

Article

Rainwater Chemistry Reveals Air Pollution in a Karst Forest: Temporal Variations, Source Apportionment, and Implications for the Forest

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Abstract: Temporal rainwater chemistry was used to reveal air pollution in the Maolan National Karst Forest Park (MNKFP), which is representative of the typical karst forest region of southwest China (SW China). The rainwater ions' sources, variations, trends, and potential environmental effects were investigated from 2007 to 2010 and from 2013 to 2014. Based on the analysis of the temporal ionic concentrations of rainwater in the MNKFP, significant variations of ions were observed, including in NH_4^+ ($9.7\sim 266.6\ \mu\text{eq L}^{-1}$) and SO_4^{2-} ($14.5\sim 1396.4\ \mu\text{eq L}^{-1}$), which were mainly controlled by variations in the source and rainfall amount; a decreased trend of rainwater pH was also observed. Accordingly, NH_4^+ , Ca^{2+} , SO_4^{2-} , and Cl^- were regarded as the most dominant ions. Typical ionic ratios and positive matrix factorization (PMF) model-based source apportionment suggested that anthropogenic inputs (coal combustion, industrial, traffic, and agricultural emissions) contributed 51% of F^- , 93% of NO_3^- , 62% of SO_4^{2-} , and 87% of NH_4^+ , while the natural sources (crustal dust and sea salt) were the main sources of Cl^- (74%), Na^+ (82%), K^+ (79%), Mg^{2+} (94%), and Ca^{2+} (93%). In combination with the reducing neutralization trend of temporal rainwater observed in the MNKFP and the potential effect of rainwater ion deposition on karst forests, more detailed monitoring of the rainfall-related deposition process is required for a better understanding of its potential environmental effects on the Earth's surface.

Keywords: karst forest; wet deposition; ion composition; source identification; neutralization trend

1. Introduction

Rainwater is the most important sink of air pollutants, such as acid gases and particulate matter (PM) [1–4]. In-cloud and below-cloud scavenging processes are the keys to the removal of air contaminants during a whole rainfall event [5,6], and the rainwater pH and chemical species are changed concomitantly [7–9]. Moreover, investigating rainwater chemical composition is helpful for understanding air quality, which can be used to explore the origins of air contaminants based on the different physical and chemical processes of these contaminants [10–12]. Typically, previous studies have classified the sources of rainwater chemical components (major ions) into three types: sea-salt input (marine sources), terrestrial dust (crustal sources), and human-made emissions (anthropogenic sources) [13–15]. In addition to source variations, factors affecting the chemical composition of rainwater include geomorphic situations, meteorological conditions, and environmental policies [4,16,17].

In southwest China, an evident heterogeneity of rainwater chemistry has been observed, in particular in karst landform areas [3,6,18]; the most widely distributed karst area is in Guizhou Province [19–21]. Since the end of the last century, this area has been regarded as an acid rain control area with a high level of acid deposition [7], and many governmental emission reduction measures have been implemented to reduce rainwater-acidifying potential and to increase neutralizing potential [22]. As one of the most

sensitive terrestrial ecosystems, the karst ecosystem has responded strongly to rainfall (especially acid rain) due to the severe karstification [23–27]. Acidified rainwater not only facilitates the migration of materials (from the surface to underground) but also accelerates the weathering process of carbonate rocks and causes intense soil erosion in a karst ecosystem. On the other hand, the weathering products (mainly calcium and magnesium) provide a source of alkaline matter for the neutralization process of rainwater [3,28]. Moreover, rainwater is an important source of nutrients (e.g., nitrogen, phosphorus, and potassium) for some barren karst ecosystems (e.g., a karst forest ecosystem) due to the weak capacity of the soil for nutrient retention [18,29].

Forests are important parts of terrestrial ecosystems and are regarded as the Earth's lungs. However, the structure and function of a forest system is significantly disturbed by atmosphere-related pollution and accompanying acid deposition [8,30–35]. Chemistry-varied rainwater can further impact biogeochemical cycles via chemical elemental redistribution in forest ecosystems [2,32]. For example, rainwater-related ion deposition significantly changes a land's carbon cycle (e.g., the soil respiration process) [36,37]. Previous studies took the Maolan National Karst Forest Park (MNKFP), the most typical karst forest in the region of southwest China (SW China), as a case to investigate rainwater chemistry based on strontium and calcium isotope constraints, and they reported on the qualitative source identification and short-term material source of rainwater [8,38]. However, only a long-term variation in the chemical components of rainwater can provide more comprehensive information on the temporal evolution of air contamination (especially local air quality), and such variation can be further applied as an indicator to assess the influences of anthropogenic and natural inputs. To our knowledge, the relatively long-term measurement-based studies on rainwater chemistry in the MNKFP have been very limited, and temporal variations in the acidifying and neutralizing potential of rainwater are also unclear in the karst forest ecosystem. Moreover, the quantitative contribution (e.g., model-based source identification) of the different sources of the rainwater components in the MNKFP has been rarely studied.

To advance the information on rainwater chemistry and its potential environmental effects in the karst forest region, the present study conducted a systematic investigation in the MNKFP based on temporal rainwater chemistry (2007–2010 and 2013–2014). The key objectives were to: (1) clarify the ionic composition of rainwater in a karst forest, (2) explore the temporal variations of rainwater ion compositions and trends in terms of acidifying and neutralizing potentials, (3) identify the source contribution of related ions, and (4) discuss the potential environmental effects of rainfall-related ion deposition on the forest ecosystem.

2. Materials and Methods

2.1. Study Area and Sampling

The MNKFP is the most representative of the karst forest landscape in the subtropical region of China. It has a landmass of 213 km² and is located in one of three globally continuous larger karst areas (southwest China karst; Figure 1) [16]. This park is distinctly encircled by a subtropical virgin evergreen forest with a forest coverage of 88.6% (elevation is 430–1078 m). Since 1996, the MNKFP has been included in the World Biosphere Reserves Network and the World Heritage List due to the primitiveness of the forest vegetation and the richness of fauna. According to government statistics, there are 2199 species of higher plants in 241 families and 870 genera in the MNKFP, such as *Taxus chinensis* and *Incense cedar*. Karst geomorphology, including karst funnels, karst depressions, karst valleys (basin), karst trough valleys, and karst hydrological landscapes, is widespread in the MNKFP. The lithology of the MNKFP is controlled by the shallow marine carbonate with sporadically distributed sandstone (Figure 1). The MNKFP is characterized by a subtropical monsoon climate (average air temperature of 15.3 °C). The wet season (from April to September) is generally the season when major rainfall events happen (~80%) [38]; the annual rainfall amount is 1750 mm.

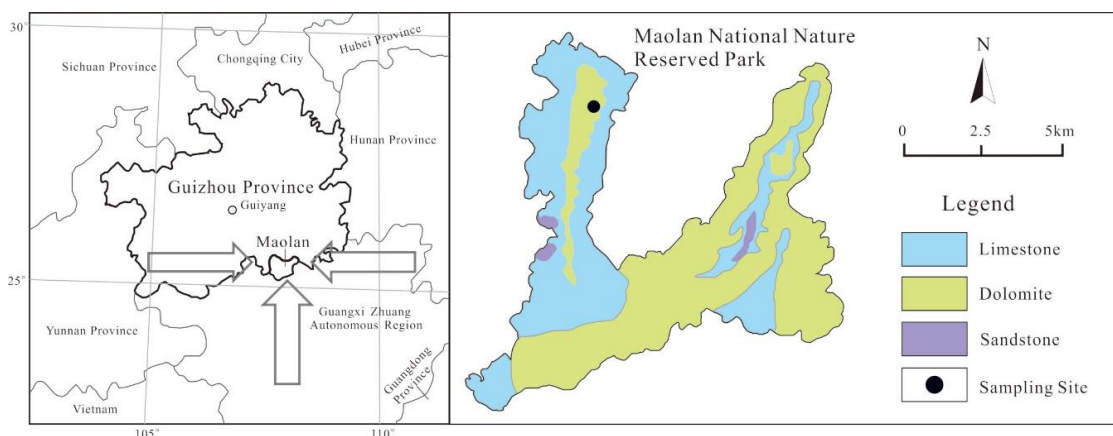


Figure 1. Background of the sampling site in the Maolan National Karst Forest Park (MNKFP).

The rainwater sampling site was selected in the northwest of the MNKFP (Figure 1). Polyethylene (PE) samplers (diameter of approximately 65 cm and volume of 20 L) were manually installed to sample the rainwater, and they were set 12 m apart over the land's surface. A lid was also used to avoid deposited dust on non-rainy days. The samplers were thoroughly washed with ultrapure water after each rainfall event. The filtration of the rainwater samples was completed using Millipore membrane filters (0.22 μm , acetate membrane, MILLIPORE, Billerica, MA, USA). After filtration, the samples were stored in a clean PE bottle and kept refrigerated at 4 $^{\circ}\text{C}$. From 2007 to 2010, a total of 104 daily rainwater samples were collected [8,38]. From August 2013 to June 2014, nine monthly mixed samples were obtained, and these were proportionally mixed based on the corresponding rainfall amount of each rainfall event in different months. The analytical data of the mixed sample represent the monthly weighted-mean values [39].

2.2. Measurement and Quality Control

The pH values of daily rainwater samples were measured by portable multiple parameter meters after collection. Both the daily rainwater samples and the monthly mixed samples were separated and saved in two clean PE bottles for detecting contents of anions and cations (nitric acid acidified, pH < 2), respectively. The pre-cleaned procedure of PE bottles was taken from the literature [40]. Ion chromatography (IC, Dionex DX-120, DIONEX, Sunnyvale, CA, USA) with an anion column (IonPac AS23, DIONEX, Sunnyvale, CA, USA) was applied to detect the major anion contents, including Cl^- , F^- , NO_3^- , and SO_4^{2-} . The detection limits of these anions were 0.04, 0.03, 0.06, and 0.10 mg L^{-1} , respectively. The inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Scientific IRIS Intrepid-II, Thermo Fisher Scientific, Waltham, MA, USA) was applied to measure the major cation contents of K^+ , Na^+ , Ca^{2+} , and Mg^{2+} . The detection limits of these cations were 0.01, 0.03, 0.04, and 0.01 mg L^{-1} , respectively. The NH_4^+ concentration of the daily rainwater samples was determined by the spectrophotometer (Nessler method) with a detection limit of 0.02 mg L^{-1} . For quality control, the measurement was performed with the replicates, standard reference materials, and procedural blanks. In brief, the measured replicate samples implied an acceptable repeatability for all ions (within 5%). The standard reference material (GB W08606, National Research Center for Certified Reference Materials, China) was regularly applied to ensure quality assurance for major ion analysis. Furthermore, the procedural blanks of detected ions were below the detection limit or <5% in the rainwater samples, indicating a reliable analytical process. Moreover, the ionic balance was also applied for the daily rainwater samples. The total cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and NH_4^+) and total anions (Cl^- , F^- , NO_3^- , and SO_4^{2-}) presented good ion balances ($R^2 = 0.94$ and $p < 0.01$), suggesting the good quality of the chemical detection [41].

2.3. Data Processing Method

The equation below was used for calculating the monthly volume-weighted mean (VWM) concentrations of each ion of previous observational data [18]:

$$C = \frac{\sum C_i P_i}{\sum P_i} \quad (1)$$

where C is the monthly VWM concentration, C_i is the ionic concentration of each sample in the same month, and P_i is the corresponding rainfall amount of each sample.

After a normal distribution test (Kolmogorov–Smirnov test) of the data of ion concentrations, the Spearman's rank correlation coefficient and principal component analysis (PCA) were performed (via SPSS 21.0) for potential source identification. More details can be found in previous studies [40,42]. The contribution of various origins to rainwater ionic species was quantified by using the model of positive matrix factorization (PMF), which is a widely used receptor model based on the ionic concentrations and corresponding uncertainty values [43]. The modeling process was concluded via EPA (Environmental Protection Agency) PMF, version 5.0. More details on the PMF model process can be found in Supplementary Materials (Text S1).

3. Results and Discussion

3.1. Rainfall Amount and pH Distribution

The yearly total rainfall amounts of the study area were 1051, 1430, 1058, 1059, 1027, and 1288 mm from 2007 to 2010 and 2013 to 2014, respectively, with a mean value of 1152 mm. These results were relatively stable during study period but much lower than the long-term (>50 years) average value of 1750 mm in the MNKFP. As shown in Figure 2, the monthly rainfall amount of each year changed significantly, with a peak in June/July, and approximately 46%–60% of the rainfall was concentrated from June to August (summer).

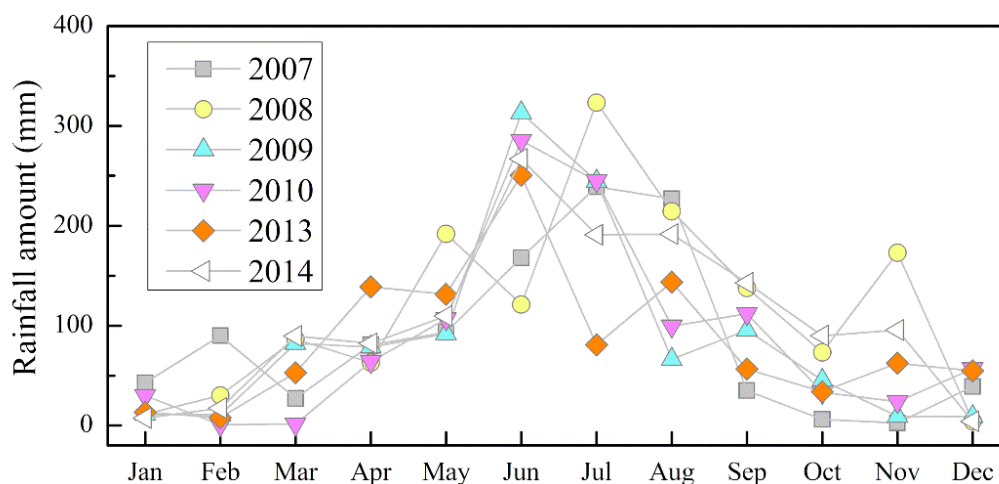


Figure 2. Monthly rainfall amount during the study period.

As illustrated in Figure 3a, rainwater pH values (frequency distribution) presented a unimodal distribution, which was quite different from the bimodal distributions of rainwater pH observed in other areas, e.g., the Mediterranean region [44]. The pH of each rainwater sample ranged from 3.8 to 7.2, with a mean value of 5.2 and a VWM value of 5.3. An intermediate pH (4.7–5.6) in Figure 3a was recorded in about 56% of rainwater samples, and acidic pH ($\text{pH} < 5.6$) accounted for 75%. This pH distribution implied the acidic characteristics of rainwater in the MNKFP. According to carbonic acid equilibrium, the rainwater HCO_3^- concentration under this pH condition was very low, and the organic anionic species (e.g., plant-released oxalate) could have led to a slight ion imbalance [45] (Section 2.2).

It is noteworthy that the reducing trend of rainwater pH in time-based linear regression (Figure 3b) was synchronously similar to that in some urban regions [46]. Overall, these results reflected that the buffer capacity of rainwater may be declining, that is, the input of acid compounds was increased and/or the input of base materials (for neutralization) was decreased. Further discussion about the neutralization process can be seen in Section 3.4.

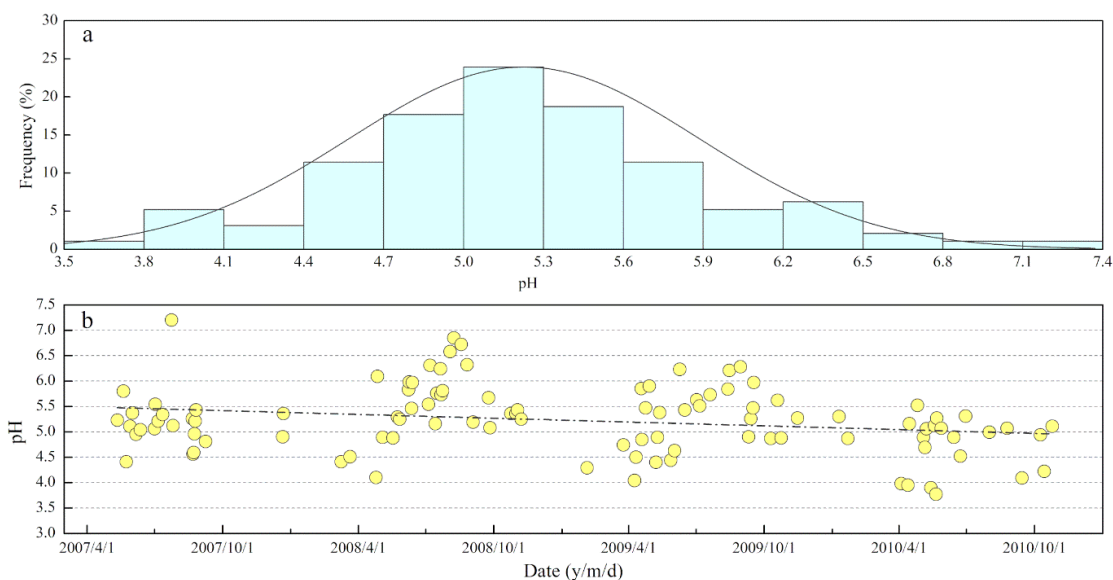


Figure 3. The pH values of rainwater (a) frequency distribution and (b) time series; $n = 104$.

3.2. Ion Compositions and Temporal Variations

3.2.1. Overview of Ion Compositions

Figure 4 illustrates the statistical results of major ion concentrations on a monthly scale, including the ranges, mean values, VWM values, and relative percentages of each ion in the study period. As expected, great variations in the concentration for each ion in rainwater were observed in the MNKFP. All the ion concentration values showed a wide range, e.g., the NH_4^+ concentration ranged from 9.7 to 266.6 $\mu\text{eq L}^{-1}$ and that of SO_4^{2-} ranged from 14.5 to 1396.4 $\mu\text{eq L}^{-1}$ (Figure 4a), which means that the arithmetic mean value could not reflect the overall level of rainwater ion concentration. Therefore, the VWM values were more appropriate for comparison [14]. Accordingly, the major ion concentrations in the MNKFP followed the order of SO_4^{2-} (79.9 $\mu\text{eq L}^{-1}$) > Cl^- (25.7 $\mu\text{eq L}^{-1}$) > NO_3^- (18.1 $\mu\text{eq L}^{-1}$) > F^- (5.0 $\mu\text{eq L}^{-1}$) and NH_4^+ (56.3 $\mu\text{eq L}^{-1}$) > Ca^{2+} (52.9 $\mu\text{eq L}^{-1}$) > Mg^{2+} (12.3 $\mu\text{eq L}^{-1}$) > K^+ (7.2 $\mu\text{eq L}^{-1}$) > Na^+ (6.6 $\mu\text{eq L}^{-1}$) (Figure 4a).

The composition percentages of anions and cations are also shown in Figure 4b,c, indicating that SO_4^{2-} , Cl^- , NH_4^+ , and Ca^{2+} were the predominant rainwater species in the MNKFP. SO_4^{2-} and Cl^- accounted for 62.1% and 20.0%, respectively, of all measured anions, making them the most and the second richest anions (Figure 4b). The highest percentage of SO_4^{2-} implied the potential impact of intense human activities [43,47]. As seen in Figure 4c, NH_4^+ , Ca^{2+} , Mg^{2+} , K^+ , and Na^+ accounted for 41.6%, 39.1%, 9.0%, 5.4%, and 4.9% of the total cations, respectively. Therefore, NH_4^+ was the leading cation, and Ca^{2+} was also a significant contributor compared to Mg^{2+} , K^+ , and Na^+ . Both agriculture and geology are responsible for cationic composition. With the accelerated development of agricultural production, continual overfertilization discharges vast NH_4 -contained pollutants into the atmospheric environment, which can be supported by the increasing application rate of synthetic nitrogen fertilizer (about 10 kg N/(km²·yr) in karst agriculture over the last few decades [48]. Furthermore, the wide distribution of carbonate is the most probable source of Ca-enriched dust, which is an important origin of rainwater Ca^{2+} [40]. In total, the NH_4^+ and Ca^{2+} concentrations made up 80.7% of the

cations, while SO_4^{2-} and Cl^- made up 82.1% of the anions. These results reflected that the secondary ammonium sulfate and ammonium nitrate in fine inorganic atmospheric aerosols are the most probably contributors of rainwater ions that could be washed out from the atmosphere by rainfall [49].

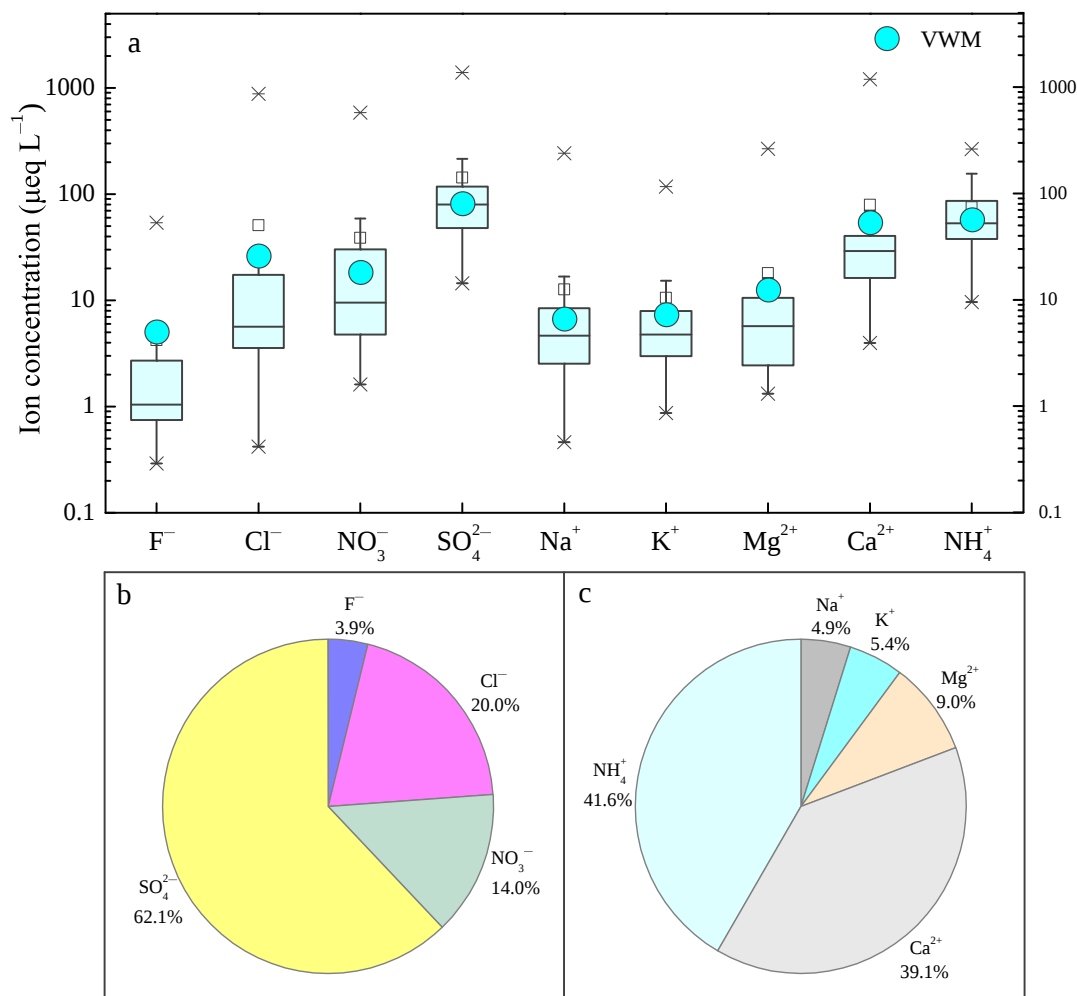


Figure 4. (a) Overview of rainwater ion concentrations ($\mu\text{eq L}^{-1}$), (b) rainwater anion composition percentages, and (c) rainwater cation composition percentages from 2007 to 2014 in the MNKFP. VWM: volume-weighted mean.

Here, we also summarize the ion concentrations of rainwater in different karst systems, such as karst city (Guiyang city) and karst agriculture (Puding), as well as the published data in different environmental types (Table 1). From the perspective of synchronous rainwater in different karst systems, the concentrations of SO_4^{2-} and Ca^{2+} concentrations in the MNKFP were much lower than those observed in karst city, agricultural areas, and the Bohemian karst region [3,28,40,50,51], and the concentrations of F^- and NO_3^- were also lower than that in karst city [40,50]. In contrast, the concentrations of Na^+ and K^+ in rainwater were similar in different karst systems. The concentrations of Cl^- , Mg^{2+} , and NH_4^+ in the MNKFP were among the corresponding ion concentrations in different karst systems (Table 1). These results can be explained by the differences of the relative intensity of human activities under various karst environmental types, such as coal combustion emissions (e.g., SO_4^{2-}), traffic emissions (e.g., NO_3^-), industrial emissions (e.g., F^-), and agricultural production intensity (e.g., NH_4^+ from nitrogen fertilizer and F^- from phosphorus fertilizer) [18,52]. Furthermore, with the acceleration of urbanization, the construction industry and other human activities continually discharge vast Ca-containing pollutants into atmosphere [43], which are responsible for higher Ca^{2+}

levels in karst urban rainwater relative to forest areas (MNKFP). The results in other inland/coastal megacities [13,43], deserts [53], mountain areas [54], and oceanic islands [55] further support the impact of different anthropogenic emission intensities on rainwater ion species (Table 1).

Table 1. Comparison of ion concentration (in $\mu\text{eq L}^{-1}$) of rainwater in the MNKFP and other published data.

Site	F [−]	Cl [−]	NO ₃ [−]	SO ₄ ^{2−}	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	NH ₄ ⁺	Rainwater Type
MNKFP (this study)	5.0	25.7	18.1	79.9	6.6	7.2	12.3	52.9	56.3	Karst forest
Guiyang 2007–2008	14.3	9.8	39.6	237.8	1.8	11.1	18.6	217.6	77.0	Karst city
Guiyang 2009–2010	19.9	5.7	26.1	274.6	10.9	10.2	62.2	349.4	35.4	Karst city
Puding 2008	2.8	54.5	17.0	152.4	10.8	9.1	3.9	155.8	33.1	Karst agriculture
Puding 2012–2013	—	17.0	12.3	168.7	7.4	4.3	18.5	112.9	32.1	Karst agriculture
Prague	2.7	18.3	72.9	129.0	8.0	23.4	10.3	319.9	—	Bohemian karst
Beijing 2011–2012	12.0	50.9	42.6	357.0	21.5	9.2	53.3	273.0	346.0	Inland megacity
Shenzhen 2008–2009	—	45.9	23.7	59.3	36.4	2.0	11.8	18.1	14.7	Coastal megacity
Alxa 2013–2015	—	202.8	69.7	471.4	232.5	34.1	72.1	663.0	167.2	Desert
Eastern Tien Shan 2003–2004	—	16.5	9.6	53.0	19.0	4.0	18.1	174.2	25.2	Mountain area
Yongxing Island 2013	—	214.4	8.9	38.0	209.7	5.8	45.6	128.8	8.7	Oceanic island

“—” denotes no data; the data sources were Guiyang 2007–2008 [50], Guiyang 2009–2010 [40], Puding 2008 [3], Puding 2012–2013 [28], Prague [51], Beijing [13], Shenzhen [43], Alxa [53], Eastern Tien Shan [54], and Yongxing Island [55].

3.2.2. Temporal Variations

In southwest China, in general, March to May, June to August, September to November, and December to February are defined as spring, summer, autumn, and winter, respectively [56]. Relatively higher total ion concentrations were found in spring, autumn, and winter, while summer was accompanied by lower concentrations (Figure 5a,b). Each cation and anion also showed similar seasonal variation trends. Though the seasonal pattern was not obvious, the variations of ion concentrations could still be explained by two factors. Firstly, seasonal variation in potential material sources is an important factor, including variations of atmospheric particulate matter (PM; high Ca²⁺ content) and atmospheric acid gases [14]. Secondly, relatively frequent precipitation in summer (rainy season) could effectively scour various species in the atmosphere and further cause a short retention time for air contaminants compared to other seasons [57], whereas more atmospheric materials can be captured by rainwater in low rain-frequency seasons [58]. Generally, in the rainfall scouring process, atmospheric materials, including sulfur and nitrogen oxides, particulate nitrate, Ca/Mg-mineral, and the new particles produced by these materials (new particle formation and gas-to-particle conversion in the process of cloud condensation nuclei, especially on the nanoscale) [59], are powerfully washed down during the early rain stage, resulting in higher ion concentrations under the condition of low rainfall amounts [39]. On the contrary, in the rainy season, without the continuing supplements of suspended materials or gaseous atmospheric pollutants, the ion concentrations of the late rain stage (prolonged and heavy rainfall event) decrease progressively and remain on a relatively low level (reflecting the in-cloud process, that is, rainwater presents a similar ion concentration to cloud-water) [5,60,61]. This decrease could also be associated with the dilution effect widely observed in rainwater research [41,62–65] that has shown a decreased ion concentration with an increased rainfall amount. Moreover, the combined influence of synoptic easterly airflow that transports a cleaner marine air mass over a region is another potential reason for lower ion concentrations during monsoons [66].

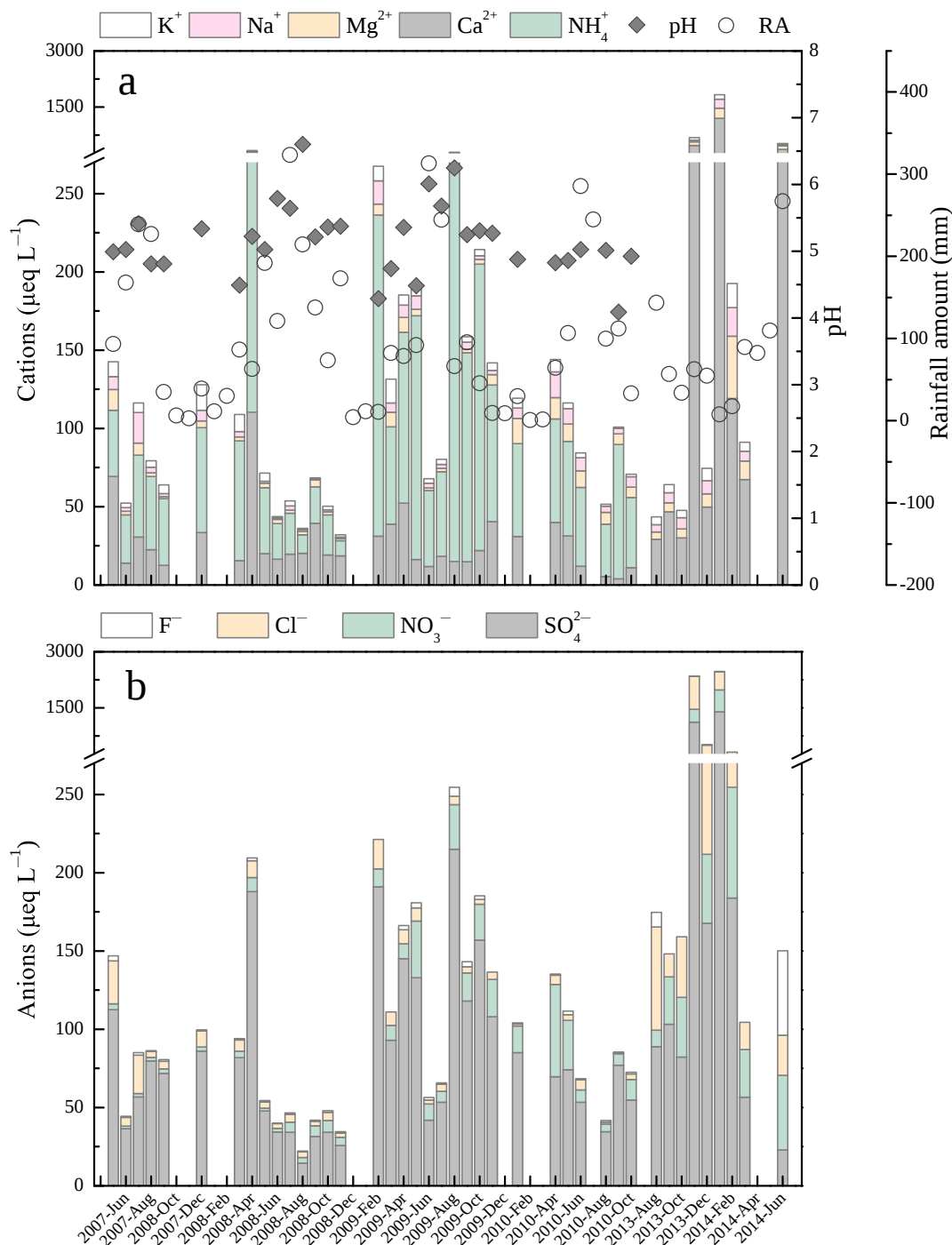


Figure 5. Monthly variations of (a) cation concentrations, rainfall amount (RA), and pH. (b) Anion concentration in the MNKFP.

3.3. Source of the Rainwater Ions

3.3.1. Source Identification

Because of similar physicochemical features and potential co-sources of some air species (e.g., sulfur and nitrogen oxides) [67], the correlation coefficient, which was applied in this study, is an effective tool for distinguishing common sources of rainwater ions. As presented in Figure 6, the rainfall amount displayed obvious negative correlations with all ions ($p < 0.01$), which further supported the vital influence of rainfall amount on ion concentration variations. Nevertheless, obvious positive

correlations were found among most of the ion species, such as $r = 0.91$ for SO_4^{2-} and NH_4^+ , $r = 0.66$ for Ca^{2+} and Mg^{2+} , $r = 0.60$ for SO_4^{2-} and Cl^- , and $r = 0.60$ for SO_4^{2-} and NO_3^- ($p < 0.01$; Figure 6). Thus, it was hard to gain further source information of these ions via correlation analysis.

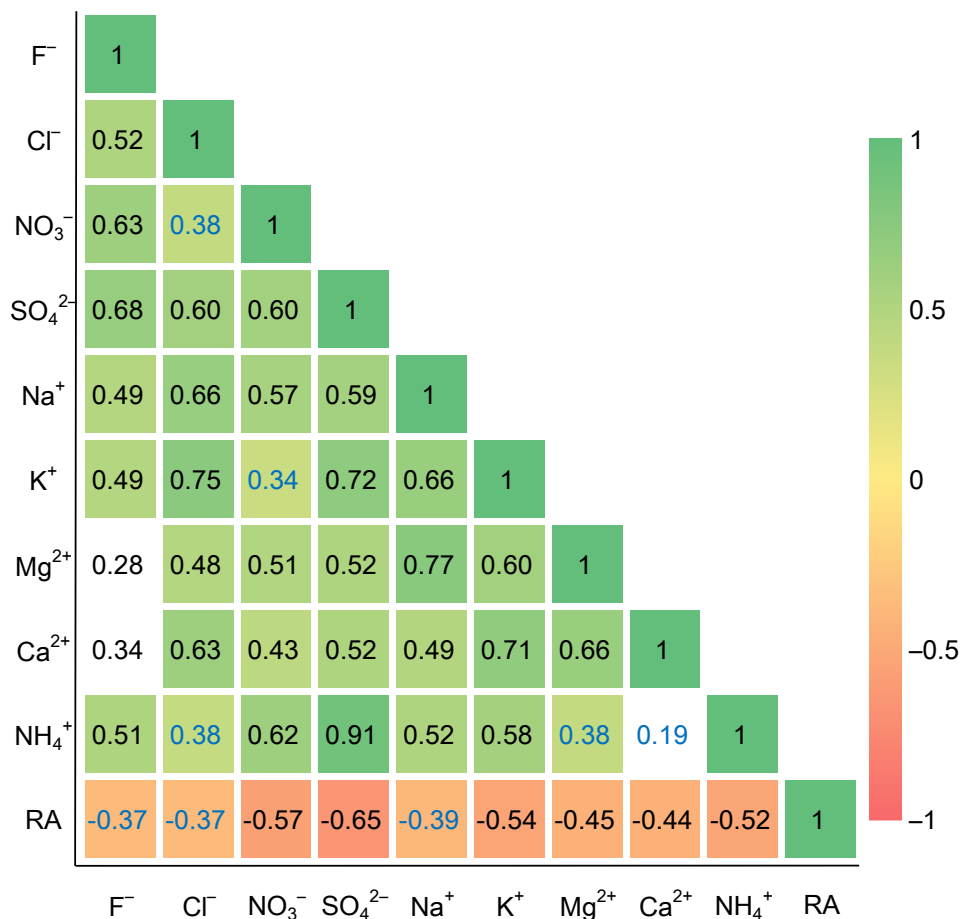


Figure 6. Spearman's rank correlation coefficients between monthly major ions in rainwater and RA; white cells denote statistically non-significant correlations ($p > 0.05$), blue font cells denote the significance level of $p < 0.05$, and other cells denote the significance level of $p < 0.01$.

To further distinguish the relationships of different rainwater ions and their sources, typical ion equivalent ratios, including $\text{SO}_4^{2-}/\text{Na}^+$, Cl^-/Na^+ , $\text{NO}_3^-/\text{Na}^+$, $\text{SO}_4^{2-}/\text{NO}_3^-$, $\text{Mg}^{2+}/\text{Ca}^{2+}$, and $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ratios, were calculated. As shown in Figure 7a, about a quarter of rainwater showed low Cl^-/Na^+ ratios (relative to seawater), while most of the rainwater presented a higher Cl^-/Na^+ ratio [68]. Overall, the Cl^-/Na^+ ratios of rainwater in the MNKFP are comparable to that in karst urban and rural regions [18,40,50]. Combined with the fact that the concentrations of rainwater Cl^- and Na^+ (typical sea-salt ions) in the MNKFP were much less than that of oceanic rainwater (Yongxing Island; Table 1) [55], we concluded that Cl^- and Na^+ were undergoing a strong depleted or dilution process during the transportation of atmospheric clouds [14], while the contributions of human activity to Cl^- and Na^+ were limited. Moreover, high $\text{SO}_4^{2-}/\text{Na}^+$ and $\text{NO}_3^-/\text{Na}^+$ ratios were observed in most of the rainwater samples (Figure 7a,b), implying a distinct influence of human input, that is, the SO_4^{2-} and NO_3^- in rainwater mainly originated from anthropogenic emissions [47]. In particular, the $\text{SO}_4^{2-}/\text{NO}_3^-$ ratios presented consistently high values (exceeding 1 up to 36.1; Figure 7c) in almost all samples, further revealing that fixed pollution emission sources were the primary contributors (e.g., local coal-burning emissions) [69,70], while the contribution of mobile sources (e.g., vehicle emissions) was relatively weakened [53,71]. It can be seen in Figure 7d that because of the low $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios (mean value 0.3), most of the samples are scattered between the calcite and dolomite dissolution line

and the calcite dissolution line, reflecting a significant impact of atmospheric dust-calcite dissolution (originated from carbonate weathering) on rainwater Ca^{2+} and Mg^{2+} [28]. In contrast, the marine contribution to rainwater Ca^{2+} and Mg^{2+} was relatively limited compared with seawater, as seen in Figure 7d. Moreover, although the ionic ratios associated with F^- , K^+ , and NH_4^+ are not plotted in Figure 7, previous studies have suggested the primary contributors on these ions. The main sources of K^+ were attributed to soil dust and biomass burning (e.g., agricultural straw burning), and the higher F^- concentration in rainwater was accounted by anthropogenic emissions [72–74]. As for rainwater NH_4^+ , agriculture-related processes, including fertilization and biomass burning, are the primary origins [52,53], as supported by the high $\text{NH}_4^+/\text{NO}_3^-$ ratios (up to 25.7 with a mean value of 10.0).

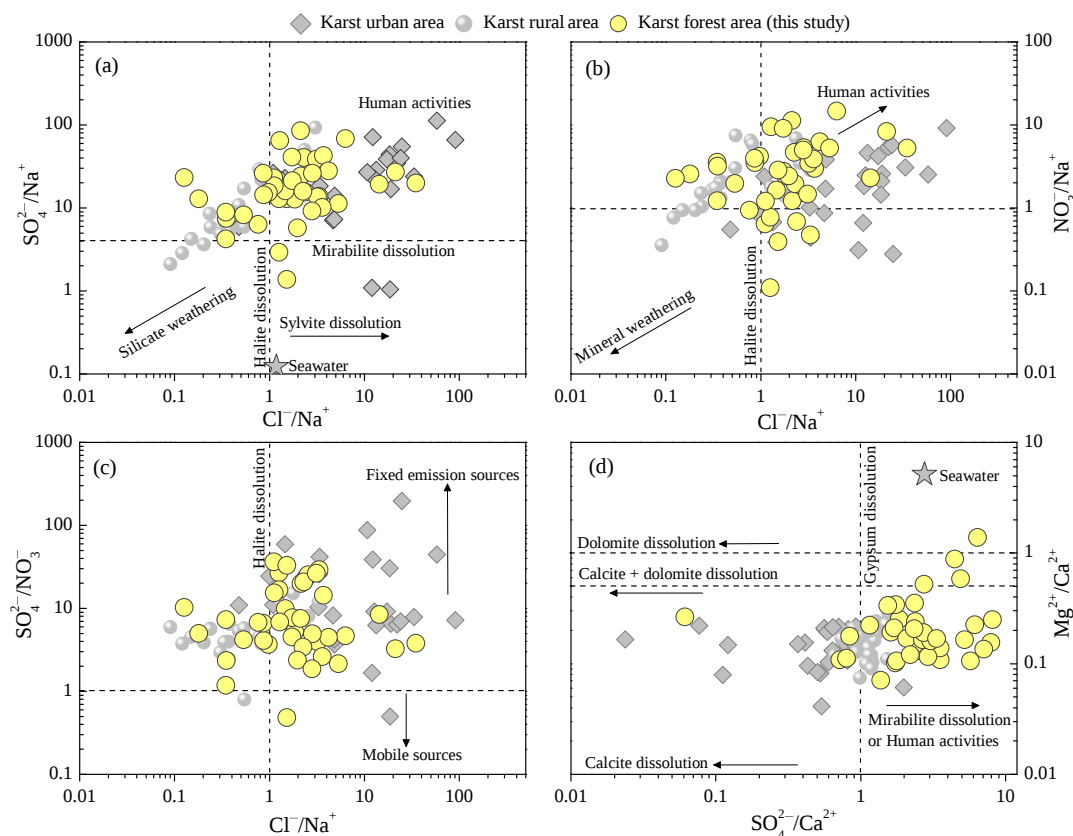


Figure 7. The relationship between the ratios of typical ions (equivalent ratio) in karst forest, urban, and rural rainwater, including $\text{SO}_4^{2-}/\text{Na}^+$ vs. Cl^-/Na^+ (a), $\text{NO}_3^-/\text{Na}^+$ vs. Cl^-/Na^+ (b), $\text{SO}_4^{2-}/\text{NO}_3^-$ vs. Cl^-/Na^+ (c), and $\text{Mg}^{2+}/\text{Ca}^{2+}$ vs. $\text{SO}_4^{2-}/\text{Ca}^{2+}$ (d) ratios. The calcite and dolomite dissolution line is the second horizontal dotted line in (d), and the calcite dissolution line is the x axis in (d). Data sources for karst urban and rural rainwater chemistry and other reference values are from [18,40,50,68].

3.3.2. Source Contributions

Based on the time series of rainwater chemistry data, two principal components (PCs) were recognized with a cumulative variance of 71%. Obviously, these two PCs could be easily distinguished as two contributors to rainwater ions, including anthropogenic emissions and natural sources. As shown in Figure 8a, PC1—highly loaded with F^- , NO_3^- , SO_4^{2-} , and NH_4^+ —explained 36% of the variance. This PC has mainly displayed certain anthropogenic emission sources, such as industrial emissions, coal combustion, traffic emissions, and agricultural emissions [72,75]. PC2 had high loadings on Cl^- , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , which was likely indicative of natural sources, such as crustal dust and sea salt [14,43]. Two contributors (factors) were further extracted from the PMF model, and the contributions of each contributor (anthropogenic and natural source) to rainwater ions are shown in Figure 8b. Anthropogenic sources contributed 51% of F^- , 93% of NO_3^- , 62% of SO_4^{2-} , and 87% of

NH_4^+ , while 74% of Cl^- , 82% of Na^+ , 79% of K^+ , 94% of Mg^{2+} , and 93% Ca^{2+} were attributed to natural sources. In combination with the previous discussion, the specific anthropogenic source contributions can be well-constrained, e.g., the contribution of vehicle emissions and coal combustion to rainwater NO_3^- were found to be no more than 93%, agriculture's contribution to rainwater NH_4^+ was less than 87%, and the soil-derived dust's contribution to Mg^{2+} and Ca^{2+} was found to be up to more than 90%.

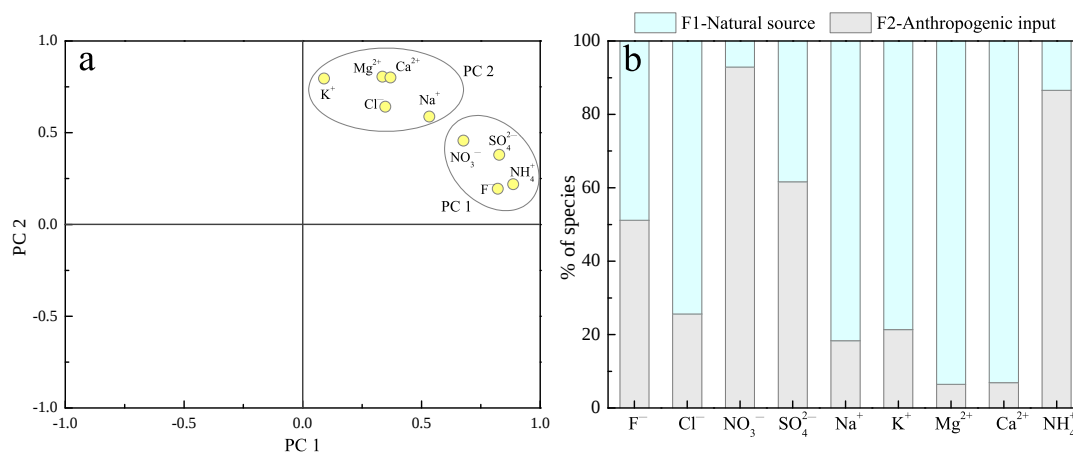


Figure 8. (a) The principal component analysis of rainwater ions and (b) positive matrix factorization (PMF)-extracted relative contribution fractions of anthropogenic and natural sources to rainwater ions in the MNKFP.

3.4. Trends in Acidifying and Neutralizing Potential

Generally, the ratio of neutralizing potential (NP) and acidifying potential (AP) is applied to reflect the rainwater neutralizing process, which is defined as the equivalent concentration ratio of (ammonia and calcium) and (nitrate and sulfate), as follows [14,76,77]:

$$\text{NP/AP} = [\text{NH}_4^+ + \text{nss-Ca}^{2+}] / [\text{NO}_3^- + \text{nss-SO}_4^{2-}] \quad (2)$$

where nss denotes the non-sea salt part of corresponding ions—the detailed calculation can be found in previous study [53]. The time series of NP/AP are shown in Figure 9a. The high value of NP/AP (1.13 on average) implied that rainwater in the MNKFP had a significant neutralization potential to adjust the high loading sulfur/nitrate-caused acidity. It is noteworthy that the NP/AP ratio presented an obvious declining trend, with the regression intercept decreasing from 1.4 to 0.9 within four years (Figure 9a), indicating that the reducing neutralization trend was probably the temporal trend for MNKFP rainwater. A similar trend was also observed in the rainwater of some urban regions [46]. Furthermore, the time series of neutralization factors (NFs; $\text{NF of } X = [X] / [\text{NO}_3^- + \text{nss-SO}_4^{2-}]$, $X = \text{NH}_4^+$, nss-Ca^{2+} , and nss-Mg^{2+}) of NH_4^+ , Ca^{2+} , and Mg^{2+} were also calculated and are plotted in Figure 9b–d. The NFs of these three ions showed large variations with ranges from 0.06 to 1.82 (0.76 on average), from 0.02 to 1.41 (0.38 on average), and from 0.004 to 0.39 (0.07 on average) of the NFs of NH_4^+ , Ca^{2+} , and Mg^{2+} , respectively, suggesting the leading role of NH_4^+ and Ca^{2+} neutralization over Mg^{2+} . Both the NFs of NH_4^+ and Ca^{2+} showed an evident decreasing trend, while the NF of Mg^{2+} presented an increasing trend over the period (Figure 9b–d). Due to the confirmation of magnesium as a representative marker of cement dust [78], the increasing trend in the NF of Mg^{2+} (although the NF was small) likely reflected the growing potential influence of construction activities on rainwater. Similar trends of NFs were also observed in urban rainwater [46]. The temporal trends of rainwater acidification and neutralization in the MNKFP (karst forest area) were different to that in the rainwater of karst urban and agricultural regions (revealing an alkaline rain trend) [18,40], which can be explained by relatively fewer alkaline substance sources, such as NH_3 volatilization from agricultural production and Ca-enriched dust from the construction industry, in the forest area.

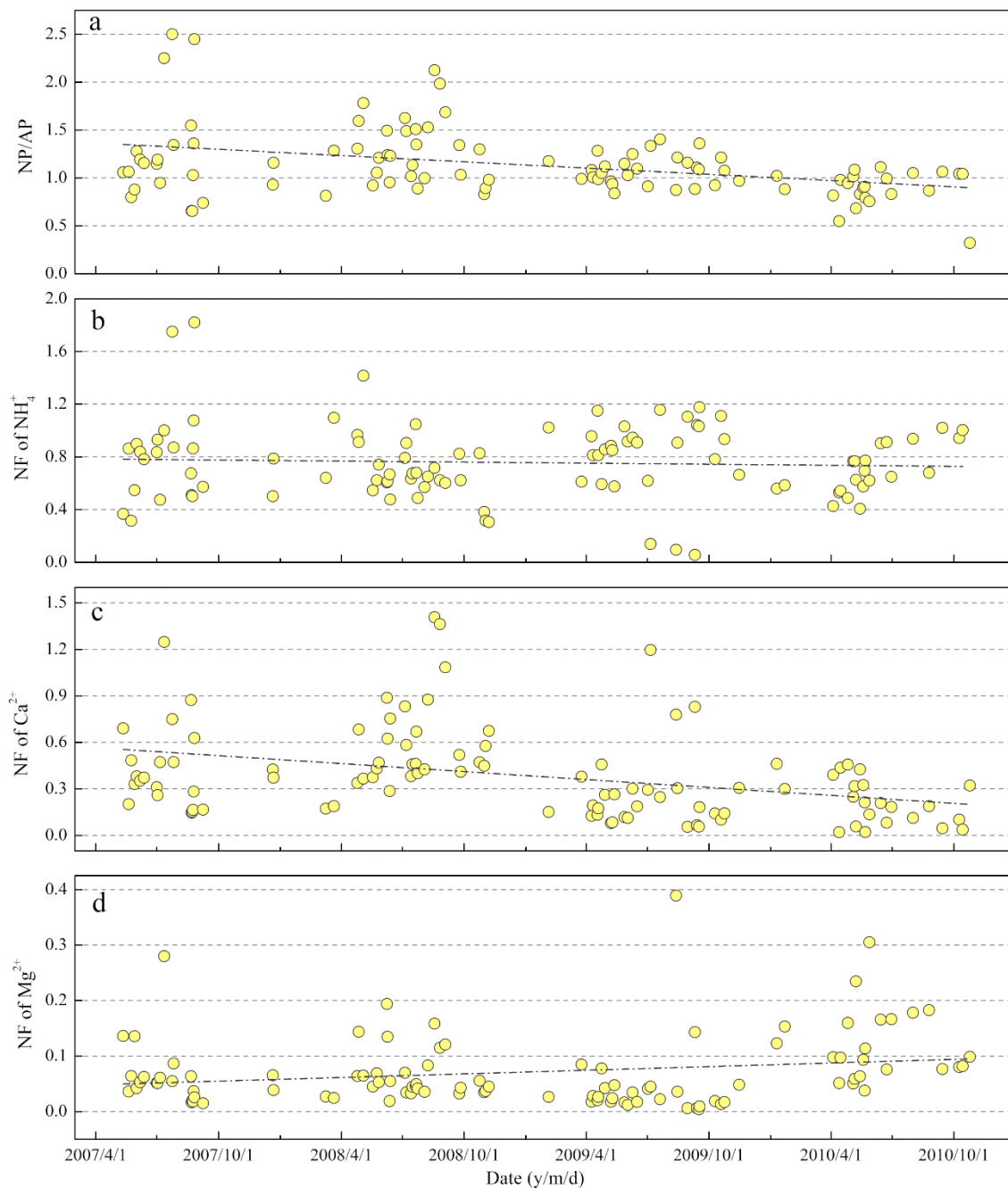


Figure 9. Time series of (a) neutralizing potential/acidifying potential (NP/AP), (b) neutralization factor (NF) of NH_4^+ , (c) NF of Ca^{2+} , and (d) NF of Mg^{2+} .

3.5. Ions Deposition Flux and Potential Environmental Effects

According to the VWM concentrations (Table 1) of each ion and the average rainfall amount (1152 mm) over the study period, the annual deposition fluxes of rainwater ions were calculated and are plotted in Figure 10. Fairly large variations in ionic deposition fluxes were observed in different ions in MNKFP rainwater with a range of 0.06 (F^-) to 0.92 (SO_4^{2-}) keq ha^{-1} . The annual wet deposition flux of total ions was calculated as 3.0 keq ha^{-1} . Though the yearly deposition flux was relatively low over China, it was equivalent to the monthly deposition flux in some heavily polluted regions ($\sim 2.5 \text{ keq ha}^{-1}$) [43,46,53,54]; however, the potential environmental effects of rainwater ions on such a karst forest ecosystem are non-negligible. As the important influence factors, wet nitrogen and acid deposition significantly the change soil respiration of the forest ecosystem, which is one of the largest

CO₂ sources to atmosphere, on a global scale [79]. A previous study found that the interactive effects of nitrogen and acid deposition significantly reduced soil respiration via the inhibition of enzyme activity and microbial biomass in forest soil caused by soil acidification [36]. Decreased soil respiration may have similarly occurred in the MNKFP (karst forest) and further impacted the global carbon cycle based on the observed trend of rainwater pH, nitrogen, and sulfur (Sections 3.1 and 3.4). In addition, other inorganic ions of rainwater, including K⁺, Na⁺, Ca²⁺, Mg²⁺, and Cl[−], together with rainwater nitrogen and sulfur, could inhibit the decomposition rates of leaf litters and the carbon and nitrogen loss of a forest system [80]. Even more remarkable is that rainfall-actuated acid deposition (as the exogenous acid) has significantly enhanced the weathering processes of carbonate rock in karst areas and further affected global climate change [81–84]. Different from economically developed and densely populated areas (wet acid deposits dominated by nitrates) [85], wet acid deposition in the karst forest (MNKFP) was found to be controlled by sulfur with a significantly high contribution of 82% in total acid deposition (Figure 10). Therefore, more attention should be paid to rainfall-related ion deposition, particularly sulfur wet deposition in the karst forest region.

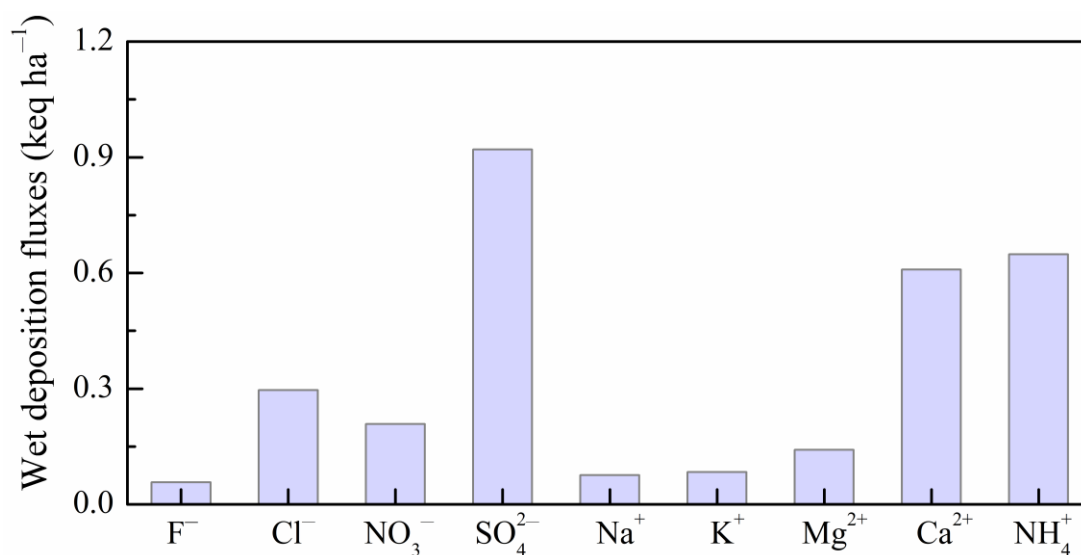


Figure 10. The annual rainwater ions deposition fluxes in the MNKFP.

4. Conclusions

In conclusion, a temporal rainwater investigation in a typical karst forest (MNKFP) was concluded to understand the variations of rainwater chemistry, sources of rainwater ions, trends in acidifying and neutralizing potentials, and environmental effects on the karst forest system. As expected, the rainwater ion composition significantly varied in the study period based on the analysis of temporal rainwater chemistry, and a reduced trend of time-based rainwater pH was also observed. In particular, the concentrations of NH₄⁺ and SO₄^{2−} ranged from 9.7 to 266.6 µeq L^{−1} and from 14.5 to 1396.4 µeq L^{−1}, respectively. NH₄⁺, Ca²⁺, SO₄^{2−}, and Cl[−] were the most dominant ions, with obvious monthly variations. Source variations and rainfall amounts were found to be the vital factors affecting rainwater ion concentration. Source identification indicated that Mg²⁺, Ca²⁺, K⁺, Cl[−], and Na⁺ were mainly controlled by natural sources, while anthropogenic inputs were the primary sources of F[−], NO₃[−], SO₄^{2−}, and NH₄⁺. The contributions were also described by a PMF model. A reducing neutralization trend of temporal rainwater was observed in the MNKFP. Given the potential effect of rainwater ion deposition on enzyme activity and microbial biomass, the decomposition of leaf litter, carbon and nitrogen loss, and carbonate rock weathering processes in a karst forest, more focus on rainfall-related ion deposition is needed.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4433/11/12/1315/s1>. [86–88] cited in supplementary.

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