{2+} and Mg^{2+} [36]. Iko station is located on the island near the cement industry in the coastal area. Generally, the rain was unevenly distributed in the basin during sampling, and some stations received less water. The variability followed the trend of the activities and the seasonality in the basin, as observed in various China regions [37].

4.3. Correlations between Major Ions in Atmospheric Deposition around Lake Kivu Basin

The strong positive correlation coefficient in dry atmospheric deposition between both SO_4^{2-} and Ca^{2+} with some ions (Table 5) can be explained by the

presence of cement industry and other anthropogenic activities. These activities in the region included road construction, blowing soil in the atmosphere, lime fabrication enterprise, forest cutting and agricultural practice in the Lake Kivu basin. In this basin, the presence of cement industry and lime fabrication enterprises near the site at Iko was the main source of SO_4^{2-} and Ca^{2+} with high deposition rates in dry deposition at Iko and Lwiro. Nitrate was positively correlated with Na^+ and K^+ with possible contribution arising from biomass burning and blowing aerosol which are common activities in the basin. Meanwhile, Bukavu and Lwiro, have high deposition rates of NO_3^- than in other sites. In India, Khare *et al.* [38] found that K^+ ion was associated with airborne particles generated by biomass burning in the basin that was also observed in this study. There was a correlation with other ions that are produced by burning in dry deposition, such as NO_3^-.

According to Coelho *et al.* [39], vehicle emissions substantially increase the atmospheric deposition of major ions, as observed in samples collected in Turkey compares with our findings in the Lake Kivu basin. In addition, the influence of local road traffic, which enhances the suspension of soil-derived particles into the atmosphere, have contributed to such increase of particles as found by Safai *et al.* [20]. It is important to note that dust carried by wind and soil plays significant role in dry deposition chemistry. The presence of several limestone mines and the cement industry in the basin contribute to the increased rates of some specific ions in dry atmospheric deposition.

The Mg^{2+}, Ca^{2+}, SO_4^{2-} ions in wet atmospheric deposition suggested the presence of crustal contributions or from cement manufacturing. This behaviour of Mg^{2+} was also found in rainwater in China [37]. The dissolution of the carbonate minerals such as calcite and dolomite, a mineral that is composed in the soil in the region, was the essential reaction that affected the rainwater composition, as found by Baker and Jickells [8]. SO_4^{2-} ions are well correlated with NH_4^+ and PO_4^{3-} and negatively correlated with pH and NO_3^- was correlated with Na^+, K^+ and EC but also negatively correlated with pH, suggesting that the acidic pH originated from the anthropogenic input. pH was only correlated to CO_3^{2-} in wet atmospheric deposition, which supported the contribution of acidity coming from H_2SO_4 and HNO_3, which was lower than the free acidity observed due to the neutralization process was responsible of acidification [40].

Sulphate and NO_3^- ions were not correlated, suggesting that the contributions of the observed deposition of these ions were either from volcanic ash or soil blowing in the atmosphere. The processes such as wind erosion, burning and tillage caused particles containing major ions to become airborne [33]. These findings confirm the influence of natural and anthropogenic sources of these ions in wet deposition around the Lake Kivu watershed. The ammonium ion is notable with its poor correlation with other major ions. It is negatively correlated with pH, suggesting that some NH_4^+ are not associated with volcanic sources but reflect agricultural activity's influence. Sodium and Mg^{2+} ions were strongly correlated, suggesting an influence from soil dust. Coelho *et al.* [39] in-

dicated that NaCl, CaSO$_4$, MgSO$_4$, MgCl$_2$, HNO$_3$, NH$_4$NO$_3$, NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$ were the predominant species combinations that could occur in the atmosphere by following the major ions in contact in the atmosphere. They could have been formed by scavenging of aerosols and reaction of gaseous species in water droplets.

4.4. Origin of Major Ions Contribution: Enrichment Factors

Enrichment factors (EF) were a useful tool in understanding atmospheric deposition in Lake Kivu. The composition of the bedrock revealed that calcium was the dominant natural element [41]. Enrichment factors of the different ions with Ca^{2+} showed a similar trend with the corresponding soil ratio EF between 0.73 - 1.94. According to Ma *et al.* [42], most of the EFs of other elements were below or close to ten, suggesting an influence from soil particles.

The EF analysis confirmed that SO$_4^{2-}$, Cl$^-$, Ca^{2+} and Mg^{2+} originated from soil and volcanic ash, biomass burning, cement industry and lime production enterprises. At the same time, Na$^+$ came mostly from biomass burning, and the more significant part of K$^+$ was from the lake (marine origin). The application of factor analysis reveals that crusting and anthropogenic activities played an important role in the distribution of ionic species in wet precipitation in the Lake Kivu basin.

Generally, lake contribution of NO$_3^-$ and NH$_4^+$ was minimal; therefore, EFs for the lake source were computed for Cl$^-$, Mg^{2+}, K$^+$, SO$_4^{2-}$ and Ca^{2+}, while EFs for soil source were computed for K$^+$, Na$^+$, Mg^{2+}, Cl$^-$, SO$_4^{2-}$ and NO$_3^-$. The EF approaching unity suggests that the elements originate from the soil. If the EF was greater than unity, it implies that a significant fraction had an origin in a different than soil/lake. Main sources of Ca^{2+}, Na$^+$ and Mg^{2+} are known to be obtained during the crusting processes and wind-blown soil [17] as revealed in Table 4. The EFs of these elements were higher than the corresponding EF in the soil in the region. These were also confirmed in the study of Barbieri *et al.* [43], who found the highest deposition concentration of Ca^{2+} ion in soil near the sampling site. The potential contribution of the cement industry and other small enterprises producing lime in the region were also contributors of Ca^{2+} ions in the dust to the atmosphere by local wind systems.

According to Rastegari *et al.* [44], the ratios Na$^+$/Ca^{2+}, SO$_4^{2-}$/Ca^{2+} and K$^+$/Ca^{2+} EF indicated a dominant soil origin for both species, while K$^+$, Mg^{2+}, SO$_4^{2-}$, Na$^+$ and Ca^{2+} contents pointed to additional sources (soil dust, fertilizers, etc.) as nitrate and sulphate displayed a nearly constant EFs indicating a common anthropogenic origin. This was also found in Lake Kivu basin where activities such as agricultural practices and cement industry are common leading to susceptibility of increased biomass burning and dust in the atmosphere, concurring with observations by Naimabadi *et al.* [45].

5. Conclusions and Recommendations

This study presents the chemical compositions of one year of dry and wet atmospheric deposition samples at different stations around the Lake Kivu basin

to help better understand their chemical characteristics and sources on the DR Congo side. Except for high Ca^{2+} and SO_4^{2-}, the atmospheric deposition rates of dissolved major ions were close to those reported for other areas worldwide. The pH in dry and wet atmospheric deposition in all the sites was at an average of 5.6, which is a normal pH for rain equilibrated with atmospheric CO_2. Major ions analyzed indicated that Ca^{2+} and Mg^{2+} were the significant alkaline species for the neutralization process. The enrichment factors and correlation analysis showed that SO_4^{2-}, Cl^-, Ca^{2+}, and Mg^{2+} originated from soil and volcanic ash, biomass burning, cement and lime industry.

In contrast, Na^+ originated mainly from biomass burning, and a greater part of K^+ was from aerosol and burning in general. K^+ was found to be provided in the basin by lake and soil contribution. SO_4^{2-} was from volcanic, soil, cement industry and lime production enterprise origins. NO_3^- was from soil and anthropogenic origins. The observed high atmospheric deposition rates of Ca^{2+} were mainly from the dust soil from agricultural practice, biomass burning and volcano ash from natural and anthropogenic sources. The main findings of this study were:

1) High deposition VWM of major ions was recorded in the dry period of the year, especially Ca^{2+} associated with high NO_3^- and SO_4^{2-} deposition.

2) pH appeared to be controlled by equilibration with atmospheric CO_2, with little influence from major ions.

3) The main sources of Ca^{2+}, Na^+ and Mg^{2+} were from the crusting processes. Wind-blown particles originated from the soil, volcanic ash, biomass burning, cement and lime industry around the Lake Kivu watershed.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Iavorivska, L., Boyer, E.W. and DeWalle, D.R. (2016) Atmospheric Deposition of Organic Carbon via Precipitation. *Atmospheric Environment*, **146**, 153-163.
https://doi.org/10.1016/j.atmosenv.2016.06.006

[2] Conradie, E.H., Van Zyl, P.G., Pienaar, J.J., Beukes, J.P., Galy-Lacaux, C., Venter, A.D. and Mkhatshwa, G.V. (2016) The Chemical Composition and Fluxes of Atmospheric Wet Deposition at Four Sites in South Africa. *Atmospheric Environment*, **146**, 113-131.

https://doi.org/10.1016/j.atmosenv.2016.07.033

[3] Budhavant, K.B., Rao1, P.S.P., Safai, P.D., Gawhane, R.D., Raju, M.P., Mahajan, C.M. and Satsangi, P.G. (2012) Atmospheric Wet and Dry Depositions of Ions over an Urban Location in South-West India. *Aerosol and Air Quality Research*, **12**, 561-570. https://doi.org/10.4209/aaqr.2011.12.0233

[4] Gatebe, C.K., Levy, R.C. and Thompson, A.M. (2012) Atmospheric Chemistry over Southern Africa. *Eos, Transactions American Geophysical Union*, **93**, 110. https://doi.org/10.1029/2012EO100008

[5] Kuik, F., Lauer, A., Beukes, J.P., Van Zy, P.G., Josipovic, M., Vakkari, V., Laakso, L. and Feig, G.T. (2015) The Anthropogenic Contribution to Atmospheric Black Carbon Concentrations in Southern Africa: A WRF-Chem Modelling Study. *Atmospheric Chemistry and Physics*, **15**, 8809-8830. https://doi.org/10.5194/acp-15-8809-2015

[6] Lunt, M.F., Palmer, P.I., Feng, L., Taylor, C.M., Boesch, H. and Parker, R.J. (2019) An Increase in Methane Emissions from Tropical Africa between 2010 and 2016 Inferred from Satellite Data. *Atmospheric Chemistry and Physics*, **19**, 14721-14740. https://doi.org/10.5194/acp-19-14721-2019

[7] Ossohou, M., Galy-Lacaux, C., Yoboue, V., Adon, M., Delon, C., Gardrat, E., Konate, I., Ki, A. and Zouzou, R. (2021) Long-Term Atmospheric Inorganic Nitrogen Deposition in West African Savanna over 16 Year Period (Lamto, Cote d'Ivoire). *Environmental Research Letters*, **16**, Article 015004. https://doi.org/10.1088/1748-9326/abd065

[8] Baker, A.R. and Jickells, T.D. (2017) Atmospheric Deposition of Soluble Trace Elements along the Atlantic Meridional Transect (AMT). *Progress in Oceanography*, **158**, 41-51. https://doi.org/10.1016/j.pocean.2016.10.002

[9] Egbueri, J.C., Mgbenu, C.N. and Chukwu, C.N. (2019) Investigating the Hydrogeochemical Processes and Quality of Water Resources in Ojoto and Environs Using Integrated Classical Methods. *Modeling Earth Systems and Environment*, **5**, 1443-1461. https://doi.org/10.1007/s40808-019-00613-y

[10] Muvundja, A. (2015) Hydrological Variability and Biogeochemistry of Particulate Organic Matter of a large Tropical Rift Lake, Lake Kivu (East Africa). Ph.D. Thesis, Université de Namur, Belgique.

[11] Bagalwa, M., Majaliwa, J.G.M., Kansiime, F., Bashwira, S., Tenywa, M. and Karume, K. (2015) Sediment and Nutrient Loads into River Lwiro, in the Lake Kivu Basin, Democratic Republic of Congo. *International Journal of Biological and Chemical Sciences*, **9**, 1678-1690. https://doi.org/10.4314/ijbcs.v9i3.46

[12] Barrus, S.M., Williams, G.P., Miller, A.W., Borup, M.B., Merritt, L.B., Richards, D.C. and Miller, T.G. (2021) Nutrient Atmospheric Deposition on Utah Lake: A Comparison of Sampling and Analytical Methods. *Hydrology*, **8**, Article 123. https://doi.org/10.3390/hydrology8030123

[13] Golterman, H.L., Clymo, R.S. and Ohnstad, M.A.M. (1978) Methods for Physical and Chemical Analysis of Freshwaters. Blackwell Scientific Publication, London.

[14] Wetzel, R.G. and Likens, G.E. (2000) Limnological Analysis. Springer, New York. https://doi.org/10.1007/978-1-4757-3250-4

[15] APHA (American Public Health Association) (1989) Standard Methods for the Examination of Water and Wastewater. 18th Edition, American Public Health Association, Washington DC.

[16] Kumar, R., Rani, A., Singh, S.P., Kumari, K.M. and Srivastava, S.S. (2002) A Long Term Study on Chemical Composition of Rainwater at Dayalbagh, a Suburban Site of Semiarid Region. *Journal of Atmospheric Chemistry*, **41**, 265-279.

https://doi.org/10.1023/A:1014955715633

[17] Cerqueira, M.R.F., Pinto, M.F., Derossi, I.N., Esteves, W.T., Santos, M.D.R., Matos, M.A.C., Lowinsohn, D. and Matos, R.C. (2014) Chemical Characteristics of Rainwater at a Southeastern Site of Brazil. *Atmospheric Pollution Research*, **5**, 253-261. https://doi.org/10.5094/APR.2014.031

[18] Kulshrestha, U.C., Kulshrestha, M.J., Sekar, R., Sastry, G.S.R. and Vairamani, M. (2003) Chemical Characteristics of Rainwater at an Urban Site of South-Central India. *Atmospheric Environment*, **37**, 3019-3069. https://doi.org/10.1016/S1352-2310(03)00266-8

[19] Cao, Y.Z., Wang, S.Y., Luo, J.Y. and Lu, S.Y. (2009) Chemical Characteristics of Wet Precipitation at an Urban Site of Guangzhou, South China. *Atmospheric Research*, **94**, 462-469. https://doi.org/10.1016/j.atmosres.2009.07.004

[20] Safai, P.D., Budhavant, K.B., Rao, P.S.P., Ali, K. and Sinha, A. (2010) Source Characterization for Aerosol Constituents and Changing Roles of Calcium and Ammonium Aerosols in the Neutralization of Aerosol Acidity at a Semi-Urban Site in SW India. *Atmospheric Research*, **98**, 78-88. https://doi.org/10.1016/j.atmosres.2010.05.011

[21] Bigabwa, J.B. (2014) Characterization of Soils Using Infra-Red Scanning in South Kivu Province, Democratic Republic of Congo. Master Thesis, Kenyatta University, Nairobi.

[22] Keresztesi, A., Birsan, M.V., Nita, I.A., Bodor, Z. and Szép, R. (2019) Assessing the Neutralization, Wet Deposition and Source Contributions of the Precipitation Chemistry over Europe during 2000-2017. *Environment Sciences Europe*, **31**, Article No. 50. https://doi.org/10.1186/s12302-019-0234-9

[23] Wang, Y., Yu, W., Pan, Y. and Wu, D. (2012) Acid Neutralization of Precipitation in Northern China. *Journal of the Air & Waste Management Association*, **62**, 204-211. https://doi.org/10.1080/10473289.2011.640761

[24] Akimoto, H., Sato, K., Sase, H., Dong, Y., Hu, M., Duan, L., Sunwoo, Y., Suzuki, K. and Tang, X. (2022) Development of Science and Policy Related to Acid Deposition in East Asia over 30 Years. *Ambio*, **51**, 1800-1818. https://doi.org/10.1007/s13280-022-01702-6

[25] Wang, W., Guan, L., Zhao, J., Sha, Z. and Fang, J. (2022) Chemical Compositions of Rainfall Water in Nyingchi City, Tibet. *Atmosphere*, **13**, Article 1021.

[26] Derry, L.A. and Chadwick, O.A. (2007) Contributions from Earth's Atmospheric to Soil. *Elements*, **3**, 333-338. https://doi.org/10.2113/gselements.3.5.333

[27] Bootsma, H.A., Bootsma, M.J. and Hecky, R.E. (1996) The Chemical Composition of Precipitation and Its Significance to the Nutrient Budget of Lake Malawi. In: Johnson, T.C. and Odada, E.O., Eds., *The Limnology, Climatology and Palaeoclimatology of East African Lakes*, Taylor & Francis Group, Oxfordshire, 251-265. https://doi.org/10.1201/9780203748978-14

[28] Stefánsson, A., Stefánsdóttir, G., Keller, N.S., Barsotti, S., Sigurdsson, A., Thorláksdóttir, S.B., Pfeffer, M.A., Eiríksdóttir, E.S., Jónasdóttir, E.B., von Löwis, S. and Gíslason, S.R. (2017) Major Impact of Volcanic Gases on the Chemical Composition of Precipitation in Iceland during the 2014-2015 Holuhraun Eruption. *Journal of Geophysical Research*: *Atmospheres*, **122**, 1971-1982. https://doi.org/10.1002/2015JD024093

[29] Lee, C., Martin, R.V., van Donkelaar, A., Lee, H., Dickerson, R.R., Hains, J.C., Krotkov, N., Richter, A., Vinnikov, K. and Schwab, J.J. (2011) SO_2 Emissions and Lifetimes: Estimates from Inverse Modelling Using *in Situ* and Global, Space-Based (SCIAMACHY and OMI) Observations. *Journal of Geophysical Researcher*, **116**,

D06304. https://doi.org/10.1029/2010JD014758

[30] Smith, S.J., van Aardenne, J., Klimont, Z., Andres, R.J., Volke, A. and Delgado Arias, S. (2011) Anthropogenic Sulfur Dioxide Emissions: 1850-2005. *Atmospheric Chemistry and Physics*, **11**, 1101-1116. https://doi.org/10.5194/acp-11-1101-2011

[31] Giannoni, S.M., Trachte, K., Rollenbeck, R., Lehnert, L., Fuchs, J. and Bendix, J. (2014) Atmospheric Salt Deposition in a Tropical Mountain Rainforest at the Eastern Andean Slopes of South Ecuador—Pacific or Atlantic Origin? *Atmospheric Chemistry and Physics*, **16**, 10241-10261. https://doi.org/10.5194/acp-16-10241-2016

[32] Pfeffer, M.A., Langmann, B. and Graf, H.F. (2006) Atmospheric Transport and Deposition of Indonesian Volcanic Emissions. *Atmospheric Chemistry and Physics*, **6**, 2525-2537. https://doi.org/10.5194/acp-6-2525-2006

[33] van der Werf, G.R., Randerson, J.T., Giglio, L., Collatz, G.J., Mu, M., Kasibhatla, P.S., Morton, D.C., DeFries, R.S., Jin, Y. and van Leeuwen, T.T. (2010) Global Fire Emissions and the Contribution of Deforestation, Savanna, Forest, Agricultural, and Peat Fires (1997-2009). *Atmospheric Chemistry and Physics*, **10**, 11707-11735. https://doi.org/10.5194/acp-10-11707-2010

[34] Hansen, M.C., Potapov, P.V., Moore, R., Hancher, M., Turubanova, S.A., Tyukavina, A., Thau, D., Stehman, S.V., Goetz, S.J., Loveland, T.R., Kommareddy, A., Egorov, A., Chini, L., Justice, C.O. and Townshend, J.R.G. (2013) High-Resolution Global Maps of 21st-Century Forest Cover Change. *Science*, **342**, 850-853. https://doi.org/10.1126/science.1244693

[35] Bootsma, H.A. and Hecky, R.E. (1993) Conservation of the African Great Lakes: A Limnological Perspective. *Conservation Biology*, **7**, 644-656. https://doi.org/10.1046/j.1523-1739.1993.07030644.x

[36] Aiuppa, A., Bonfanti, P. and D'Alessandro, W. (2003) Rainwater Chemistry at Mt. Etna (Italy): Natural and Anthropogenic Sources of Major Ions. *Journal of Atmospheric Chemistry*, **46**, 89-102. https://doi.org/10.1023/A:1024878323823

[37] Xiao, H.W., Xiao, H.Y., Luo, L., Shen, C.Y., Long, A.M., Chen, L., Long, Z.H. and Li, D.N. (2017) Atmospheric Aerosol Compositions over the South China Sea: Temporal Variability and Source Apportionment. *Atmospheric Chemistry and Physics*, **17**, 3199-3214. https://doi.org/10.5194/acp-17-3199-2017

[38] Khare, P., Goel, A., Patel, D. and Behari, J. (2004) Chemical Characterization of Rainwater at a Developing Urban Habitat of Northern India. *Atmospheric Research*, **69**, 135-145. https://doi.org/10.1016/j.atmosres.2003.10.002

[39] Coelho, C., Allen, A., Fornaro, A., Orlando, E., Grigoletto, T. and Campos, M. (2011) Wet Deposition of Major Ions in a Rural Area Impacted by Biomass Burning Emissions. *Atmospheric Environment*, **45**, 5260-5265. https://doi.org/10.1016/j.atmosenv.2011.06.063

[40] Morales-Baquero, R., Pulido-Villena, E. and Reche, I. (2013) Chemical Signature of Saharan Dust on Dry and Wet Atmospheric Deposition in the South-Western Mediterranean Region. *Tellus B*: *Chemical and Physical Meteorology*, **65**, e18720. Https://Doi.Org/10.3402/Tellusb.V65i0.18720

[41] Tuttle, M.L., Kockwood, J.P. and Evans, W.C. (1990) Natural Hazard Associated with Lake Kivu and Adjoin Areas of the Virunga Volcanic Field, Rwanda and Zaire, Central Africa; Final Report. United States Department of the Interior Geological Survey, Reston. https://doi.org/10.3133/ofr90691

[42] Ma, H., Shi, G. and Cheng, Y. (2020) Accumulations Characteristics of Metals and Metalloids in Plants Collected from Ny-Alesund, Arctic. *Atmosphere*, **11**, Article 1129. https://doi.org/10.3390/atmos11101129

[43] Barbieri, M., Nigro, A. and Sappa, G. (2015) Soil Contamination Evaluation by Enrichment Factor (EF) and Geo-Accumulation Index (Igeo). *Senses and Sciences*, **2**, 94-97.

[44] Rastegari, M.M., Keshavarzi, B. and Sorooshian, A. (2019) Influence of Natural and Urban Emissions on Rainwater Chemistry at a Southwestern Iran Coastal Site. *Science of the Total Environment*, **668**, 1213-1221. https://doi.org/10.1016/j.scitotenv.2019.03.082

[45] Naimabadi, A., Shirmardi, M., Maleki, H., Teymouri, P,, Goudarzi, G., Shahsavani, A., Sorooshian, A., Babaei, A.A., Mehrabi, N., Baneshi, M.M., Zarei, M.R., Lababpour, A. and Ghozikali, M.G. (2018) On the Chemical Nature of Precipitation in a Populated Middle Eastern Region (Ahvaz, Iran) with Diverse Sources. *Ecotoxicology and Environmental Safety*, **163**, 558-566. https://doi.org/10.1016/j.ecoenv.2018.07.103