The climatic characteristics and formation mechanism of acid rain in Guilin, China

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Abstract. A comprehensive study on climatic conditions and the chemical compositions of the rainwater had been undertaken from 2011 to 2015. Over 200 samples were taken and analyzed for pH in each year. Particularly, 240 samples taken in 2015 were analyzed for major ions. The results showed that the average frequency of acid rain in Guilin City was as high as 60% from 2011 to 2015. The order of the anion and cation concentration in precipitation was SO₄²⁻>NO₃⁻>Cl⁻>F⁻, Ca²⁺>NH₄⁺>K⁺>Na⁺>Mg²⁺, respectively. Ca²⁺ plays an important catalytic role on the photochemical conversion process of SO₄²⁻. The formation of a large number of sulfates led to the occurrence of acid rain in Guilin. The adverse meteorological conditions in the winter and spring season were found to be a main reason for most serious acid rain pollution episodes during this period.

1. Introduction

Acid rain refers to acidic precipitation with the pH of less than 5.6, which is one of the major environmental problems in the world(Xie, Du et al. 2009). The northern Guangxi is a basin with typical “karst” landform. There are many mountains in the northern of Guangxi. Pollutants could be easily blocked by the trumpet topography in the area due to wind direction and landform. As the most typical city in the region, Guilin has a subtropical monsoon climate with abundant rainfall and sufficient illumination. Emissions of urban traffic, living and industrial pollutants make acid substances easily accumulate in the environment, especially in rainy winter days. In recent years, serious acid rain has been formed in north of Guangxi.

Because of the special topography, the north of Guangxi has excellent tourism resources. Guilin is one of the most important international tourist cities in China. Air quality plays a vital role for economic development progress of this region. Research activities focused on acid rain in Guilin had been conducted in recent ten years. Hongbo Zhang and his team analyzed the chemical characteristics of atmospheric precipitation in karst area of Guilin. The results showed that there was a good positive correlation between SO₄²⁻ and NO₃⁻, Ca²⁺, Mg²⁺(Zhang, Yu et al. 2012). The source of acid transport in acid rain had been proved to be mainly caused by human factors(Guo, Yu et al. 2016). Although many researches had undertaken studies of status of acid rain, there are few reports explored the formation and main influencing factors of acid rain in typical cities of Karst landform in the northern Guangxi. Based on the precipitation data during 2011-2015 years in Guilin, the process of acid rain and its main influencing factors were analyzed in the study. In addition, the key components and main pollutants in acid rain occurrences were determined. This work has a great significance for acid rain...
pollution control and management, coping strategies, protection of regional environmental resources, and protection of urban economic development.

2. Materials and Methods

2.1. Overview of the study area
The northern Guangxi is located in the southwestern part of China and is located at the southern end of the Xianggui Corridor, southwest of the Nanling Mountains. As a national key environmental city, it is also a famous tourist city. There are no heavy industries in Guilin. However, monitoring data has shown acid rain pollution is serious in the region. Compared with the heavy industrial city of Liuzhou in central Guangxi and the large southern city of Nanning, acid rain occurrence is even worse in Guilin (Guo., 2017; Huang et al., 2004) Figure 1 shows the sampling locations at Guilin.

![Sampling locations at Guilin, China](image)

2.2. Sources of data
The data used in this article are all from the precipitation monitoring data of the Guilin Environmental Monitoring Central Station in 2015 and the 2011-2015 environmental quality report of Guilin.

3. Results and Analysis

3.1. Precipitation results and analysis during monitoring
Table 1 shows the statistics of precipitation monitoring data in Guilin during 2011-2015. The total number of precipitation samples from 2011 to 2015 was 1197, of which the total number of acid rain occurrence was 758. The average frequency of acid rain reached 63.32% with the average pH of 4.93. The acid rain pollution was serious. During the five-year period, the precipitation pH ranged from 3.46 to 8.29. The most serious of acid rain pollution occurred in 2012 with the acid rain frequency of 78.7%. Although compared with the reported data in 2008 (Guo, Yu et al. 2016), the average annual precipitation pH value decreased further by 6.89%.

### Table 1 Statistical Table of Monitoring Results of Rainfall in Guilin City, 2011-2015

| project      | 2011    | 2012    | 2013    | 2014    | 2015    |
|--------------|---------|---------|---------|---------|---------|
| pH range     | 3.46-8.12 | 3.65-7.2 | 3.98-7.28 | 3.74-8.29 | 4.13-7.44 |
| pH average   | 4.71    | 4.66    | 5.04    | 4.85    | 5.23    |
| Acid rain frequency % | 72.8    | 78.7    | 56.3    | 64      | 42.5    |
| Number of samples | 228    | 272    | 224    | 233    | 240    |

Figure 2 shows the variation of acid rain seasons in Guilin during 2011-2015. It can be seen from Figure 2 that there is a significant seasonal variation in acid rain occurrence in Guilin. Acid rain pollution in winter is more serious than in summer. The highest frequency of acid rain was observed in the first quarter of 2011-2015. During the observation period of 2011-2015, the order of acid rain frequency in different seasons is follow: the first quarter (84.1%) > the second quarter (64.2%) > the fourth quarter (64.1%) > the third quarter (29.0%). The acid rain frequency of the whole observation period was reached to over 60% in Guilin, around double than in Nanning (Huang and Wang 2014).

Figure 3 shows the change of mean monthly pH and average monthly frequency of acid rain in 2015 in Guilin. The results indicates that the pH values of precipitation are lower than 5.6 except for April, July, August, September and October. In January, the lowest pH value of precipitation was measured at 4.64. The highest frequency of acid rain reached 82.4% in March. The lowest values of precipitation pH and the maximum frequency of acid rain appeared in winter and spring. The seasonal distribution characteristics of acid rain are consistent in most areas of China, especially in southern cities (Guoying Qin 2001, Yu, Kuo et al. 2015). In Guilin, The time distribution of precipitation is
uneven: rainy in summer but less in autumn and winter. It is often rainy in spring, acid rain is serious, but between July and October, the strong rainfall season, the pollution of acid rain has been alleviated.

Fig.3. Monthly variation of pH, monthly precipitation and acid rain frequency in Guilin in 2015

3.2. Analysis of Precipitation Ion Concentration in Guilin in 2015

Table 2 shows the ion concentration in precipitation in Guilin in 2015. The anions in precipitation were mainly $\text{SO}_4^{2-}$, which accounts for 59.6% of the total anions in precipitation. Moreover, the concentration of $\text{NO}_3^-$ was also high, accounting for 26.2% of the total anions in precipitation. The order of the anion concentration in precipitation is follow $\text{SO}_4^{2-}>\text{NO}_3^->\text{Cl}^->\text{F}^-$. The concentration ratio of $\text{SO}_4^{2-}$ to $\text{NO}_3^-$ is 2.28. Therefore, the main anion in precipitation was sulfuric acid ions. The precipitation in Guilin was classified as sulfuric sulfate acid rain. The main cations in the atmospheric precipitation are $\text{Ca}^{2+}$. The average annual concentration of cations reached 2.522mg/L, accounting for 46.2% of the total cations in precipitation.

Table 2 The main ion concentration in precipitation in Guilin City in 2015 (mg/L)

| Month | $\text{SO}_4^{2-}$ | $\text{NO}_3^-$ | $\text{F}^-$ | $\text{Cl}^-$ | $\Sigma_{\text{anionic}}$ | $\text{NH}_4^+$ | $\text{Ca}^{2+}$ | $\text{Mg}^{2+}$ | $\text{Na}^+$ | $\text{K}^+$ | $\Sigma_{\text{cation}}$ |
|-------|-----------------|-----------------|-------------|-------------|-----------------|-------------|-------------|-------------|-------------|-------------|------------------|
| 1     | 14.6            | 5.48            | 0.215       | 0.867       | 21.162          | 1.31        | 5.79        | 0.317       | 0.34         | 0.383       | 8.14             |
| 2     | 6.19            | 3.59            | 0.115       | 0.873       | 10.768          | 1.27        | 2.55        | 0.221       | 0.278        | 0.379       | 4.698            |
| 3     | 10.7            | 5.76            | 0.165       | 4.67        | 21.295          | 1.46        | 5.26        | 0.449       | 0.815        | 2.590       | 10.574           |
| 4     | 9.7             | 3.34            | 0.159       | 4.04        | 17.239          | 1.33        | 3.62        | 0.341       | 1.88         | 2.710       | 9.881            |
| 5     | 2.5             | 1.2             | 0.069       | 0.634       | 4.403           | 0.621       | 0.737       | 0.124       | 0.667        | 0.546       | 2.695            |
| 6     | 1.79            | 0.951           | 0.062       | 0.232       | 3.035           | 0.401       | 0.637       | 0.044       | 0.151        | 0.154       | 1.387            |
| 7     | 3.7             | 1.62            | 0.114       | 0.42        | 5.854           | 0.684       | 1.79        | 0.075       | 0.609        | 0.229       | 3.387            |
| 8     | 3.45            | 1.46            | 0.1         | 0.344       | 5.354           | 0.658       | 1.597       | 0.074       | 0.153        | 0.207       | 2.689            |
| 9     | 9.93            | 3.25            | 0.274       | 0.823       | 14.277          | 0.965       | 4.52        | 0.156       | 0.18         | 0.319       | 6.14             |
| 10    | 3.63            | 1.42            | 0.107       | 0.337       | 5.494           | 0.429       | 1.756       | 0.06        | 0.189        | 0.177       | 2.611            |
| 11    | 2.27            | 1.07            | 0.073       | 0.286       | 3.699           | 0.315       | 0.911       | 0.058       | 0.115        | 0.156       | 1.555            |
| 12    | 3.53            | 1.16            | 0.101       | 0.673       | 5.464           | 0.332       | 1.09        | 0.183       | 0.504        | 0.152       | 2.261            |
The maximum of SO$_4^{2-}$ was measured at 14.6mg/L in January, 2015 (Figure 4). In the winter and spring (the first quarter), the concentration of SO$_4^{2-}$ was much higher than the annual average. This period was also the season with the highest frequency of acid rain in Guilin. The monitoring result shows that the acid rain probably fell into the category of sulfate acid rain probably in Guilin.

In general, we usually use the sulfur oxygen ratio (SOR) and the nitrogen oxidation ratio (NOR) to express to the transformation from SO$_2$/NO$_x$ to SO$_4^{2-}$/NO$_3^-$ (Yuan, Li et al. 2015). The specific formula is as follows:

$$\text{SOR} = \frac{n(\text{SO}_4^{2-})}{n(\text{SO}_4^{2-}) + n(\text{SO}_2)}$$

$$\text{NOR} = \frac{n(\text{NO}_3^-)}{n(\text{NO}_3^-) + n(\text{NO}_2)}$$

The SOR during the monitoring period was 0.43, much higher than 0.1. This indicates that the secondary transformation of SO$_2$ in Guilin is very significant (Huang, Liu et al. 2016). In contrast, the NOR was only 0.05 during the monitoring period, less than 0.1. Thus, the conversion of NO$_2^-$ to NO$_3^-$ due to photochemical oxidation reaction was negligible. Consequently, SO$_4^{2-}$ mainly comes from the secondary conversion of SO$_2$. The high concentration of SO$_2$ probably resulted from no definite ban on domestic coal burning in Guilin. Compared with the other two seasons, residents heating with coal produced more SO$_2$ in the winter and spring. Secondly, Guilin had low wind speed and a large thickness of atmospheric inversion layer in the winter and spring (Pan, Chen et al. 2018). Pollutants tend to accumulate in large amounts in the environment with low precipitation intensity.

3.3. Causes of Acid Rain in Guilin City in 2015

The above data shows that Guilin region suffered from severe sulfuric acid rain pollution. The high concentration of SO$_4^{2-}$ in the atmosphere of Guilin was mainly derived from the secondary conversion of SO$_2$. Table 3 shows the correlation coefficient between chemical components in precipitation.
observed in 2015. The highest value of 0.980 implied that Ca\(^{2+}\) had highly positive relationship with SO\(_4^{2-}\). This result indicates that Ca\(^{2+}\) played an important role in formation of typical sulfate acid rain.

Table 3. Correlation coefficient between chemical components in precipitation observed in 2015

|          | SO\(_4^{2-}\) | NO\(_3^{-}\) | F\(^{-}\) | Cl\(^{-}\) | Ca\(^{2+}\) | NH\(_4^{+}\) | Na\(^{+}\) | K\(^{+}\) | Mg\(^{2+}\) |
|----------|--------------|-------------|--------|--------|---------|---------|--------|--------|---------|
| SO\(_4^{2-}\) | 1            |             |        |        |         |         |        |        |         |
| NO\(_3^{-}\) | 0.932**     | 1           |        |        |         |         |        |        |         |
| F\(^{-}\)   | 0.861**     | 0.711**    | 1      |        |         |         |        |        |         |
| Cl\(^{-}\)  | 0.566*     | 0.657*    | 0.335  | 1      |         |         |        |        |         |
| Ca\(^{2+}\) | 0.980***   | 0.949***  | 0.877**| 0.590* | 1        |         |        |        |         |
| NH\(_4^{+}\) | 0.856**    | 0.924**  | 0.640* | 0.719**| 0.858** | 1        |        |        |         |
| Na\(^{+}\)  | 0.333      | 0.286     | 0.132  | 0.771**| 0.267   | 0.489   | 1      |        |         |
| K\(^{+}\)   | 0.508*     | 0.581*   | 0.268  | 0.986**| 0.519*  | 0.684*  | 0.836**| 1      |         |
| Mg\(^{2+}\) | 0.816**    | 0.889**  | 0.528* | 0.863**| 0.801** | 0.867** | 0.597* | 0.806**| 1       |

**.Correlation is significant at 0.01 level(1-tailed).
*.Correlation is significant at 0.05 level(1-tailed).

Previous studies indicated SO\(_3^{2-}\) was generated due to attachment and absorption of SO\(_4^{2-}\) on the surface of the particulates of CaCO\(_3\) presented in the atmosphere in a humid environment. And these ions were oxidized to sulfate acid substance in the end. This process was the main cause of sulfate acid rain(Zhu, Shang et al. 2010). Because of the weathering of carbonate rocks and the effect of soil dust, the content of Ca\(^{2+}\) in the atmospheric particulates and precipitation was high in Guilin(Yu, LI et al. 2012), resulting in favorable conditions for the mass production of sulfates. Furthermore, the high annual average humidity of Guilin (the average humidity was 56% and the relative humidity was above 65% in winter and spring) accelerated the generation of sulfate acid substances. The terrain of Guilin is surrounded by mountains and low concave in the central region. In winter and spring, the pollutants were difficulty spread under local meteorological conditions. Consequently, serious acid rain pollution were regularly observed in the two seasons in Guilin.

4. Conclusions
(1) The occurrence of acid rain pollution in Guilin had obvious seasonal variations. The seasonal acid rain pollution degree was follow the first quarter>the second quarter>the fourth quarter>the third quarter. The frequency of acid rain with the average annual pH of 4.93 reached 63.32% during 2011 to 2015.

The water-soluble ions in the 2015 precipitation of Guilin were ranked as follows: SO\(_4^{2-}\)>NO\(_3^{-}\)>Cl\(^{-}\)>F\(^{-}\); Ca\(^{2+}\)>NH\(_4^{+}\)>K\(^{+}\)>Na\(^{+}\)>Mg\(^{2+}\).

(2) SOR was 0.43 indicated that the secondary conversion of SO\(_2\) contributed to formation of SO\(_4^{2-}\). Guilin had typical sulfate acid rain.

(3) The correlation coefficient between SO\(_4^{2-}\) and Ca\(^{2+}\) in precipitation was 0.980 in Guilin in 2015. It indicated that the presence of large amounts of Ca\(^{2+}\) had a significant catalytic effect on the generation of acid rain substances. This kind of catalysis reaction with local suitable humidity conditions and meteorological conditions lead to serious acid rain pollution in Guilin region in winter and spring.

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