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Chemistry and source identification of wet precipitation in a rural watershed of subtropical China

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Abstract South China is one of the regions severely suffering from acid rain in the world. However, few systematic studies of rural precipitation chemistry have been performed in comparison with the extensive studies on their urban counterparts of this region. In order to characterize the current acid rain status and identify its possible sources in the rural area of South China, we analyzed precipitation collected event by event from a rural forested watershed in southern Anhui Province between March 2007 and February 2010. The results showed that the concentrations of major ions within precipitation in the studied rural area were significantly lower than those reported for the urban areas of the same latitude in China. Nevertheless, the precipitation acidity (with an average pH value of 4.49) and the frequency of acid rain (95%) were considerably high. The relatively high ratio of $(SO_4^{2-}+ NO_3^-)/(Ca^{2+}+NH_4^+)$ was the main cause of acid rain in this rural area, as SO_2 and NO_x were the main precursors of acid rain, while Ca^{2+} and NH_4^+ acted as the dominant neutralizers to the acidity. Source identification indicated that Ca^{2+} and Mg^{2+} mainly were derived from alkaline dust, SO_4^{2-}, NO_3^- and NH_4^+ originated mainly from anthropogenic sources such as industrial and agricultural activities, most Na^+, Cl^-, K^+ and some of Mg^{2+} were derived from the sea. The results suggested that the major ions within precipitation in the rural area of South China were related to the meso-scale and long-range transport of particles and aerosols in the air.

Key words acid rain; precipitation chemistry; source identification; rural area; South China

1 Introduction

Acid rain has been recognized as an increasing important environmental problem in China over the last decades. Many years of record economic growth have been accompanied by increasing energy demand and rocketing emissions of pollutants. As a result, the acidity of the precipitation in China as well as the area affected by acid rain has increased rapidly during the recent years. For instance, acid rain influenced 16% of the Chinese territory in 2008 and occurred most frequently in South China, where over 70% of cities were suffering from acid precipitation (Ministry of Environmental Protection of China, 2009). In South China, the average pH of precipitation was reported to be usually below 4.6 and even reached as low as 3.6 in some urban environments (Larssen et al., 1999; Zhang Miaoyun et al., 2007; Cao Yuzhen et al., 2009). High acidity of rainfall has been proved to have adverse impacts on forests, freshwaters and soils, kill terrestrial and aquatic organisms as well as cause damage to buildings and having impacts on human health (Krug and Frink, 1983; Schindler, 1988; Likens et al., 1996).

Previous monitoring studies carried out in South China have sought to characterize the chemical composition of acid precipitation (Seip et al., 1999; Xu Y.G. et al., 2001; Huang Yilong et al., 2008a). These studies revealed that the precursors of acid rain were mainly SO_2 and NO_x were derived from the combustion of fossil fuel and traffic emissions; however, most of these reports were reconnaissance studies, and the provenance of pollutants as well as the mechanisms of pollutant transportation remained poorly understood. Due to increased emissions and long-range transportation of atmospheric pollutants, acid precipitation has also been reported for thought-to-be-pristine rural areas in South China (Ao Ziqiang et al., 2007). However, relatively few systemic studies of precipitation chemistry have been performed in the rural areas for this region as compared with the extensive studies in the urban environments. Consequently, there is a clear and urgent need for a more comprehensive understanding of precipitation chemistry in these areas. The outcomes of such an investigation will be valuable to decision-makers in their attempts to curb the effects of acid rain.

In the present study, the chemical composition and acidity of precipitation in a rural area of South China were analyzed based on precipitation samples collected continuously from March 2007 to February 2010. Factors influencing precipitation acidity, as well as the seasonal variability of precipitation chemistry were discussed. The objectives of this paper were to gain a better understanding of precipitation chemistry in rural area with mainly forestry and agricultural activities, to identify the possible sources contributed to its chemical composition, and finally to furnish data that were useful for estimating chemical weathering rates and modeling aqueous processes which will be involved in our future research.

2 Materials and methods

2.1 Study area

The monitoring site is located in a rural area of southern Anhui Province in South China (30°33′ N, 118°2′ E), near the outlet of Fengxingzhuang (FXZ) forested watershed with an area of 3.59 km^2 (Fig. 1). It lies in the southern part of lower reaches of the Yangtze River, which is more than 100 km away from any large urban-industrial area. This region is subjected to a typical Asian monsoon climate: mild springs (March to May) with frequent, light rainfall; hot and humid summers (June to August) with strong southeasterly monsoon breezes from the sea; and relatively cool and dry autumns (September to November) and winters (December to February) are influenced by the northwestern monsoonal winds from northern China (DingYihui and Johnny, 2005; Wang Pinxian et al., 2005). The mean annual temperature is 16.5℃ and the mean annual precipitation is 1585 mm.

2.2 Sampling and chemical analysis

Precipitation was monitored and collected from March 2007 to February 2010, using a weather station (Watchdog Model 900ET Weather Station, Spectrum Technologies Inc., USA) and an automated wet/dry deposition collector (PSC-Ⅲ, Qingdao PR Instrument Co., China), respectively, which were installed on the rooftop (5 m height above the ground) of a small house in the FXZ forested watershed. Rainfall, solar radiation, relative humidity, wind speed and direction, air and soil temperature were recorded by a data logger in the weather station every 15 minutes and the data were retrieved weekly. Precipitation, collected continuously during each rain event by the automated wet/dry deposition collector, was sampled at weekly intervals. A total of seventy-five precipitation samples were collected during the monitoring period.

Precipitation samples were analyzed as soon as transported back to laboratory. pH values were determined in unfiltered solutions at 25℃ by pH meter (PHS-3C, Shanghai REX Instrument Factory, China). Then the samples were filtrated (0.45 μm membrane filter) into plastic bottles and stored in the refrigerator at 4℃ for chemical analysis. Ca^{2+}, Mg^{2+}, K^+ and Na^+ were measured using atomic absorption spectroscopy (Varian Spectra AA220, Varian Australia Pty Ltd., Australia); SO_4^{2-}, NO_3^- and Cl^- were determined using ion chromatography (ICS-900, Dionex Corporation, USA); NH_4^+ was analyzed using the indophenol blue method followed by colorimetry (Clesceri et al., 1998). Concentrations of H^+ were obtained from pH values. The monthly volume-weighted mean (VWM) concentrations of major ions ($\overline{C}$) were calculated according to the corresponding period using the formula, $\overline{C}=(\sum_{i=1}^{n} CiQi)/(\sum_{i=1}^{n} Qi)$, where Qi is the rainfall amount (mm) and Ci is the measured concentration (μeq/L) of a given anion or cation.

3 Results

3.1 Acidity of precipitation

Precipitation in the FXZ forested watershed was acidic. The pH ranged from 3.66 to 5.80, with a mean of 4.49 (Fig. 2). The frequency of acid precipitation reached 95% of total rainfall, indicating that severe atmospheric pollution has affected the rural area of South China. Specifically, about 55% of rainfall had a pH lower than 4.5, and more than 40% of rainfall had a pH ranging from 4.5 to 5.5, while only 5% of rainfall had a pH higher than 5.5 (Fig. 2). There was an obvious seasonal variation of pH in precipitation, i.e., pH values during the summer were much higher than those during the winter, which was similar to the results observed in other regions of South China (Zhang Fuzhu et al., 1996; Huang Kan et al., 2008b).

3.2 Ionic composition of precipitation

Ionic composition of precipitation in the FXZ forested watershed during the monitoring period was listed in Table 1. To ensure the reliability of analytical data and assess whether any ions with notable concentrations have been overlooked, the balance between anions with cations must be checked at first. Data were generally considered acceptable if the concentration ratio of total anions to total cations (∑-/∑+) measured in precipitation was in the range of 1±0.25 (Keene et al., 1986). The equivalent concentration of total anions correlated well with that of total cations (r=0.86, p<0.01, n=75) in the present study, with an average concentration ratio (∑-/∑+) of 0.91, indicating that all the major components in precipitation were measured. The concentrations of major ionic species for the three monitoring years were in the following order: SO_4^{2-}>Ca^{2+}>Cl^->H^+>NH_4^+>NO_3^->Na^+>Mg^{2+}>K^+ (Table 1). The average concentrations of SO_4^{2-}, Cl^- and NO_3^- were 89.92, 60.69 and 43.92 μeq/L with maximum of 421.18, 140.24 and 140.53 μeq/L, respectively (Table 1). Among the anions, SO_4^{2-} occurred in the highest concentration, which was due to the fact that coal still remains as the major energy source in China (British Petroleum, 2010) and the contribution of coal burning to sulfur oxide is significant. Nevertheless, the concentrations of SO_4^{2-} in the FXZ forested watershed were much lower than those reported for urban areas of China (Table 1). Ca^{2+}, H^+ and NH_4^+ were the predominant cations in precipitation, with the average concentrations of 77.88, 49.20 and 47.99 μeq/L, respectively (Table 1). These levels were slightly higher than those obtained from the remote sites, but were significantly lower than those reported for urban areas in China (Tang Aohan et al., 2005; Li Chaoliu et al., 2007; Huang Kan et al., 2008b; Huang Deyin et al., 2009) (Table 1).

Table 1 Chemical composition of precipitation in the FXZ forested watershed compared with other monitoring sites in China (μeq/L)

Ion	FXZ forested watershed				Other monitoring site			
					Remote	Urban		
	Average	Minimum	Maximum	Standard deviation	Tibet[a]	Beijing[b]	Shanghai[c]	Guangzhou[d]
SO_4^{2-}	89.92	9.45	421.18	62.59	15.50	346.60	199.59	202.19
Cl^-	60.69	31.58	105.50	14.89	19.17	91.70	58.34	21.13
NO_3^-	43.92	9.79	140.53	25.57	10.37	65.50	49.80	52.26
Ca^{2+}	77.88	3.99	534.68	78.01	65.58	346.20	203.98	131.38
H^+	49.20	1.58	218.78	45.20	0.26	0.18	32.21	32.24
NH_4^+	47.99	2.63	143.85	27.61	18.13	125.38	80.68	66.47
Na^+	19.57	4.35	108.74	17.80	15.44	64.01	50.11	18.21
Mg^{2+}	9.91	0.16	88.38	15.42	7.43	84.70	29.64	9.02
K^+	8.10	2.56	25.58	4.71	14.49	5.30	14.89	9.11

[a] Li Chaoliu et al., 2007; [b] Tang Aohan et al., 2001; [c] Huang Kan et al., 2008b; [d] Huang Deyin et al., 2009.

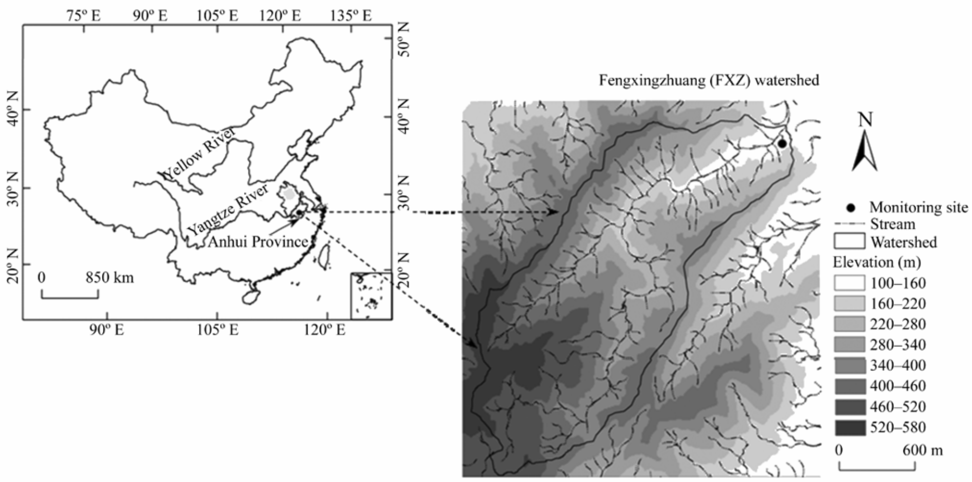

Fig. 1. Location of monitoring site in the Fengxingzhuang (FXZ) forested watershed of South China.

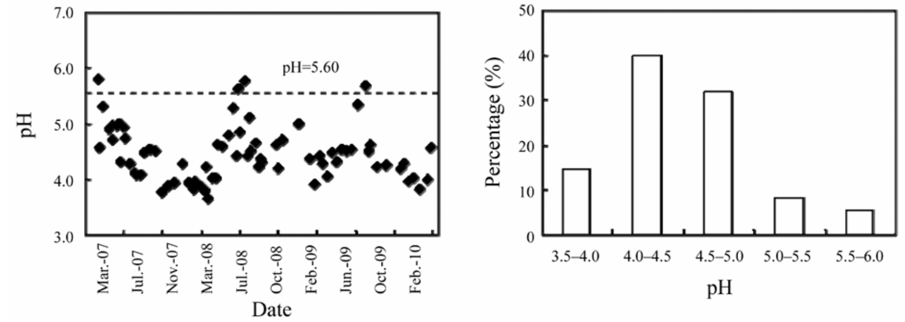

Fig. 2. Temporal variation and frequency distribution of pH values in precipitation.

3.3 Temporal variations in ionic concentrations

The monthly volume-weighted mean (VWM) concentrations of major ions in precipitation were higher in the dry season (October to March) than those in the rainy season (April to September) (Fig. 3), indicating that rainfall amount had a dilution effect on precipitation chemistry, as confirmed by the significant correlation between monthly total VWM ionic concentrations and rainfall amount (r=0.37, p<0.05, n=36). The precipitation chemistry may also be partially dependent on the residence time of suspended particles in the air. During the dry season, suspended particles persisted in the air for a long period, thereby accumulated to relatively high levels. Consequently, during the small rainfall events in the dry season, their incorporation enhanced ionic concentrations in precipitation. In contrast, during the rainy season suspended particles, which scavenged by the frequent precipitation decreased ionic concentrations in precipitation in the corresponding period. Nevertheless, Na^+ had higher concentrations in the summer than in the autumn. The dispersion of sea salts in atmospheric aerosols during the southeast monsoon could be an important contribution to the relatively high concentrations of Na^+ in summer, though there were frequent, large rainfall events. Ca^{2+} and Mg^{2+} also had higher concentrations in spring and summer than in autumn, which may be due to the invasion of alkaline dust from the northern China during the spring (Liu Xiaodong et al., 2004) and from intensive construction activities in the southern China during summer (Larssen et al., 2006). In addition, relatively high concentrations of NH_4^+ and NO_3^- occurred in August, despite of its relatively high rainfall amount, reflecting increased emissions of NH_3 from agricultural activities and NO_x from power production and transportation in the corresponding period.

4 Discussion

4.1 Factors controlling the acidity of precipitation

Because the pH of unpolluted natural water in equilibrium with dissolved CO_2 is not less than 5.60, rain water with pH below this value is considered as acid rain. High frequency of acid precipitation was observed in the FXZ forested watershed during the monitoring period (Fig. 2). Previous studies have shown that the principal cause of acid precipitation in South China was the anthropogenic emission of SO_2, which were hydrolyzed and oxidized to form strong acids (H_2SO_4) in precipitation (Zhang Fuzhu et al., 1996; Fan Houbo et al., 1999). However, strong correlations were observed between the acidity of precipitation and concentrations of NO_3^- and SO_4^{2-} in the present study (r=0.73 and 0.58 respectively, p<0.01, n=75), indicating that emissions both of SO_2 and NO_x played a central role in the development of acid precipitation. The results also suggested that acid rain in this area had changed from sulfuric acid rain type to sulfuric-nitric complex type of acid rain, which can be explained by the expansion of industrial activity as well as the rapid increase of motor vehicles in the past decades (National Bureau of Statistics of China, 2008). The occurrence of acid precipitation in the FXZ forested watershed, which is more than 100 km away from any large urban-industrial area, implied that acid precipitation in this region was primarily caused by long-rang transport of pollutants.

As demonstrated above, SO_2 and NO_x were the main precursors of acid precipitation in the FXZ forested watershed. If all of the SO_4^{2-} and NO_3^- in precipitation was assumed to occur as free acids, the corresponding pH value of precipitation in the FXZ forested watershed, as calculated by adding the equivalent concentrations of base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+) to the measured H^+ concentration (Table 1), would be 3.67, which was 0.82 less than the measured value. Thus, the measured concentration of hydrogen ion within precipitation was not (only)a measurement of the original acidity, but most likely reflected the acidity after neutralization by atmospheric bases as emphasized in other reports (Wang Wenxin and Wang Tao, 1996; Larssen and Carmichael, 2000). The neutralization role of base cations can be evaluated by the neutralization factor (NF) using the equation $NF_X=X/(SO_4^{2-}+NO_3^-)$, where X is the base cation of interest (Kulshrestha et al., 1995). The neutralization factors were 0.58 for Ca^{2+}, 0.41 for NH_4^+, and very small values for other bases such as Mg^{2+} (0.08). Therefore, Ca^{2+} and NH_4^+ were the dominant neutralizers corresponding to their high concentrations in precipitation (Table 1). This interpretation was further supported by the strong linear correlation between (H^++Ca^{2+}+NH_4^+) and (SO_4^{2-}+NO_3^-) (r=0.84, p<0.01, n=75).

It can be concluded that the ratio of SO_4^{2-}+NO_3^-/Ca^{2+}+NH_4^+ could be used as an index of acidity in precipitation from the above analysis. The ratio of SO_4^{2-}+NO_3^-/Ca^{2+}+NH_4^+ in the dry season (with an average value of 1.36) was higher than that in the rainy season (with an average value of 1.18) during the monitoring period, which exactly corresponded to the seasonal variation of precipitation acidity (Fig. 2). In addition, there was a significant positive correlation between pH of precipitation and rainfall amount (r=0.43, p<0.01, n=75), showing that rainfall amount had a dilution effect on precipitation acidity. This further explained why precipitation during the rainy season had a relatively high pH value (Fig. 2).

4.2 Source identification of major ions in precipitation

Particles, gases, and aerosols in the atmosphere, which can be scavenged by precipitation, are commonly regarded as determinants of precipitation chemistry. Previous studies have shown that there were three main sources of ions in precipitation: terrestrial, marine, and anthropogenic (Keene et al., 1986; Likens and Bormann, 1995; Laudon et al., 2004; Rogora et al., 2004). In order to find the possible associations between ions, and consequently, the potential sources of nutrients in precipitation, the correlation coefficients between various ions were calculated (Table 2). Na^+ correlated well with Cl^- (r=0.84, p<0.01, n=75) indicating that they originated from the same source such as sea salt. Similarly, strong correlations have been found between Ca^{2+} and Mg^{2+} (r=0.83, p<0.01, n=75), K^+ and Na^+ (r=0.81, p<0.01, n=75), suggesting the common origin of these ions from earth crust and sea, respectively. The relative strong correlations between Ca^{2+} and SO_4^{2-} (r=0.76, p<0.01, n=75), Mg^{2+} and SO_4^{2-} (r=0.57, p<0.01, n=75), Mg^{2+} and NO_3^- (r=0.62, p<0.01, n=75), Ca^{2+} and NO_3^- (r=0.55, p<0.01, n=75) probably resulted from the reactions of acids (HNO_3 and H_2SO_4) with alkaline compounds which were carried into the atmosphere by wind-blown dust (HanYongxiang et al., 2005). Besides, the acidic anions NO_3^- and SO_4^{2-} were well correlated (Table 2) because of the co-emission of their precursors (SO_2 and NO_x) and the similarity of their behaviors in precipitation. As discussed above, H^+ correlated well with NO_3^- and SO_4^{2-}, implying that the acidity of precipitation was mainly caused by sulfuric and nitric acids.

To estimate the marine contribution in precipitation composition, assuming that all of the Na^+ in precipitation were derived from sea salt and using the molar ratios of Na^+:K^+:Ca^{2+}:Mg^{2+}:Cl^-:SO_4^{2-}:NO_3^-= 1:0.02:0.04:0.23:1.17:0.12:0.00002 in sea water (Millero, 1974), we calculated that sea salt accounted for an average of 100%, 5%, 1%, 45%, 51%, and 0.0004% of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and NO_3^- in precipitation, respectively. The result suggested that the majority of NO_3^-, SO_4^{2-}, K^+ and Ca^{2+}, almost half of Cl^- and Mg^{2+} in precipitation were anthropogenic or terrestrial in origin. For instance, there were point sources of HCl inputs to the atmosphere from small-sized pulp mill workshops ran by local farmers since the southern Anhui region has been the hometown of the unique Xuan paper (Wu Shixin, 2008).

Table 2 Matrix of Pearson correlation coefficients for major ions in precipitation

	NO_3^-	SO_4^{2-}	Cl^-	H^+	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}
NO_3^-	1								
SO_4^{2-}	0.43**	1							
Cl^-	0.18	-0.02	1.00						
H^+	0.73**	0.58**	0.13	1					
NH_4^+	0.38**	0.26*	-0.10	-0.06	1				
K^+	0.40**	0.20	0.30**	0.38**	0.18	1			
Na^+	0.42**	0.17	0.84**	0.31**	0.13	0.81**	1		
Ca^{2+}	0.55**	0.76**	0.20	0.61**	0.12	0.41**	0.39**	1	
Mg^{2+}	0.62**	0.57**	0.04	0.56**	-0.03	0.43**	0.41**	0.83**	1

* Correlation is significant at the 0.05 level (two-tailed); ** Correlation is significant at the 0.01 level (two-tailed).

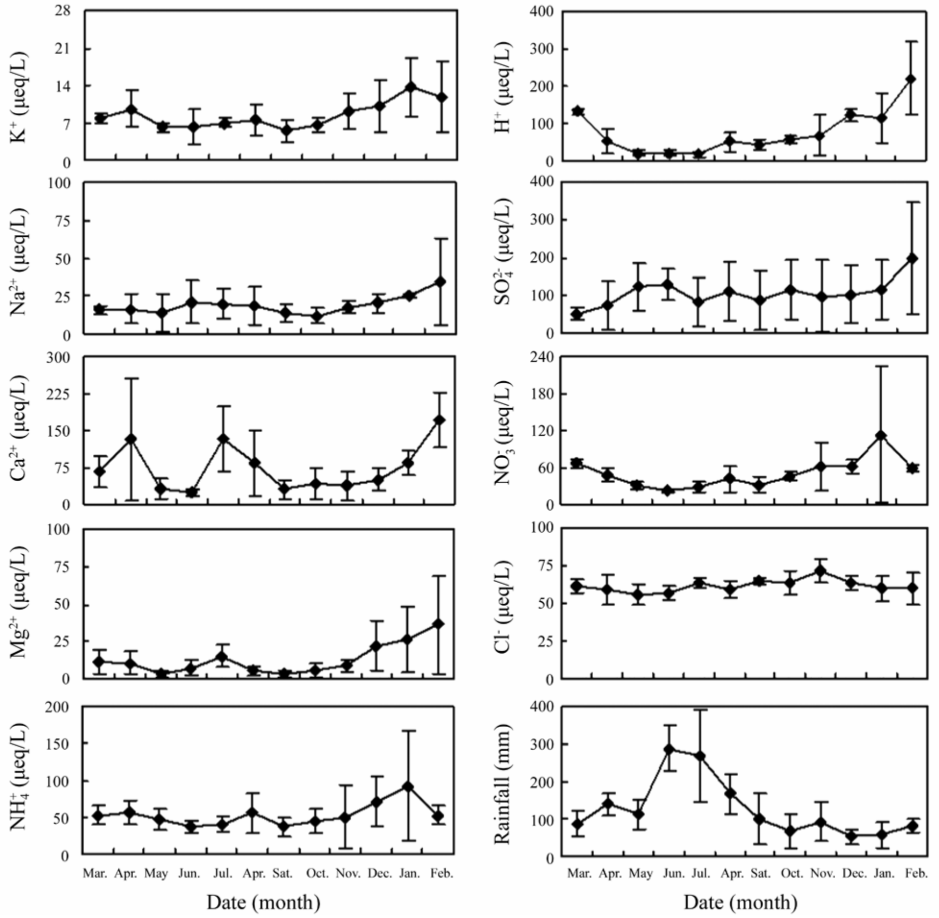

Fig. 3. Temporal variations in monthly rainfall amount and volume-weighted mean (VWM) concentrations of major ions. The data points are mean values of three years and vertical bars are standard errors.

The principal component analysis was applied to identify the proportion of each source for the major ions in precipitation (Table 3). Three factors, which totally explained 76.59% of the variance, were extracted from the data. The first factor (PC1) explained 32.14% of the total variance, showing high loadings for SO_4^{2-}, NO_3^-, Ca^{2+} and Mg^{2+}, which represented sources from industrial activities and alkaline dust. SO_4^{2-} and NO_3^- almost were entirely derived from industrial activities, such as the extensive use of coal and oil which accounted for more than 90% of the energy production in China in 2009 (British Petroleum, 2010). Ca^{2+} and Mg^{2+} mainly originated from alkaline dust, which has many potential sources, including windblown dust and anthropogenic sources such as industrial and construction activities. The second factor (PC2) with a variation of 27.80% showed high loadings for Na^+, Cl^-, K^+ and Mg^{2+}, which was associated with marine sources such as sea salts. The third factor (PC3) accounted for 16.65% of the total variance showing high loadings for NH_4^+ and NO_3^-, of which these ions were related to agricultural activities. The results suggested that the major ions within precipitation in the rural area of South China were directly related to the meso-scale and long-range transport of particles and aerosols in the air.

Table 3 Rotated component matrix for major ions in precipitation

Variable	PC1	PC2	PC3
NO_3^-	0.46	0.05	0.47
SO_4^{2-}	0.88	-0.06	0.24
Cl^-	-0.03	0.62	-0.33
NH_4^+	-0.03	0.04	0.93
K^+	0.24	0.87	0.21
Na^+	0.21	0.84	0.13
Ca^{2+}	0.89	0.26	0.04
Mg^{2+}	0.83	0.56	-0.09
Variance (%)	32.14	27.80	16.65
Source	Industrial activity and alkaline dust	Sea salt	Agricultural activity

5 Conclusions

The acidity of precipitation was considerably high in the studied forested watershed with a mean pH value of 4.49, and the frequency proportion of acid precipitation of total rainfall was 95% during the monitoring period, indicating that the severe atmospheric pollution has affected the rural area of South China. The chemical composition of precipitation was characterized by high concentrations of SO_4^{2-}, NO_3^-, Ca^{2+} and NH_4^+. SO_4^{2-} and NO_3^- were the main precursors of acid precipitation, while Ca^{2+} and NH_4^+ acted as the dominant neutralizers to the acidity. Concentrations of major ions in this rural area were significantly lower than those reported for urban areas of South China. The monthly volume-weighted mean concentrations of major ions in precipitation were higher in the dry season than those in the rainy season, and the temporal variations of ion concentrations were influenced by source strength, rainfall amount and the residence time of suspended particles in the air. Source identification indicated that Ca^{2+} and Mg^{2+} were mainly derived from alkaline dust, SO_4^{2-}, NO_3^- and NH_4^+ originated mainly from anthropogenic sources such as industrial and agricultural activities, most Na^+, Cl^-, K^+ and some of Mg^{2+} were derived from the sea. The results suggested that the major ions within precipitation in the rural area of South China were related to the meso-scale and long-range transport of particles and aerosols in the air.

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