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Chemical and sulfur isotopic characteristics of precipitation in a representative urban site, South China: implication for anthropogenic influences

Fangwen Zheng[1,2] · Wenbo Rao[1] · Xiaodong Chu[3] · Hua Bai[2] · Sanyuan Jiang[4]

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Abstract

Nanchang, the capital of Jiangxi Province, is a major constituent of the South China Acid Rain Zone. In this study, the chemical and sulfur isotopic compositions of precipitation in this region were investigated during 2015–2016 to clarify the origin of major chemicals. The pH was < 5.6 for 72.6% of precipitation events, reflecting the predominance of acid rain. SO_4^{2-}, Ca^{2+}, NH_4^+, and NO_3^- were the four main ions, occupying 77% of the total ions in precipitation. SO_4^{2-} and NO_3^- were the dominant acidifying species while Ca^{2+} and NH_4^+ were the dominant neutralizing species. Overall, the concentrations of ions in precipitation were lower in the rainy months than in other months. Compared with foreign cities, the concentrations of ions in precipitation, particularly SO_4^{2-} and NO_3^-, were significantly higher in Nanchang, indicating the effect of anthropogenic pollution. Factor analyses showed that in precipitation, anthropogenic pollutants controlled SO_4^{2-}, NO_3^-, and NH_4^+ whereas K^+, Mg^{2+}, and Ca^{2+} originated from rock weathering, and Cl^- was dominantly of marine origin. Based on the sulfur isotope data, it was further found that precipitation SO_4^{2-} was associated with the use of northern Chinese coal in Nanchang and homogeneous oxidation was a major mechanism affecting $\delta^{34}S$ fluctuations in precipitation SO_4^{2-} with time. This work provides deep insights into the formation of acid rain and is helpful for guiding air quality protection in South China.

Keywords Major ions · Sulfur isotopic composition · Precipitation · Source identification · Acid rain

Introduction

With rapid economic growth and massive emissions of pollutants, acid rain has been a major environmental problem in China since the late 1980s (Kuribayashi et al. 2012). It was reported that precipitation pH values were < 4.5 for more than half of the cities of South China and less than 7 in many cities of northern China (Wu and Han 2015; Wu et al. 2016). Sulfur dioxide (SO_2), which can be converted into sulfate (SO_4^{2-}) dissolved in precipitation, is an important precursor of acid rain, originating from fossil fuel combustion, industrial emissions, and biomass burning (Yu et al. 2016). SO_2 emissions in China have had a significantly increasing trend since 1980, reaching over 33 million tons in 2006 (Duan et al. 2016). To prevent acid pollution, the Chinese government has made great efforts in energy structure changes, energy savings, and emission reductions since the mid-1990s. As a result, SO_2 emissions started to decrease in 2006 but still remained at historically higher levels (Kurokawa et al. 2013). Therefore, the provenance, transport, and deposition of air pollutants associated with acid rain are still topics of concern in China (Gu et al. 2014; Niu et al. 2017).

Precipitation constitutes a natural pathway for removing atmospheric pollutants and captures soluble components from gases and particles in the atmosphere (Lynam et al. 2014; Sinha et al. 2008; Han et al. 2019). Dissolved ions in precipitation are usually of natural or anthropogenic origin. For example, Ca^{2+} and Mg^{2+} are considered to be derived from soil dust while SO_4^{2-} and NO_3^- are produced by human activities

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✉ Wenbo Rao
raowenbo@163.com

[1] College of Earth Sciences and Engineering, Hohai University, Nanjing 210098, China

[2] Nanchang Institute of Technology, Nanchang 330099, China

[3] Jiangxi Institute of Geo-Environment Monitoring, Nanchang 330095, China

[4] Nanjing Institute of Geography and Limnology, CAS, Nanjing 210008, China

such as coal combustion and vehicle exhaust (Ciężka et al. 2016). Therefore, precipitation chemistry can help us understand the cycles of air pollutants. Moreover, it is fundamental for assessing air quality. Sulfate (SO_4^{2-}) is a dominant acidic component in acid rain and usually has different sources with different $\delta^{34}S$ values (Novák et al. 2001; Mukai et al. 2001; Norman et al. 2004). Furthermore, sulfur isotope fractionation occurs during atmospheric oxidation of SO_2 to SO_4^{2-} (Harris et al. 2013). Therefore, the use of sulfur isotopes can provide information on the provenance and formation of sulfate in precipitation. Precipitation chemistry with sulfur isotopes has been widely used to trace the provenance, transport, and deposition of air pollutants in the world, including China (Sinha et al. 2008; Wu and Han 2015; Górka et al. 2017; Han et al. 2019). Nevertheless, sulfur isotopic and chemical investigations of precipitation are still incipient in China, considering its large area affected by acid rain.

Nanchang, the capital of Jiangxi Province, lies in the South China Acid Rain Zone (Duan et al. 2016). Chemical and isotopic studies on air pollutants dissolved in precipitation in Nanchang are limited (Xiao et al. 2011). In this study, precipitation samples were collected during 2015–2016 in Nanchang to (1) ascertain the chemical and sulfur isotopic characteristics of precipitation, (2) determine the origin of major chemicals and (3) explore sulfur isotopes as tracers of dissolved sulfates.

Study area

Nanchang, with a population of approximately 7 million residents, is located to the southwest of Lake Poyang (Fig. 1). It is subtropically wet and mild, with a mean annual temperature and precipitation of 18 °C and 1600 mm, respectively, in Nanchang, according to meteorological data (http://www.weather.com.cn/). It usually rains from April to July. The dominant wind is southerly in summer and northerly in winter. The urban land area, local population, fertilizer use, coal consumption, and industrial GDP increased by 2.3 times, 17%, 12%, 200% , and 760%, respectively from 2005 to 2015 in Nanchang according to statistical data (http://tjj.jiangxi.gov.cn).

Samples and methods

Sampling and pretreatment

Precipitation samples were collected on the roof of a teaching building at the Nanchang Institute of Technology during Nov. 2015 and Oct. 2016. Prior to use, the sampler was cleaned with 2 N HCl solution and 18.2 MΩ·cm Milli-Q water. Between rain events, the sampler was closed to avoid dry deposition. In total, 95 samples were taken for chemical analysis. Of these, 71 samples were enough for sulfur isotope analysis. All samples were filtered through a 0.45-μm Millipore membrane. The filtrate was separated into three aliquots for each sample: one was directly used for anion measurement, one was acidified to $pH < 2$ with 2 N HCl solution for cation measurement, and the remaining aliquot was acidified to $pH < 2$ for sulfur isotopic analysis after it was poisoned with $HgCl_2$ solution to inhibit microbial activities. The third aliquot was further treated to obtain purified $BaSO_4$ powder samples for $\delta^{34}S$ determination according to the method of Xiao et al. (2011).

Chemical and sulfur isotopic analyses

The pH and Ec (electrical conductivity) values were measured in situ by a digital pH meter (PHJS-4A, Jisi, China) with an error of 0.01 and a digital conductivity meter (DDS-IIA, Xiangtian, China) with an error of 1 μS/cm, respectively. Major cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) were measured by inductively coupled plasma atomic emission spectroscopy (ICP 6300, Thermo, USA). Major anions (F^-, $C1^-$, NO_3^-, SO_4^{2-}) were measured by using ion chromatography (ICS-2100, Dionex, USA). Reagent and procedural blanks were analyzed in parallel with sample treatments using identical procedures. The analytical precision was better than ± 3%. The NH_4^+ concentration was determined by using the Nessler colorimetric-spectrophotometric method with an analytical precision of better than ± 5%. The H^+ concentration was calculated using the equation, $H^+ = 10^{pH}$ (μeq/L).

Sulfate $\delta^{34}S$ analysis was performed on an EA-IRMS (EA3000, IsoPrime, Germany) mass spectrometer at the Institute of Geochemistry, Chinese Academy of Sciences. The analytical procedure was described in detail by Grassineau et al. (2001). The $\delta^{34}S$ data were reported on the VCDT scale after normalization using three international standards (IAEA-SO5, IAEA-SO6 and NBS127). The standard deviation for $\delta^{34}S$ determination was below 0.2‰ ($n = 10$, one sigma). The sulfur isotopic composition was calculated as follows:

$$\delta^{34}\,S(‰) = \left(^{34}\,S/^{32}S\right)_x / \left(\left(^{34}\,S/^{32}S\right)_{VCDT} - 1\right) \times 1000,$$

where x and VCDT stand for samples and Vienna Canyon Diablo Troilite (standard material), respectively.

Statistical treatment and backward trajectory analysis

The volume-weighted mean (VWM) values of the species (pH, ions and $\delta^{34}S$) were calculated by the formula: $X_{VWM} = (X_1\ P_1 + X_2\ P_2 + \ldots + X_i\ P_i)/(P_1 + P_2 + \ldots P_i)$, where

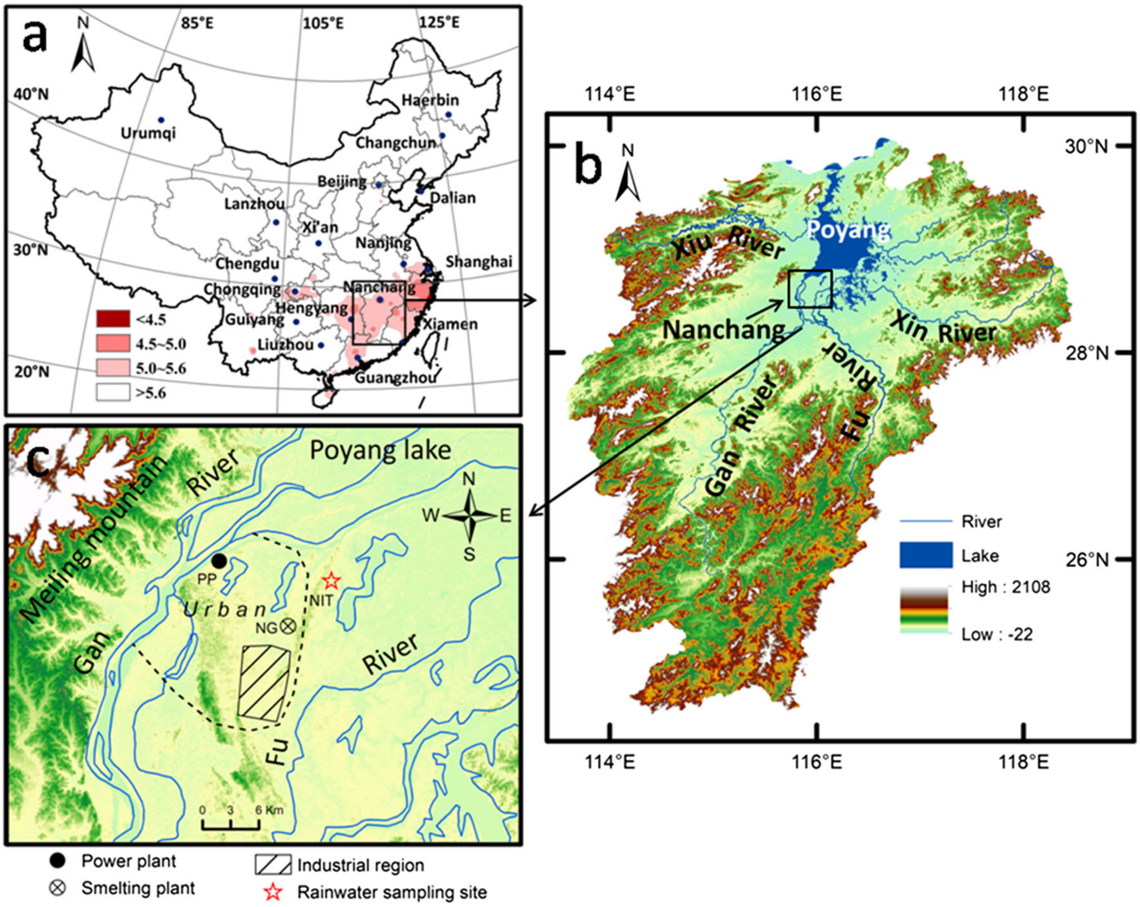


Fig. 1 Map showing **a** the pH distribution during 2016 in China, **b** the area of Jiangxi Province, and **c** the Nanchang region and the sampling point. The pH data were from China National Environmental Monitoring Center (http://www.cnemc.cn/)

P_i is the precipitation amount corresponding to the ith sample and X_i is the concentration of the species in the ith sample.

The HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model devised by the NOAA Air Resources Laboratory (https://ready.arl.noaa.gov/HYSPLIT.php) was used to calculate each backward trajectory of air masses during precipitation events for a 72-h duration with a final level of 1000 m above ground level. The percent frequency of wind was calculated by $\left(\sum_{i=1}^{n} W_i\right)/W_t$, where W_i means the ith occurrence of wind in a given area and W_t is the total occurrences of wind in all areas during a given season. The amount (percentage) of precipitation was determined by $\left(\sum_{i=1}^{n} P_i\right)/P_t$, where P_i means the ith precipitation amount in a given area and P_t is the total precipitation in all areas during a given season. The SO_4^{2-} concentration or $\delta^{34}S$ was described by $\left(\sum_{i=1}^{n} X_i \times P_i\right)/P_t$, where X_i and P_i are the SO_4^{2-} concentration ($\delta^{34}S$) and amount of the ith precipitation measurement, respectively, in a given area.

Results and discussion

pH, Ec, and ionic composition of precipitation

The pH values of precipitation samples collected during 2015–2016 in Nanchang ranged from 3.6 to 7.0 with a VWM value of 5.1 (Table 1), and the values were lower and higher than 5.6 for 72.6% and 27.4% of the samples, respectively (Table S1). Samples with pH values below 5.6 reflect the impact of anthropogenic pollution, whereas samples with pH values above 5.6 indicate the addition of alkaline species (Charlson and Rodhe 1982). Overall, precipitation pH values were lower in the rainy months than in the other months (Fig. 2). The VWM pH value of precipitation in Nanchang approximated those reported for Chengdu and Nanjing, and was higher than those in other large cities of South China but lower than those in cities of North China (Table S2). Compared with overseas monitoring data, the precipitation pH value in Nanchang was higher than those in New York and Tokyo, close to that in Belgium but lower than those in other cities (Table S2). The Ec values of precipitation samples

Table 1 The statistical results of various species ($\mu eq \cdot l^{-1}$) in precipitation samples from Nanchang during 2015–2016

Species	Number	Min	Max	Median	Mean	VWM [a]	S.D.
pH	95	3.64	7.02	5.02	5.16	5.12	0.74
H^+	95	0.1	229.1	9.55	20.63	18.81	35.44
F^-	95	0	33.79	1.68	4.53	1.64	6.79
Cl^-	95	3.3	280.0	19.15	23.62	15.90	30.24
SO_4^{2-}	95	15.69	645.6	87.08	124.2	67.65	110.5
NO_3^-	95	2.11	257.4	38.23	63.46	30.94	58.21
Ca^{2+}	95	8.35	1015	56.00	115.9	47.93	160.5
K^+	95	0.16	21.63	2.63	3.90	1.80	3.86
Mg^{2+}	95	0.93	66.64	8.36	12.00	6.72	11.37
Na^+	95	0	42.39	11.26	13.04	10.11	9.73
NH_4^+	95	8.44	336.7	46.56	61.88	37.17	49.19
TZ^+ [b]	95	35.21	1448	151.7	227.4	122.5	212.0
TZ^- [c]	95	32.73	1201	151.1	215.8	116.3	190.7
Total ions	95	69.07	2649	297.7	443.3	238.7	401.2
Ec ($\mu S \cdot cm^{-1}$)	95	3.0	86.0	17	24.82	15.59	19.28
$\delta^{34}S$(‰)	71	− 1.0	4.52	2.47	2.43	2.60	1.24

[a] The volume-weighted mean value. [B] The sum of ($Ca^{2+} + Mg^{2+} + K^+ + Na^+ + NH_4^+ + H^+$). [c] The sum of ($F^- + SO_4^{2-} + Cl^- + NO_3^-$)

ranged from 3 to 86 $\mu S\ cm^{-1}$ with a VWM of 16 $\mu S\ cm^{-1}$, and only approximately 16% of the values were greater than 50 $\mu S\ cm^{-1}$ during 2015–2016 in Nanchang (Table 1). The Ec value of precipitation in Nanchang was roughly similar to those in cities of South China but lower than those in cities of North China (Han et al. 2010; Wu et al. 2016; Niu et al. 2017).

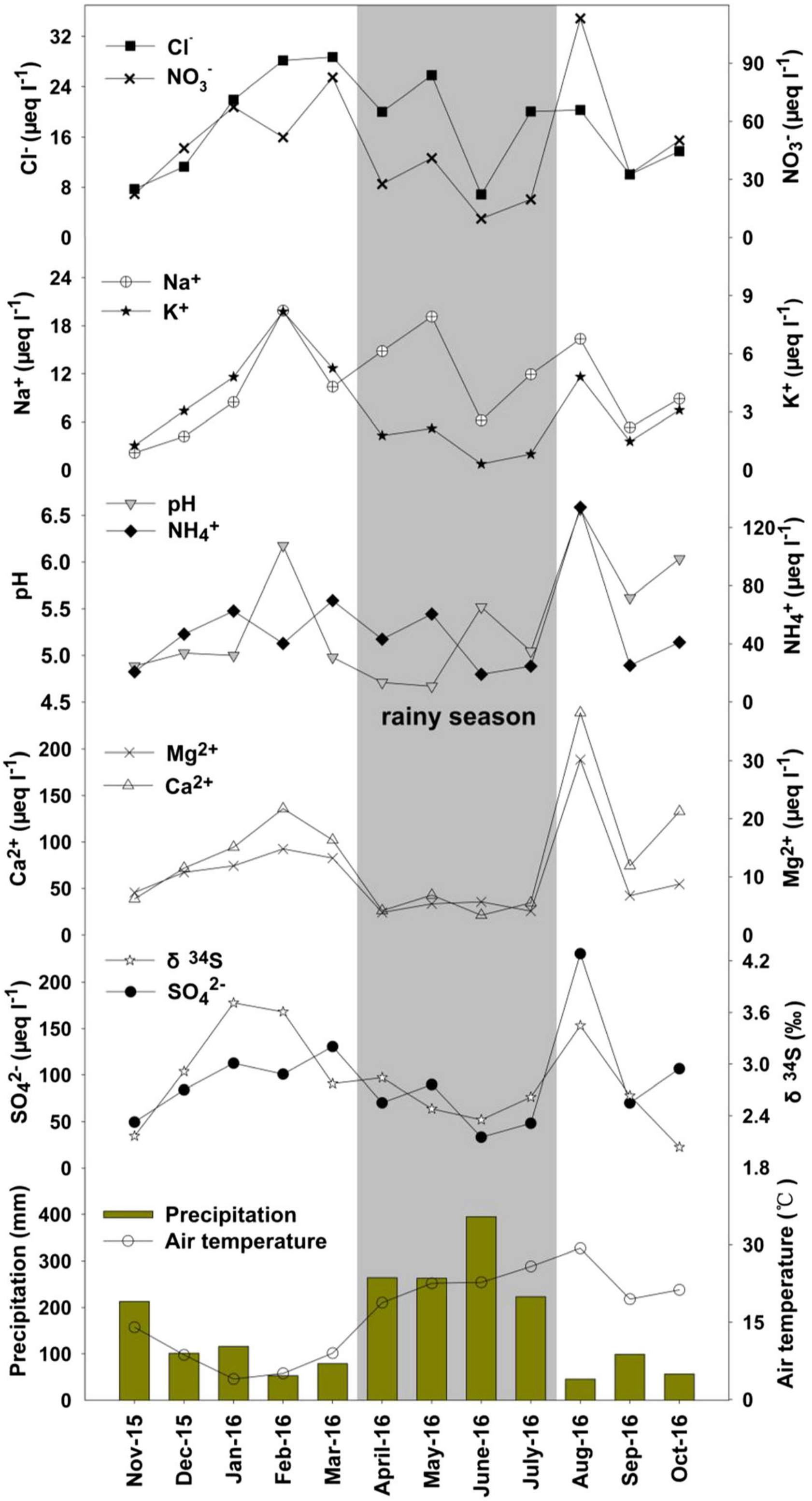
The total cation concentrations (TZ^+) varied from 35 to 1448 $\mu eq\ l^{-1}$, and the total anion concentrations (TZ^-) varied from 32.7 to 1201 $\mu eq\ l^{-1}$ (Table 1). The mean equivalent ratio of TZ^-/TZ^+ was 0.95. The small imbalance between cations and anions was attributed to unmeasured anionic species such as bicarbonate, acetate, and formate. On average, the concentrations of measured ionic species in precipitation decreased in the order of $SO_4^{2-} > Ca^{2+} > NH_4^+ > NO_3^- > H^+ > Cl^- > Na^+ > Mg^{2+} > K^+ > F^-$ (Table 1). The former four ions were the dominant constituents, accounting for 77% of the total ions in precipitation (Fig. S1). NO_3^- and SO_4^{2-} explained 84.9% of the total anions and were thus the main acidifying factors while Ca^{2+} and NH_4^+ comprised 69.43% of the total cations and were thus the main neutralizing factors (Fig. S1). The VWM values of chemical species in precipitation were lower than the arithmetic mean values, implying links between low ion concentrations and high precipitation. In addition to pH, the concentrations of ions such as SO_4^{2-}, NO_3^-, Ca^{2+}, and NH_4^+ were lower in the rainy months than in the other months (Fig. 2). Among cities in China, the precipitation of Nanchang was moderate in terms of ion concentrations (Table S2). The SO_4^{2-}, NO_3^-, Ca^{2+}, and NH_4^+ concentrations of precipitation in Nanchang were higher than those in Maolan, which is located in the acid rain zone of China (Table S2). The ion concentrations of Nanchang precipitation, especially SO_4^{2-} and NO_3^-, were also significantly higher than those of some megacities in Europe and America (Table S2). These results show that the precipitation chemistry of Nanchang was affected to a large degree by anthropogenic pollution.

Origin of major ions in precipitation

Based on factor analyses with varimax rotation of standardized component loadings, three major factors with eigenvalues > 0.9 were extracted for the precipitation chemistry of Nanchang and accounted for 77.7% of the total variance (Table 2).

Factor 1 was characterized by high positive loadings for major anions (SO_4^{2-} and NO_3^-) and major cations (Ca^{2+}, Mg^{2+}, K^+, and NH_4^+) and a negative loading for precipitation amount (Table 3). There were positive correlations between SO_4^{2-}, NO_3^-, and NH_4^+ (Table 3). Furthermore, SO_4^{2-} and NO_3^-, which are usually considered to be two sensitive indicators of anthropogenic pollution (Ciężka et al. 2016), were remarkably enriched in precipitation relative to marine and crustal sources (Table S3). In addition, NH_4^+ in precipitation has been ascribed to biomass burning, fertilizer usage, and human excrement (Ciężka et al. 2016). Therefore, the high loadings for SO_4^{2-}, NO_3^-, and NH_4^+ implied the predominance of acid and alkaline pollutants from anthropogenic sources. Ca^{2+}, Mg^{2+}, and K^+ were positively correlated with one another and were concentrated in precipitation compared with seawater values (Table 3 and Table S3). Ca^{2+} and Mg^{2+} result from silicate weathering and are also enriched in carbonate dust (Han et al. 2019). K^+ could be sourced partly from

Fig. 2 The variations of various species in monthly precipitation in Nanchang during 2015–2016



biological burning because it was correlated with NH_4^+ (Table 3). However, K^+ in precipitation was mainly related to the weathering of silicates in soil dust since sylvites are scarce in Nanchang. Therefore, the high loadings of K^+, Ca^{2+}, and Mg^{2+} were associated with crustal sources. Factor 1 revealed two aspects: (1) crust-sourced dust and anthropogenic particulates were jointly carried into the atmosphere by wind, which was supported by positive correlations of major anions with major cations (Table 3), and (2) there was a dilution effect of precipitation on ion concentrations because

Table 2 Factor loadings and the variance extracted by the varimax-rotated factor analysis for the 2015–2016 precipitation in Nanchang

	Factor 1	Factor 2	Factor 3
SO_4^{2-}	*0.744**	*0.509**	0.355
NO_3^-	*0.802**	0.405	0.275
F^-	*0.730**	0.262	0.326
Cl^-	0.168	*0.870**	0.190
Ca^{2+}	*0.634**	0.464	*0.547**
Mg^{2+}	*0.774**	0.341	0.390
K^+	*0.771**	0.364	0.220
Na^+	0.214	*0.718**	− 0.262
NH_4^+	*0.549**	*0.665**	0.078
pH	0.155	− 0.069	*0.848**
Ec	*0.777**	0.207	0.085
Rainfall	*− 0.720**	0.008	0.332
Eigenvalue	7.1	1.3	0.95
% variance	59.15	10.62	7.9
% cumulative	59.15	69.77	77.67

* Factor loadings > 0.50 are in italics and are considered significant

almost all ions were negatively correlated with precipitation amount to some degree (Table 3).

Factor 2 showed positive loadings on Cl^-, Na^+, SO_4^{2-}, and NH_4^+ (Table 2). Cl^- was positively correlated with SO_4^{2+} and NH_4^+ and had a certain correlation with Na^+ (Table 3). Moreover, Cl^- was slightly and significantly enriched in precipitation relative to the seawater and crust values, respectively (Table S3). Therefore, Cl^- in precipitation originated partly from anthropogenic pollution but was predominantly of marine origin. Na^+ is the best reference ion for seawater; however, its EF_{crust} value is 0.371 (Table S3). Thus, a small amount of Na^+ in precipitation could be from crustal sources. As a whole, the positive loadings for Cl^-, Na^+, SO_4^{2-}, and NH_4^+ reflected a combined effect of sea salt and anthropogenic sources.

Factor 3 had positive loadings for Ca^{2+} and pH (Table 2). Ca^{2+} increased as the pH value increased with a correlation coefficient of $r = 0.51$ (Table 3). Ca^{2+} is a typical alkaline cation of crustal origin, and pH is an indicator of precipitation acidity (Al-Khashman 2005). Therefore, factor 3 emphasized the effect of acid rain on Ca-bearing materials, including construction materials, surface soils, and rocks.

Sulfur isotopes as tracers of SO_4^{2-} in precipitation

Sulfur isotopic characteristics

The $\delta^{34}S$ value of SO_4^{2-} in Nanchang precipitation during 2015–2016 ranged from − 1.0‰ to + 4.5‰ (Table 1), similar to the values reported by Xiao et al. (2011). On average, precipitation $\delta^{34}S$ values in Nanchang approximated the values in the Three Gorges Reservoir and were higher than those in Guiyang but lower than those in most other domestic cities (Mukai et al. 2001; Xiao et al. 2014; Wu and Han 2015). Compared with foreign cities (Panettiere et al. 2000; Tichomirowa et al. 2007), precipitation $\delta^{34}S$ values were lower in Nanchang. In addition, the precipitation $\delta^{34}S$ values in Nanchang were roughly higher in the dry months than in the rainy months (Fig. 2), which was similar to the sulfur isotopic pattern of precipitation in Guiyang and Japan (Ohizumi et al. 1997; Xiao et al. 2014).

Table 3 Pearson correlation coefficients of chemical species in the Nanchang precipitation during Nov. 2015 to Oct. 2016

	pH	H^+	F^-	Cl^-	SO_4^{2-}	NO_3^-	Ca^{2+}	K^+	Mg^{2+}	Na^+	NH_4^+	δ^{34} S	Ec	P
H^+	*− 0.66***													
F^-	0.31**	− 0.04												
Cl^-	0.12	0.04	0.39**											
SO_4^{2-}	0.34**	0.03	*0.75***	*0.62***										
NO_3^-	0.28**	0.05	*0.72***	*0.50***	*0.94***									
Ca^{2+}	*0.51***	− 0.18	*0.69***	*0.65***	*0.95***	*0.87***								
K^+	0.28**	0.07	*0.75***	0.45**	*0.80***	*0.81***	*0.73***							
Mg^{2+}	0.35**	− 0.12	*0.83***	*0.50***	*0.86***	*0.84***	*0.83***	*0.84***						
Na^+	− 0.06	0.28**	0.29**	0.45**	0.41**	0.36**	0.29**	0.44**	0.28**					
NH_4^+	0.11	0.11	*0.59***	*0.69***	*0.76***	*0.74***	*0.66***	*0.61***	*0.67***	0.43**				
δ^{34} S	− 0.24*	0.09	− 0.05	0.11	− 0.21	− 0.20	− 0.32**	0.07	− 0.17	0.06	− 0.11			
Ec	0.14	0.22*	*0.58***	0.30**	*0.73***	*0.72***	*0.64***	*0.61***	*0.67***	0.30**	*0.56***	− 0.23		
P ^{a}	− 0.04	− 0.04	− 0.33**	− 0.20	− 0.39**	− 0.43**	− 0.32**	− 0.42**	− 0.36**	− 0.23*	− 0.38**	0.14	− 0.36**	
T ^{b}	0.19	0.03	− 0.14	0.01	0.02	− 0.08	0.04	− 0.25*	− 0.11	0.20*	0.02	− 0.41**	0.16	0.18

The values, which are > 0.5 or < -0.5, are highlighted in italics

**Correlation is significant at the 0.01 level. *Correlation is significant at the 0.05 level. ^{a} Precipitation amount and ^{b} Air temperature

Sulfur isotopic constraint on the provenance of SO_4^{2-}

Precipitation SO_4^{2-} usually has multiple potential sources with different sulfur isotopic compositions, as shown in Fig. 3. Active volcanoes do not occur in Nanchang and surrounding areas. Sea spray and marine biogenic sulfur are isotopically different from Nanchang precipitation (Fig. 3). Therefore, these three potential sources contributed little to Nanchang precipitation. Southwesterly, southerly, and easterly winds were dominant, and the frequency of wind directions agreed with the precipitation amount (Fig. 4a, b). However, the frequency of wind directions were not associated with $\delta^{34}S$ and the concentration of SO_4^{2-} (Fig. 4c, d), suggesting a local source of SO_4^{2-} in Nanchang precipitation. Continental biogenic S, originating from waters, wetlands, and soils (Novák et al. 2001; Wu and Han 2015), has a lower $\delta^{34}S$ value than the SO_4^{2-} in Nanchang precipitation (Fig. 3). Furthermore, anthropogenic SO_2 emissions were significantly correlated with atmospheric SO_2 concentrations during 2012–2015 (Fig. 5a). It was thus concluded that anthropogenic SO_2 emissions contributed much to precipitation SO_4^{2-}, but continental biogenic S emissions did not.

Anthropogenic SO_2 is emitted from fossil fuel combustion, ore smelting, vehicle emission, and so on (Górka et al. 2017). The usages of coal and oil comprised approximately 69% and 17% of the annual total energy consumption, respectively, during 2012–2015 in Nanchang (Fig. 5b). Moreover, industrial SO_2 emissions comprised > 98% of anthropogenic SO_2 emissions (Fig. 5c). Smelters are rare in Nanchang. Therefore, coal combustion was a dominant contributor to precipitation SO_4^{2-} in Nanchang, which was supported by the $\delta^{34}S$ value of precipitation falling in the range of coal values (Fig. 3). The proportion of local:northern Chinese:imported coals used in Jiangxi Province was generally maintained at 1:2:0.4 from 2012 to 2015, showing stable sources of coal consumption (Fig. 5d). On average, the three types of coals were different in terms of $\delta^{34}S$ values and sulfur concentrations: − 3.1‰ and 0.9% for local coal (Hong et al. 1992); + 6.6‰ and 0.77% for northern Chinese coal (Motoyama et al. 2011); and + 6.7‰ and 0.19% for imported coal from Australia and Indonesia (Smith and Batts 1974; Motoyama et al. 2011). Through calculation, the relative contributions of sulfur emissions from the burning of local, northern Chinese, and foreign coals occupied 36%, 61%, and 3%, respectively. Therefore, the burning of northern Chinese coal was dominant affecting precipitation SO_4^{2-} in Nanchang.

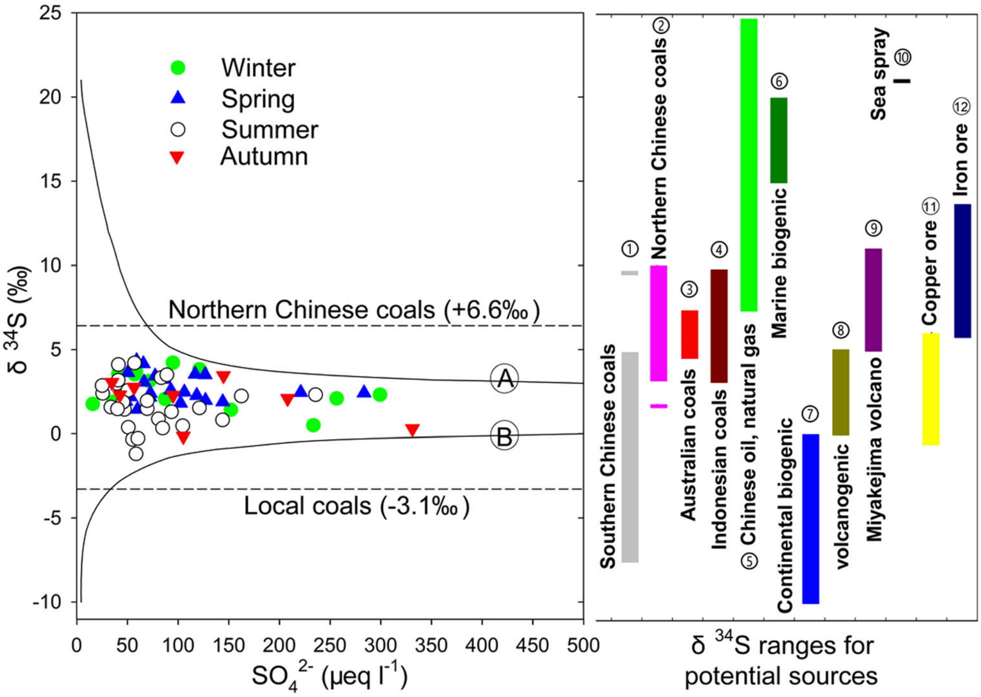


Fig. 3 The plot of $\delta^{34}S$ vs. SO_4^{2-} for precipitation events. Curve A: mixing between pollutant sulfate and seawater sulfate (Ohizumi et al. 1997). Curve B: mixing between pollutant sulfate and continental biogenic sulfur (Panettiere et al. 2000). The data of local coals were from Hong et al. (1992). ① Southern Chinese coals (Motoyama et al. 2011). ② Northern Chinese coals (Motoyama et al. 2011). ③ Australian coals (Smith and Batts 1974). ④ Indonesian coals (Motoyama et al. 2011). ⑤ Chinese oil and natural gas (Maruyama et al. 2000). ⑥ Marine biogenic source (Amrani et al. 2013). ⑦ Continental biogenic source (Panettiere et al. 2000; Norman et al. 2004). ⑧ Volcanogenic source (Nielsen et al. 1991). ⑨ Miyakejima volcano (Imai et al. 2007). ⑩ Sea spray (Amrani et al. 2013). ⑪ Copper ore, Jiangxi of China (Liu et al. 2013). ⑫ Iron ore, Jiangxi of China (Xu et al. 2016)

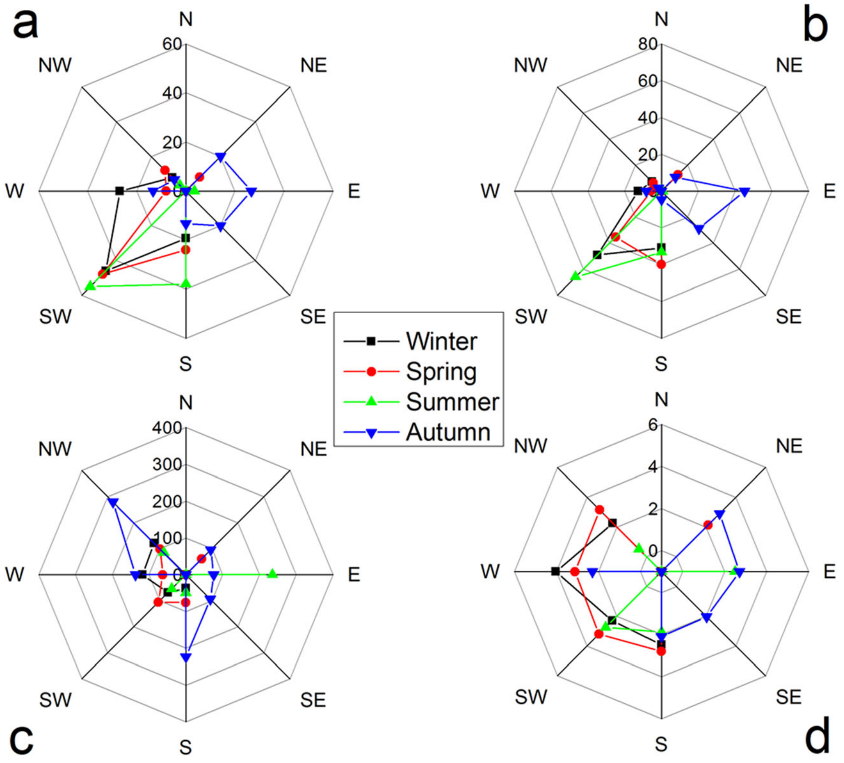


Fig. 4 Spider diagrams showing **a** frequent percentage of wind, **b** amount percentage of precipitation, **c** SO_4^{2-} concentration in precipitation, and **d** precipitation $\delta^{34}S$ value at 1000 m above ground level in each direction for four seasons in Nanchang during 2015–2016

The causes for sulfur isotopic variation between dry and wet months

Precipitation $\delta^{34}S$ seasonality is commonly caused by several mechanisms: (1) the removal of aerosol particles and soluble gases by raindrops below clouds (Xiao et al. 2014), (2) seasonal variation in sulfate sources (Mukai et al. 2001), (3) isotope fractionation during the oxidation of SO_2 to SO_4^{2-} (Harris et al. 2013), and (4) fluctuations in anthropogenic S from coal burning (Górka et al. 2017).

As shown in Table 3, no notable correlation existed between the $\delta^{34}S$ value and amount of precipitation in Nanchang. In addition, coal combustion was the dominant contributor to precipitation SO_4^{2-} and had constant sources in Jiangxi Province, as elucidated in the former paragraph. Therefore, the former two mechanisms had a minimal effect on $\delta^{34}S$ fluctuations in precipitation in Nanchang.

Oxidation of SO_2 to SO_4^{2-} is responsible for precipitation $\delta^{34}S$ seasonality and has two pathways: homogeneous and heterogeneous (Harris et al. 2013). Górka et al. (2017) thought that sulfates in precipitation originated mainly from secondary emissions in Wroclaw, ranging from ~80% during the nonheating period to ~60% during the heating period. As in Wroclaw, power plants are not equipped with desulfurization units in Nanchang. Therefore, secondary emissions should be a major contributor to the total sulfate content of precipitation in Nanchang. Furthermore, sulfate $\delta^{34}S$ in precipitation should have a corresponding response if the $\delta^{34}S$ of secondary sulfate changes significantly with ambient temperature, reflecting heterogeneous oxidation. Otherwise, sulfate $\delta^{34}S$ in precipitation should have no response to ambient temperature, indicating homogeneous oxidation. Atmospheric temperature was not significantly correlated with precipitation $\delta^{34}S$ in Nanchang (Table 3), showing the control of homogeneous oxidation on the $\delta^{34}S$ value of Nanchang precipitation during the whole year.

Homogeneous oxidation of SO_2 leads to isotopically lighter S accumulation in the resulting sulfate, whereas heterogeneous oxidation of SO_2 causes isotopically heavier S enrichment in droplets (Novák et al. 2001). In summer (Jun. to Aug.), with a mean air temperature of 28.2 °C, the photochemical production of gaseous oxidants was high and SO_2 solubility was low (Saltzman et al. 1983); more SO_2 was thus converted to SO_4^{2-} by homogeneous oxidation, causing lower $\delta^{34}S$ values in precipitation except in August (Fig. 6). In winter (Dec. to Feb.), with a mean air temperature of 6.6 °C, homogeneous oxidation became weaker, accompanied by heterogeneous oxidation, resulting in higher $\delta^{34}S$ values in precipitation (Fig. 6).

The summers were hot, with the highest temperature approaching 40 °C in Jiangxi (Fig. 6). Thus, a large amount of electricity was needed for air conditioning and agricultural irrigation, which was inferred from the coal consumption of power plants during summer (particularly August). Coal consumption for electricity increased from June to August and then decreased from August to September, and the $\delta^{34}S$ of precipitation SO_4^{2-} also changed similarly (Fig. 6).

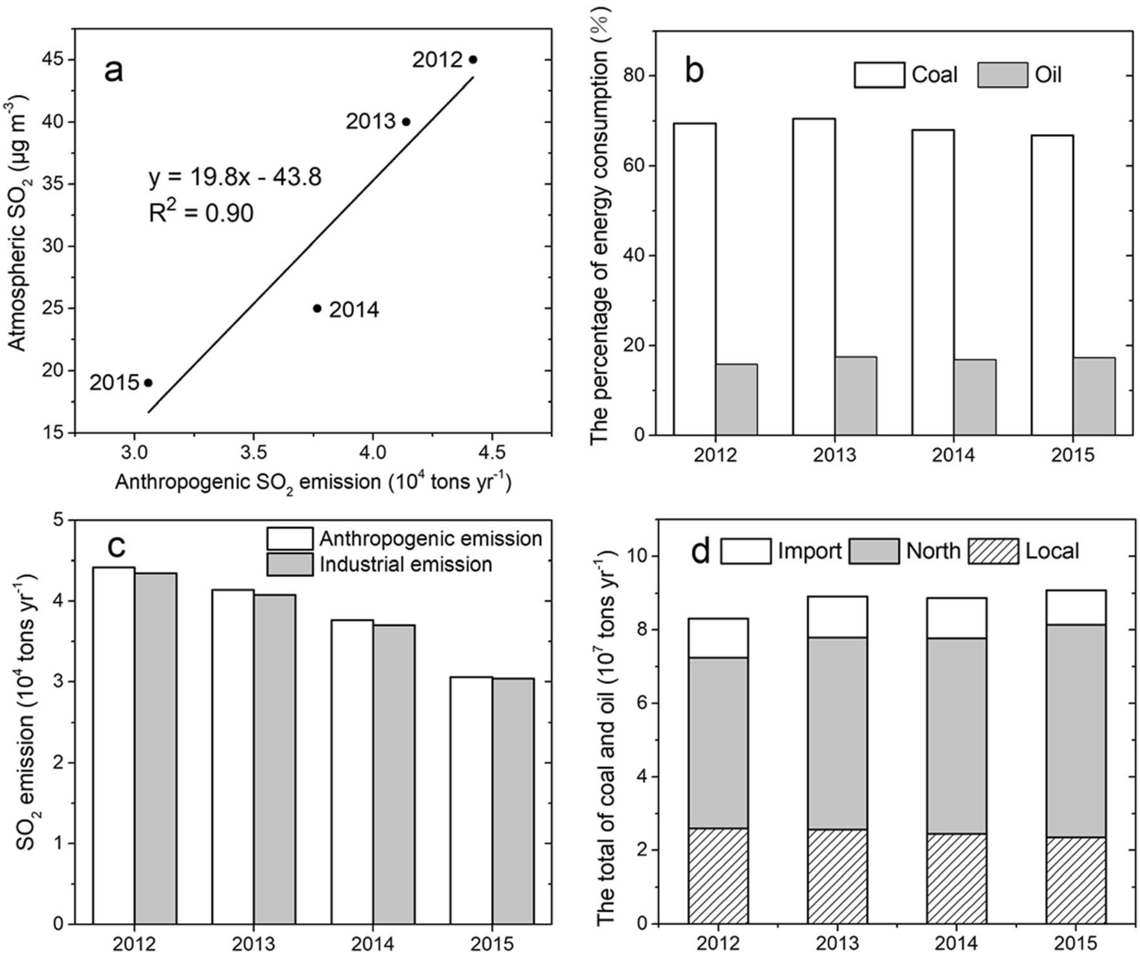


Fig. 5 Diagrams showing **a** atmospheric SO_2 concentrations versus anthropogenic SO_2 emissions in Nanchang, **b** the percentages of coal and oil in the total energy consumption in Jiangxi Province, **c** industrial and anthropogenic SO_2 emissions in Nanchang, and **d** the proportion of different energy consumption sources in Jiangxi Province. The data of atmospheric SO_2 concentrations in Nanchang were from Department of Ecology and Environment of Jiangxi Province (http://sthjt.jiangxi.gov.cn/) and other data were from Statistic Bureau of Jiangxi (http://tjj.jiangxi.gov.cn/)

Moreover, the precipitation δ^{34}S value was positively correlated with coal consumption in summer (coal consumption = $209.5 \times \delta^{34}S - 267.9$, $R^2 = 0.99$). Therefore, anthropogenic S emissions from coal-burning power plants affected the δ^{34}S

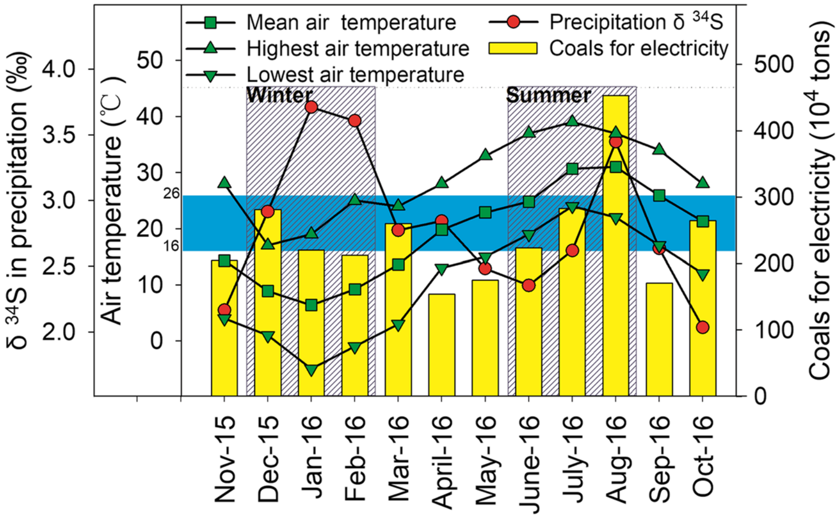


Fig. 6 Variations of air temperature, coals for electricity, and precipitation δ^{34}S values with month during 2015–2016. Air temperatures of 16–26 °C are the suitable temperatures to human beings, at which heating and air conditioning were not needed. The data for air temperature and coals for electricity in Jiangxi Province were from the China Weather website (http://www.weather.com.cn/) and the Jiangxi Energy Bureau website (http://www.cma.gov.cn/), respectively

seasonality of precipitation in Nanchang. However, the precipitation $\delta^{34}S$ value was inversely correlated with coal consumption in winter (coal consumption = − 84.9 × $\delta^{34}S$ + 527.6, $R^2 = 0.95$) (Fig. 6), probably due to the oxidation of SO_2 to SO_4^{2-}.

Conclusions

The chemical and sulfur isotope compositions of precipitation were investigated in Nanchang, South China, during 2015–2016 in this study. The pH values of precipitation in Nanchang ranged from 3.6 to 7.0, and 72.6% of the values were < 5.6, indicating the severity of acid rain. The Ec values in Nanchang varied from 3 to 86 μS cm^{-1}, similar to those in cities of South China. Precipitation was characterized by SO_4^{2-}, NO_3^-, Ca^{2+}, and NH_4^+ in Nanchang. SO_4^{2-} and NO_3^- were the two main acidifying factors, whereas Ca^{2+} and NH_4^+ were the major neutralizing species. As observed for the pH value, the chemical species of precipitation all showed lower values in the rainy months than in other months. Compared with foreign cities, the concentrations of ions in precipitation were higher in this region, reflecting the effect of anthropogenic pollution. SO_4^{2-}, NO_3^-, and NH_4^+ in precipitation were controlled by anthropogenic pollutants. K^+, Mg^{2+}, and Ca^{2+} could mainly originate from the weathering of silicates and/or carbonates. Cl^- in precipitation originated partly from anthropogenic pollution but was predominantly of marine origin. The $\delta^{34}S$ value of SO_4^{2-} fluctuated from − 1.0‰ to + 4.5‰, and its variation trend with time was opposite to pH in Nanchang precipitation. The use of northern Chinese coal was considered to be the most dominant contributor to precipitation SO_4^{2-} in Nanchang. The oxidation of SO_2 to SO_4^{2-}, particularly homogeneous oxidation, was the most dominant mechanism affecting precipitation $\delta^{34}S$ fluctuations with time. Our findings give deep insights into the origin of atmospheric pollutants in South China and are helpful for local governments to improve air quality. Our work may also provide a significant reference for acid rain studies in other regions. Our current work only focused on 1 year of precipitation events. In the future, a long-term precipitation monitoring program should be conducted to systematically explore the multiyear variations in precipitation chemistry and air pollutants.

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