Research Article

Chemical Characteristics of Precipitation in a Typical Urban Site of the Hinterland in Three Gorges Reservoir, China

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Major water-soluble ions were analyzed for two-year precipitation samples in Wanzhou, a typical urban site of the hinterland of Chinese Three Gorges Reservoir. The pH values of the precipitation were in the range of 4.0 to 8.3, and the volume-weighted mean (VWM) value was 5.0. The concentration order of anions and cations was as follows: $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{F}^-$ and $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$, respectively. Good correlations were found between SO_4^{2-} and NH_4^+ , SO_4^{2-} and Ca^{2+} , NO_3^- and NH_4^+ , and NO_3^- and Ca^{2+} , implying their co-occurrence in the precipitation, most likely as $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)\text{HSO}_4$, NH_4NO_3 , CaSO_4 , and $\text{Ca}(\text{NO}_3)_2$. The sum of all measured ions was $416.4 \mu\text{eq L}^{-1}$, indicating serious air pollution in Wanzhou. NH_4^+ and Ca^{2+} were the most important ions neutralizing the acidic compounds in the precipitation; their major sources included agricultural activity and crustal dust. Local anthropogenic activities, for example, coal burning and traffic related sources, contributed most of SO_4^{2-} and NO_3^- . The equivalent concentration ratio of $\text{SO}_4^{2-}/\text{NO}_3^-$ was 4.5, indicating that excessive emission of sulfur was the main reason leading to the precipitation acidity in Wanzhou. However, this ratio was lower than the ratio (5.9) in 2000s in Wanzhou, indicating that the contribution of nitric acid to the acidity of precipitation was strengthening.

1. Introduction

Precipitation is an important means of scavenging airborne pollutants, including in-cloud scavenging (rainout) and below-cloud scavenging (washout) [1]. With the accelerated urbanization and industrialization, excessive pollutants have emitted into the atmosphere in China, for example, nitrogen oxides (NO_x), sulfur dioxide (SO_2), and particulate matter (PM). These pollutants can dissolve in precipitation and then return to surface through wet deposition. Precipitation that contains a large amount of pollutants would cause a series of negative ecological effects on the surface ecosystem, for

example, soil acidification, eutrophication, and biodiversity reduction.

It has been observed that precipitation was contaminated worldwide because of the excessive emission of atmospheric pollutants. These pollutants can change the chemical characteristics of precipitation during the scavenging process depending on the solubility [2]. Chemical compositions of precipitation were influenced by the type of pollutant, meteorology, and topographic structure. Therefore, different regions have very different chemical composition in precipitation. Generally, Na^+ and Cl^- are abundant along coastal areas [3]; Ca^{2+} and Mg^{2+} are abundant in inland areas [4];

FIGURE 1: The sampling site in Wanzhou.

SO_4^{2-} and NO_3^- are abundant in industrial or urban areas [5, 6].

Because large amount of coal combustion increased the SO_2 concentration in the atmosphere over the past 30 years, China has become the largest acid rain region in the world [7]. Extensive acid rain was observed in the southern and southwest China in the 1990s, and it has extended to the eastern and central areas [5]. Northern China had a higher concentration of acidic ions in the precipitation than that in the south, but the pH of precipitation was almost higher than the threshold value of acid rain ($\text{pH} = 5.6$) in Northern China, because there were enough alkaline substances (e.g., alkaline particles and NH_3) which can neutralize the acidic components. It was estimated that the pH of precipitation would decrease by a factor of 1.85 pH units in the absence of alkaline neutralization in Northern China [8]. Acid precipitation would cause huge damage to environment, including acidification of soil and water, death of animals and plants, and weathering of buildings and artifacts [9]. The sum of economic loss resulting from acid deposition in China reached RMB 176.42 billion yuan in 2000 according to the evaluation from Chinese Research Institute of Environment [10].

Chongqing has been one of the most serious acid rain polluted regions in China since the late 1970s. Simian Mountain and Jinyun Mountain in Chongqing were believed to be relatively clean in the sense of air pollution, but the average pH values of precipitation in the two areas were 4.3 and 4.8 in 1991-1992, respectively [11]. As the stringent national air pollution regulations were established to decrease the emission of SO_2 , the SO_4^{2-} concentration in precipitation in Chongqing has been decreasing since 2007 [12]. However, the alleviation of the acid rain pollution was not so evident, likely due to the increase of NO_x emission [13].

Wanzhou is located in the northeastern Chongqing and is the biggest city in the hinterland of the Three Gorges

Reservoir Area (TGRA), being 327 kilometers away from downtown Chongqing and 283 kilometers away from Three Gorges Dam. In the light of the important and sensitive location in the Three Gorges Reservoir, two-year precipitation samples were collected in urban Wanzhou and the major ions were analyzed. The aim of this paper is to gain better understanding of precipitation chemistry in the hinterland of TGRA and to identify its major sources.

2. Experiments

2.1. Descriptions of Sampling Site. Wanzhou lies at the east of Sichuan Basin with a population about one million. The urban area of the city is basically built along the two mountainous banks of Yangtze River. Wanzhou has a subtropical monsoon wet climate with four distinct seasons. The average annual temperature is 18.6°C . In Wanzhou, there is a mild climate with an annual average precipitation amount of ~ 1200 mm, among which $\sim 70\%$ are concentrated in the period between May and September. Because of the topographic condition, Wanzhou is the region with the lowest wind speed in China, and the average wind speed is 0.81 m s^{-1} between 2014 and 2015 (automatic weather station's data at the sampling point).

Sampling of atmospheric precipitation was performed on the rooftop of a teaching building with nine floors in Chongqing Three Gorges University (Figure 1). This sampling site is surrounded by residential areas, and three kilometers away from the downtown Wanzhou and about 600 m away from Yangtze River. To the west of the sampling site, there is a hill with dense vegetation and a few cultivated lands. To the east, there is a major street road (about 100 m away). Next to the sampling site, a weather station (Lufft WS500-UMB, Germany) and atmospheric particle monitor (Thermo TEOM1405, USA) were equipped to obtain meteorological data and particle data, respectively, including wind speed and

direction, temperature, air pressure, relative humidity, total solar radiation, and mass concentrations of PM_{2.5} and PM₁₀.

2.2. Sample Collection and Analyses. The samples of precipitation were collected with a dry-wet deposition autosampler (APS-3A, Changsha Xianglan Scientific Instrument Co., Ltd.). There is a movable lid which can be stimulated by a wetness sensor to open the funnel of 300 mm in diameter for collection of precipitation during precipitation. Precipitation samples were collected on each rainy/snowy day between 9:00 a.m. and 9:00 a.m. the next day. After the samples were taken to the laboratory, 10 mL of each sample was taken to determine pH value (pHS-3C, Shanghai Leici Instrument Factory, China) and electrical conductivity (EC) value (sen-ION5, Hach, USA). Before each measurement, standard buffer and standard NaCl solution were used to calibrate the pH meter and conductivity meter. The remaining solution of samples was filtered with 0.45 μ m pore diameter membrane filter and then kept in 4°C for subsequent testing.

The anion components, including F⁻, Cl⁻, NO₃⁻, and SO₄²⁻, were analyzed by using ion chromatography (ICS-900, Dionex Company, USA), with an IonPac AS19-HC column, 25 mM NaOH eluent, and ASRS300 suppresser. The detection limits for these anions are 0.03 mg L⁻¹, 0.03 mg L⁻¹, 0.1 mg L⁻¹, and 0.1 mg L⁻¹, respectively. K⁺, Na⁺, Ca²⁺, and Mg²⁺ were analyzed by flame atomic absorption spectrophotometer. To eliminate spectral interference, cesium nitrate and lanthanum nitrate as deionizing agents were added to the potassium and sodium calibration solutions and the calcium and magnesium calibration solutions, respectively. The detection limits for K⁺, Na⁺, Ca²⁺, and Mg²⁺ were 0.013 mg L⁻¹, 0.008 mg L⁻¹, 0.02 mg L⁻¹, and 0.0025 mg L⁻¹, respectively. NH₄⁺ were analyzed by Spectrophotometry Method of Sodium Hypochlorite-Salicylic Acid in accordance with the national standard method of China (GB 13580.11-92). In this method, NH₄⁺ reacted with hypochlorite and salicylic acid to produce stable blue compound, whose absorbance was determined at the wavelength of 698 nm by using UV-visible spectrophotometer (T6, Purkinje General Instrument Co. Ltd., China). The lowest concentration detected by this method for NH₄⁺ was 0.01 mg L⁻¹. The recoveries for all ions detected here were in the range of 80%–120% and the relative standard deviation was less than 5% for reproducibility test. A total of 207 valid samples were analyzed. After statistical analyses described in Section 2.4, the monthly data included meteorological factors, PM_{2.5}, PM₁₀, precipitation amount, pH, anions, and cations, which are presented in the supplementary material (available here).

2.3. Quality Control and Assurance. In the process of ion analysis, Standard Reference Materials, produced by National Research Center for Certified Reference Materials, China, were routinely analyzed to guarantee the data quality. Six samples were removed because their data were outside the range of ($m - 3\delta$, $m + 3\delta$), which was often used to exclude outliers [22], and where m denotes averaged value; δ means standard deviation. The Pearson correlation between anions and cations was 0.97 ($p < 0.01$), suggesting credible data

quality. And the data were also considered acceptable because the ratio of total cations (H⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, and NH₄⁺) and total anions (F⁻, Cl⁻, NO₃⁻, and SO₄²⁻) is 1.05, which is within the range of 1 ± 0.25 [23].

2.4. Statistical Analysis. The volume-weighted mean (VWM) pH value was calculated by

$$\overline{\text{pH}} = -\log [\text{H}^+] = -\log \left[\frac{\sum_{j=1}^n 10^{-\text{pH}_j} \cdot Q_j}{\sum_{j=1}^n Q_j} \right], \quad (1)$$

where $\overline{\text{pH}}$ is the VWM pH value in a month/season/year, pH_j is the pH value of j th precipitation, and Q_j (mm) is the amount of j th precipitation. The ionic concentration of precipitation was calculated by

$$\overline{C}_i = \frac{\sum_{j=1}^n C_{ij} \cdot Q_j}{\sum_{j=1}^n Q_j}, \quad (2)$$

where $\overline{C}_i$ ($\mu\text{eq L}^{-1}$) is the VWM concentration of i th ion in a month/season/year and C_{ij} ($\mu\text{eq L}^{-1}$) is the concentration of i th ion in j th rainfall.

The non-sea salt (nss) values of any particular ion were calculated from the measured concentrations of the ions of interest using sodium ion as the reference element. This process was implemented under the assumption that all sodium is derived from marine sources [23]. The equation for the non-sea salt contribution can be written as

$$[\text{nss-X}]_i = [X_i] - [\text{Na}^+]_i \times \left[\frac{[X]}{[\text{Na}^+]} \right]_{\text{sea salt}}, \quad (3)$$

where $[\text{nss-X}]_i$ ($\mu\text{eq L}^{-1}$) is the concentration of nss concentration of species X in sample i , $[X_i]$ is the total measured concentration of chemical species X in sample i , $[\text{Na}^+]_i$ ($\mu\text{eq L}^{-1}$) is the concentration of Na⁺ in sample i , and $\{[X]/[\text{Na}^+]\}_{\text{sea salt}}$ is the ratio of these species as measured in seawater [23].

2.5. Back Trajectories and PSCF Analysis. Cluster analysis of backward air-mass trajectories and potential source contribution function (PSCF) analysis were performed using TrajStat software on the sample date during this study period [24]. The meteorological data used for the analysis were from the Global Data Assimilation System (GDAS) of National Centers for Environmental Prediction (NCEP). The 72-hour backward trajectories of the air parcels arriving at 00:00 UTC at 1200 m elevation above the ground level were clustered. The PSCF values corrected by a weight factor were then calculated using the mean concentration for three anthropogenic ions (SO₄²⁻, NH₄⁺, and NO₃⁻) [25]. The results were displayed as maps with each grid cell equal to 0.5° latitude by 0.5° longitude in size.

3. Results and Discussion

3.1. Precipitation Amount, EC, and pH Distribution. The annual precipitation amounts were 1189.2 mm and 1081.1 mm

FIGURE 2: (a) Monthly precipitation amount, VWM pH, and (b) pH frequency distribution of the precipitation in Wanzhou.

in 2014 and 2015, respectively. As shown in Figure 2(a), monthly mean precipitation amount varied markedly with a peak in the summer and about 70% of the precipitation occurred during the period from May to September. These results were consistent with the long-term average precipitation levels and seasonal variations in Wanzhou [26].

The EC values of single precipitation varied in the range of $3.4 \mu\text{S cm}^{-1}$ to $234.0 \mu\text{S cm}^{-1}$ with an average of $35.9 \mu\text{S cm}^{-1}$, which was larger by a factor of 2.5 than that ($14.6 \mu\text{S cm}^{-1}$) measured at the global atmospheric background site in Mt. Waliguan Mountain [27]. However, this value was comparable to those measured in many other cities, such as $42.2 \mu\text{S cm}^{-1}$ in Shenzhen [28] and $66.5 \mu\text{S cm}^{-1}$ in Beijing [6], indicating that anthropogenic impacts on the atmospheric environment in Wanzhou could not be neglected.

The pH values of a single precipitation sample ranged from 4.0 to 8.3 with a VWM value of 5.0, lower than the pH of typical natural rainwater (5.6). As for the frequency of acid precipitation (Figure 2(b)), there were 46.9% of precipitation with the pH lower than 5.6. Additionally, 26.1% of precipitations had pH lower than 5.0, and 11.6% were strongly acidic with pH lower than 4.5. It is worth noting that the arithmetic mean pH value of precipitation was 5.7 during the two-year study period, which was a little higher than the average (5.5) observed during the period of 2001–2009 [15]. This is an indication of the mitigation trend in acidification of precipitation in Wanzhou.

3.2. Chemical Composition of the Precipitation. Figure 3 presented the statistical results of ion concentrations and percentage share of each ion. The most abundant ions were SO_4^{2-} , Ca^{2+} , NH_4^+ , and NO_3^- . The average concentration of NH_4^+ together with Ca^{2+} reached $151.6 \mu\text{eq L}^{-1}$ and accounted for 68.4% of the total cations. The average concentration of SO_4^{2-} plus NO_3^- was $246.51 \mu\text{eq L}^{-1}$ which

occupied 91.3% of all anions. Among the precipitation components, SO_4^{2-} was the most abundant single ion, accounting for 36.3% of the total ions, followed in decreasing order by, NO_3^- , Cl^- , and F^- . For the cations, NH_4^+ and Ca^{2+} were followed in decreasing concentration by Na^+ , K^+ , H^+ , and Mg^{2+} . The total VMW concentration of the measured ions was $416.4 \mu\text{eq L}^{-1}$ in Wanzhou, indicating the serious air pollution in the hinterland of TGRA.

The sum of SO_4^{2-} , NO_3^- , and NH_4^+ , which were the main anthropogenic ions in precipitation, accounted for 71.4% of the total ionic equivalents, while H^+ accounted for 3.6%, demonstrating that anthropogenic sources predominated in the contributions to precipitation ions. Ca^{2+} and Mg^{2+} , regarded as two kinds of main crustal-related ions, occupied together 32.5% of total ionic equivalents, indicating that crustal-derived elements had key contribution to the neutralization of the acid precipitation. nss-SO_4^{2-} and nss-Ca^{2+} accounted for 96.1% and 98.5% of the total sulfate and total calcium, respectively. Thus, the impact of sea salt on the wet deposition in Wanzhou was negligible.

The equivalent ratio of $([\text{Ca}^{2+}] + [\text{NH}_4^+])/([\text{SO}_4^{2-}] + [\text{NO}_3^-])$ was further used to evaluate the degree of influence by the anthropogenic activities. The ratio of $([\text{Ca}^{2+}] + [\text{NH}_4^+])/([\text{SO}_4^{2-}] + [\text{NO}_3^-])$ in the precipitation in this study reached 0.79, which conformed with the ratio (0.80) in the period between 2001 and 2009 in Wanzhou [15]. It is noted that this ratio was lower than that measured in Lin'an (0.97), Longfengshan (1.27), and Shangdianzi (0.96), three regional background atmospheric stations of World Meteorological Organization (WMO) in Yangtze River Delta, Northeast China, and North China, respectively [29]. This comparison reflected that there was more influence from anthropogenic activities on the precipitation in Wanzhou.

As compared in Table 1, the concentration levels of the ions associated with human activities (SO_4^{2-} , NO_3^- ,

TABLE 1: VWM concentrations of major inorganic ions in the precipitation in Wanzhou and some selected areas (unit: $\mu\text{eq L}^{-1}$).

Areas	Periods	pH	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	Ca ²⁺	Na ⁺	K ⁺	Mg ²⁺	SO ₄ ²⁻ /NO ₃ ⁻	References
Wazhou	2014–2015	5.0	3.2	15.1	35.1	156.9	89.6	62.1	24.4	20.1	9.9	4.5	This study
Zigui	2009	4.9	ND ^b	11.8	63.2	177.2	90.6	142.6	11.7	7.5	18.3	2.8	[14]
Wanzhou	2001–2009	5.5 ^a	8.4	25.3	43.7	258.3	126.6	114.4	27.0	12.7	29.2	5.9	[15]
Okinawa, Japan	2003–2005	4.9	ND ^b	351	7.0	53.9	9.5	25.2	308	9.4	63.9	7.7	[16]
New Jersey, USA	2006–2007	4.6	1.1	10.7	14.3	19.0	24.4	3.0	10.9	1.3	1.6	1.3	[17]
Delhi, India	2011–2013	6.4	10.7	42.9	50.5	91.6	23.7	198.6	26.8	5.3	69.2	1.8	[4]
Beijing	2001–2005	6.0	15.4	34.9	106.0	314.0	236.0	209.0	22.5	13.8	48.4	3.0	[6]
Guiyang	2008–2009	4.2	14.5	20.7	7.3	265.6	112.8	182.9	13.9	9.6	10.5	36.4	[5]
Guangzhou	2005–2006	4.5	12.0	21.0	51.8	202	66.2	131.0	18.0	9.0	9.0	3.9	[18]
Lijiang	1989–2006	6.1	ND ^b	11.6	3.6	32.6	11.4	50.2	2.5	ND ^b	7.7	9.1	[19]
Shenzhen	1986–2006	5.0	4.5	37.9	22.1	74.3	35.2	77.7	40.3	7.2	9.7	3.4	[20]
Chengdu	2008	5.1	6.2	8.9	156.2	212.8	150.5	196.6	1.4	6.6	16.2	1.4	[21]

^aArithmetic mean value; ^bnot determined.

FIGURE 3: (a) Statistics of ions' concentration and (b) percentages of ions' VWM concentration ($\mu\text{eq L}^{-1}$) in the precipitation in Wanzhou. The box plots indicate the minimum, 10th and 25th percentiles, median, 75th and 90th percentiles, maximum, and average (square) of each ion.

and NH₄⁺) in Wanzhou were lower than those in Beijing, Guiyang, Guangzhou, but significantly higher than those reported in Japan, India, and North America. In the case of the soil derived calcium, Wanzhou had much lower values than Beijing, Guiyang, Guangzhou, and Chengdu. In comparison with Zigui, which is located in the head region of TGRA, the concentrations of SO₄²⁻ and NH₄⁺ were very similar in the two areas, whereas NO₃⁻ presented much low concentration in Wanzhou. It is noted that K⁺ concentration was much higher in this study compared to other areas and the historical value, likely due to enhanced biomass burning in the immediate vicinity of the site.

Compared to the period from 2001 to 2009, all the ions except K⁺ in this study exhibited decreasing trends. This was likely attributed to the implementation of industrial restructuring and emission reduction policies by local government. A typical example was that the emission amount of sulfur

dioxide had been decreased from 26,400 t in 2008 to 17,388 t in 2015 [30], about one-third reduction within seven years.

3.3. Temporal Variations of pH and Major Ionic Concentration. Figure 4 showed the seasonal variations of the EC, pH, and precipitation amount in Wanzhou. In winter, the pH was 4.9 and the precipitation amount was 12.8 mm; both were the lowest, while the EC was the highest with the value of 55.9 $\mu\text{S cm}^{-1}$. By contrast, the lowest EC and highest precipitation amount occurred in summer and were 18.5 $\mu\text{S cm}^{-1}$ and 161.1 mm, respectively. This indicated that the dilution effect played an important role in determining analyte concentrations in the precipitation. The seasonal variation of pH was significant in the following order with a decrease trend: spring > summer > autumn > winter. The enhanced fugitive dust, which contained many alkaline substances because of the windy weather, and local farming

FIGURE 4: Seasonal variations of the two-year average EC, pH, and precipitation amount in Wanzhou.

might be responsible for the highest precipitation pH in spring.

Figure 5 showed the monthly and seasonal variations in VWM concentration of ions in the precipitation in Wanzhou; both monthly and seasonal concentrations of each ion were subject to large variability. Both higher loadings of crustal-related and anthropogenic ions usually appeared during the dry months from November to April, while lower loadings appeared in rainy months. This variation of ionic concentration might be related to the seasonal distribution of air-mass origins, precipitation intensity, and emissions of pollutants. In the dry months, enhanced coal combustion caused the anthropogenic emissions of gaseous pollutants and particles. Taking SO_4^{2-} as an example, the seasonal variation was completely consistent with the variation of its gaseous precursor, SO_2 [31]. Additionally, atmospheric particles might play an important role in contribution of ions in

precipitation, since the sum of monthly ionic concentrations was well correlated ($r = 0.59$, $p < 0.01$) with the PM_{10} concentration in Wanzhou. Furthermore, the plentiful rains during rainy periods enhanced dilution effect of precipitation on ionic mass, as indicated by the negative correlations with precipitation volume (correlation coefficient $r = -0.15$ to -0.37).

3.4. Acid Neutralization and the Form of Acidity. The neutralization between the acidic components and basic components determines the pH value of the precipitation. Balasubramanian et al. presented an equation for calculation of fractional acidity ($\text{FA} = [\text{H}^+]/([\text{SO}_4^{2-}] + [\text{NO}_3^-])$) in precipitation [32]. On the other hand, neutralization factor (NF) was widely used to evaluate the acid neutralization efficiency by alkaline ions in precipitation: $\text{NF}_{X_i} = [\text{X}_i]/([\text{SO}_4^{2-}] + [\text{NO}_3^-])$, where X_i is the chemical component of interest and all of the ion concentrations are expressed in $\mu\text{eq L}^{-1}$ [8, 33]. In Wanzhou, the FA value was 7.3%, which means 92.7% of the acidity had been neutralized. The NF values for NH_4^+ , Ca^{2+} , Na^+ , K^+ , and Mg^{2+} during the 2-year period were 0.46, 0.32, 0.13, 0.11, and 0.05, respectively, revealing that NH_4^+ and Ca^{2+} were the major basic ions for the neutralization of the acidity. Nevertheless, the neutralization effect of NH_4^+ and Ca^{2+} in precipitation in Wanzhou was much lower than that in Northern China, where the NF values accounted for 0.71 and 0.72, respectively [8].

In this paper, the equivalent ratio of $[\text{SO}_4^{2-}]/[\text{NO}_3^-]$ was utilized to assess relative contributions of SO_4^{2-} and NO_3^- in the acidity of precipitation. As shown in Table 1, the $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio (4.5) in this study was much higher than those in all other Chinese cities except Guiyang, which is the capital city of Guizhou province suffering serious acid rain since late 1970s. This suggested that the precipitation acidity in Wanzhou was dominantly from excessive emission of sulfur. On the other hand, the ratio was lower than that determined during 2001–2009 in Wanzhou [15], indicating the relatively reinforced contribution of nitric acid to precipitation acidity.

3.5. Air-Mass Back Trajectories and PSCF Analysis.

Figure 6(a) showed the five air-mass clustering trajectories arriving at the sampling site and Table 2 showed the VWM concentrations of NH_4^+ , SO_4^{2-} , and NO_3^- of each cluster. It can be seen that all air masses converged to southern Wanzhou and finally entered Wanzhou. Cluster 1 and cluster 2, two short-distance transport trajectories, were the most important air-mass trajectories, which accounted for 39.8% and 35.7% of all the trajectories, respectively. The concentrations of NH_4^+ , SO_4^{2-} , and NO_3^- in cluster 1 and cluster 2 were lower than that in cluster 3, cluster 4, and cluster 5. The trajectories in cluster 3, moving from the Yunnan Province to Wanzhou via Guizhou province, represented for 11.2% of air masses, and the precipitation in this cluster contained moderate concentrations of NH_4^+ , SO_4^{2-} , and NO_3^- .

Precipitation in cluster 4 and cluster 5 occurred mainly in winter and spring, respectively. The trajectories accounted

TABLE 2: VWM concentrations of NH_4^+ , SO_4^{2-} , and NO_3^- in precipitation for the six trajectory clusters during 2014-2015 in Wanzhou (unit: $\mu\text{eq L}^{-1}$).

Cluster	NH_4^+	SO_4^{2-}	NO_3^-
(1) 39.8%	85.29	134.19	24.65
(2) 35.7%	83.37	118.81	25.98
(3) 11.2%	92.97	145.66	29.19
(4) 9.2%	97.62	206.74	56.51
(5) 4.1%	90.34	184.53	40.63

FIGURE 5: (a) Monthly variations and (b) seasonal variations in the VWM concentration of ions in the precipitation in Wanzhou.

for only 9.2% and 4.1% of the total trajectories, respectively, while the cluster-mean concentrations of NH_4^+ , SO_4^{2-} , and NO_3^- were the highest in the five clusters. This could have been due to the low precipitation amount and to the traversal of the clusters through high-emission areas. For example, cluster 4 and cluster 5 passed over Chongqing city and Xi'an city, respectively, both of which suffered severe air pollution [34, 35]. The potential source contribution areas of SO_4^{2-} , NH_4^+ , and NO_3^- were shown in Figures 6(b)–6(d). SO_4^{2-} , NH_4^+ , and NO_3^- possessed similar potential areas of source contribution. These areas were predominately concentrated on the southeast of Wanzhou, the junction region of Chongqing, Hubei province, and Hunan province. In addition, the areas in the northeast of Wanzhou had some contributions as well. Therefore, it can be concluded that the anthropogenic ions in the precipitation in Wanzhou were mostly from local sources and surrounding areas. In winter and spring, however, there was a small amount of pollutants input into Wanzhou through long distance.

3.6. Factor Analysis of Ions in Precipitation. Varimax-rotated factor analysis was utilized for the investigation of the major

sources of chemical species in the precipitation (Table 3). Three factors were identified with the cumulative variance more than 85%. And the communalities of all the ions are no less than 0.60, indicating that these extracted factors are reasonable. There was a strong correlation between Mg^{2+} , Ca^{2+} , and Na^+ with factor 1 accounting for 34% of the total variance, pointing to the common occurrence of these ions from crustal origin. Additionally, factor 1 had a moderate relation with SO_4^{2-} , NO_3^- , and F^- , implying that this factor was also likely associated with certain anthropogenic sources, such as industrial emissions, fossil fuel combustion, and fugitive dust. Factor 2 accounted for 31% of the total variance with high loadings for SO_4^{2-} , NO_3^- , NH_4^+ , and F^- , suggestive of the secondary pollution formed from their precursors in the atmosphere. The correlation coefficients were significant in statistics ($p < 0.01$) between the following ions: SO_4^{2-} and NH_4^+ (0.68), SO_4^{2-} and Ca^{2+} (0.59), NO_3^- and NH_4^+ (0.53), and NO_3^- and Ca^{2+} (0.70). Therefore, these ions in the precipitation mainly existed as the compounds of CaSO_4 , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)\text{HSO}_4$, NH_4NO_3 , and $\text{Ca}(\text{NO}_3)_2$. Therefore, SO_4^{2-} and NO_3^- were always in neutralized forms [36]. In addition, factor 3 was indicated by high loading

FIGURE 6: Cluster analysis (a) and potential source areas for SO_4^{2-} (b), NH_4^+ (c) and NO_3^- (d) in Wanzhou.

for Cl^- and K^+ , implying the sources of biomass burning [37].

4. Conclusions

The chemical compositions of daily precipitation in Wanzhou, a typical urban area located in the hinterland of the TGRA, were investigated during the period of January 2014 to December 2015. The main findings can be summarized as follows:

(1) The pH of two-year precipitation samples in Wanzhou ranged from 4.0 to 8.3 with a volume-weighted mean (VWM) value of 5.0. About 46.9% of the precipitation samples had a pH lower than 5.6 and 26.1% samples had a pH lower than 5.0, and 11.6% of precipitation was strong in acidity with the

pH below 4.5. EC ranged from 3.4 to $234.0 \mu\text{S cm}^{-1}$, with the VWM value of $35.9 \mu\text{S cm}^{-1}$.

(2) SO_4^{2-} was the most abundant ion with the VWM concentration of $156.9 \mu\text{eq L}^{-1}$, accounting for 74.6% of total anions, followed in decreasing order by NO_3^- , Cl^- , and F^- . The precipitation acidity was predominantly neutralized by NH_4^+ and Ca^{2+} , whose sum contributed 68.4% to the total cations. There were good relations between the following pairs of ions: SO_4^{2-} and NH_4^+ , SO_4^{2-} and Ca^{2+} , NO_3^- and NH_4^+ , and NO_3^- and Ca^{2+} , indicating their coexistence in precipitation, mostly as $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)\text{HSO}_4$, CaSO_4 , NH_4NO_3 , and $\text{Ca}(\text{NO}_3)_2$.

(3) Long-distance inputs of air pollutants were less in Wanzhou. NH_4^+ and Ca^{2+} were mainly originated from local

TABLE 3: Varimax-rotated principal factor analysis of ions in the precipitation of Wanzhou.

Variable	Factor 1	Factor 2	Factor 3	Communality
Cl ⁻	0.08	0.15	0.89	0.83
K ⁺	0.15	-0.01	0.92	0.87
Mg ²⁺	0.95	0.15	0.29	0.94
Na ⁺	0.54	0.44	0.37	0.72
NH ₄ ⁺	-0.01	0.91	0.07	0.84
SO ₄ ²⁻	0.45	0.81	0.06	0.86
NO ₃ ⁻	0.59	0.65	0.16	0.80
Ca ²⁺	0.92	0.26	0.13	0.93
F ⁻	0.47	0.72	0.07	0.74
Variance (%)	33.6	31.3	20.5	
Cumulative (%)	33.6	64.9	85.4	

agricultural activities and crust fraction, respectively. Cl⁻ and K⁺ were mainly derived from the biomass burning near the sampling site. SO₄²⁻ and NO₃⁻ were primarily associated with local anthropogenic activities, such as coal burning and traffic emissions.

(4) The levels of ionic concentrations in precipitation in Wanzhou were similar to that in the head region of the TGRA. However, most ion concentrations were lower than that in 2000s, revealing the improvement of the air pollution in Wanzhou.

Conflicts of Interest

The authors declare no conflicts of interest.

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Supplementary Materials

Table S1: monthly data of ionic concentration of precipitation, mass concentration of particulate matter, and meteorological factors in Wanzhou. (*Supplementary Materials*)

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