Characterization of Winter Haze Episodes and Their Formation Mechanism in Guilin, China

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Abstract. Three heavy haze pollution episodes could be observed in Guilin in winter. The sources and evolutionary mechanisms of the haze pollution episode that occurred from December 23, 2014 to February 10, 2015 were analyzed. The meteorological parameters and daily concentrations of $PM_{2.5}$, sulfate, nitrate, and ammonium were measured. The results showed that the mass concentrations of the sulfate, nitrate, and ammonium increased with increasing $PM_{2.5}$ levels. Sulfate was the most abundant secondary water-soluble inorganic species, which contributed to about 20% of the $PM_{2.5}$ mass concentration. The catalytic oxidation of SO_2 to SO_4^{2-} in the presence of NO_x and Ca^{2+} played a considerable role on the severe winter haze episodes in Guilin.

1. Introduction

Haze is defined as a weather phenomenon that leads to atmospheric visibility less than 10 km due to the moisture, dust, smoke, or vapor in the atmosphere. Since 1970s, the problem of haze was generally concerned by researchers. Previous studies reported that the formation of haze was closely linked to the meteorological and atmospheric conditions [1-2]. In addition, fine particulate matter (PM) such as $PM_{2.5}$, referring to the PM with an aerodynamic diameter less than or equal to 2.5 μm, is the key factor for the increase in haze pollution. The increase of $PM_{2.5}$ concentrations due to human activities was demonstrated to cause the formation of haze [3-4]. Also, high concentrations of secondary species (i.e., SO_4^{2-}, NO_3^-, NH_4^+) can be formed from the photochemical reactions of air pollutants from anthropogenic sources), which accounts for the majority of severe hazes in many cities [5-6].

Guilin is an international famous tourist city. The air quality is always concerned by public. In recent years, the haze episode appeared frequently in the Guilin area owing to the rapid development of industrial, transportation and construction industry, , which had a great impact on human's life and health as well as an adverse effect on Guilin's tourist industry.

Previous studies investigated the characteristics of long-term change in haze events in Guilin and discussed the effect of local weather conditions on the formation of haze [7-9]. However, no systematic analysis of the formation mechanism of the heavy haze was performed. To the best of our knowledge, no study reported the chemical components of aerosols during the haze evens in Guilin. In this study, the heavy haze event occurring in winter was monitored. The possible formation

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mechanisms of haze pollution were illustrated based on the continuous hour observation of $PM_{2.5}$ and gaseous pollutants, and their chemical compositions.

2. Methods

The Sampling points were set up on the open rooftops of an office building (about 25 meters above ground level) at Guilin Environment Monitoring Central Station, Guilin (Figure 1). The continuous monitoring of mean hourly concentration of $PM_{2.5}$ was conducted by an aerosol particle mass analyzer. The offline samples were collected daily by the quartz and teflon membrane from December 23, 2014 to February 10, 2015 in parallel with the on-line data. Ion chromatography (IC) was used to analyze water-soluble anions and cations.

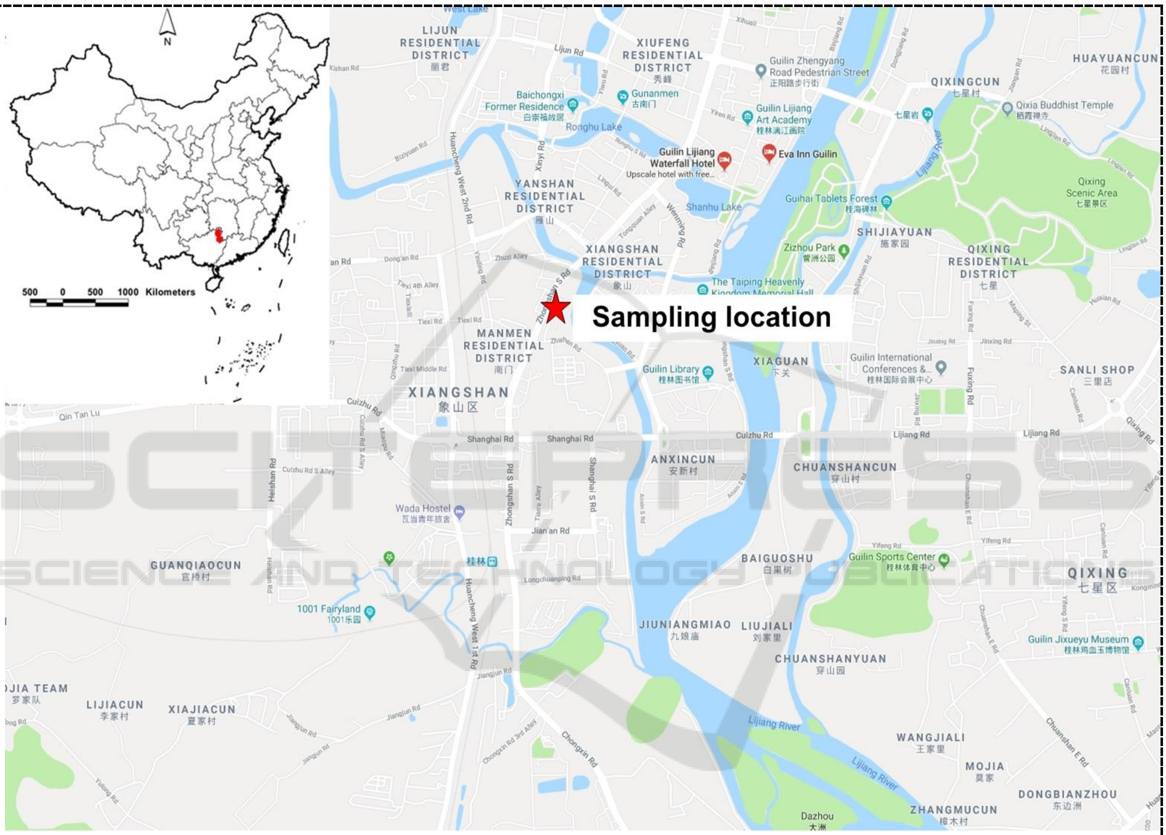

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Figure 1. Sampling locations at Guilin, China.

3. Results and discussion

3.1. Characteristics of meteorological conditions during the monitoring period

Figure 2 illustrates the temporal variations of visibility and major meteorological parameters including wind speed, wind direction, temperature, and relative humidity during the observation period. The temperature ranged from 4 ℃ to 17 ℃ with an average value of 10 ℃, while the relative humidity was in the range of 31%−94% with an average value of 66%. The pressure was 1024.9 hPa. The wind speed was 0.6−3.9 m/s with an average value of 1.7 m/s. The predominant wind direction was north or northeast, accounting for 74.6% of observation days (50 days). There were 29 days of precipitation, and the cumulative precipitation was 54.3 mm. Visibility was 0.80 km to 17.4 km, and the average value is 6.04 km. However, only 5 days had a high visibility above 10 km. In this study, the haze episodes are defined according to the Chinese standard of "Observation and forecasting levels of haze" (QX/T 113-2010), and the details are listed in Table 1. As a result, a total of 34 haze days were observed without the influence of precipitation weather, which can be classified into 1 moderate haze day, 16 slight haze days, 17 mild haze days and 16 non-haze days.

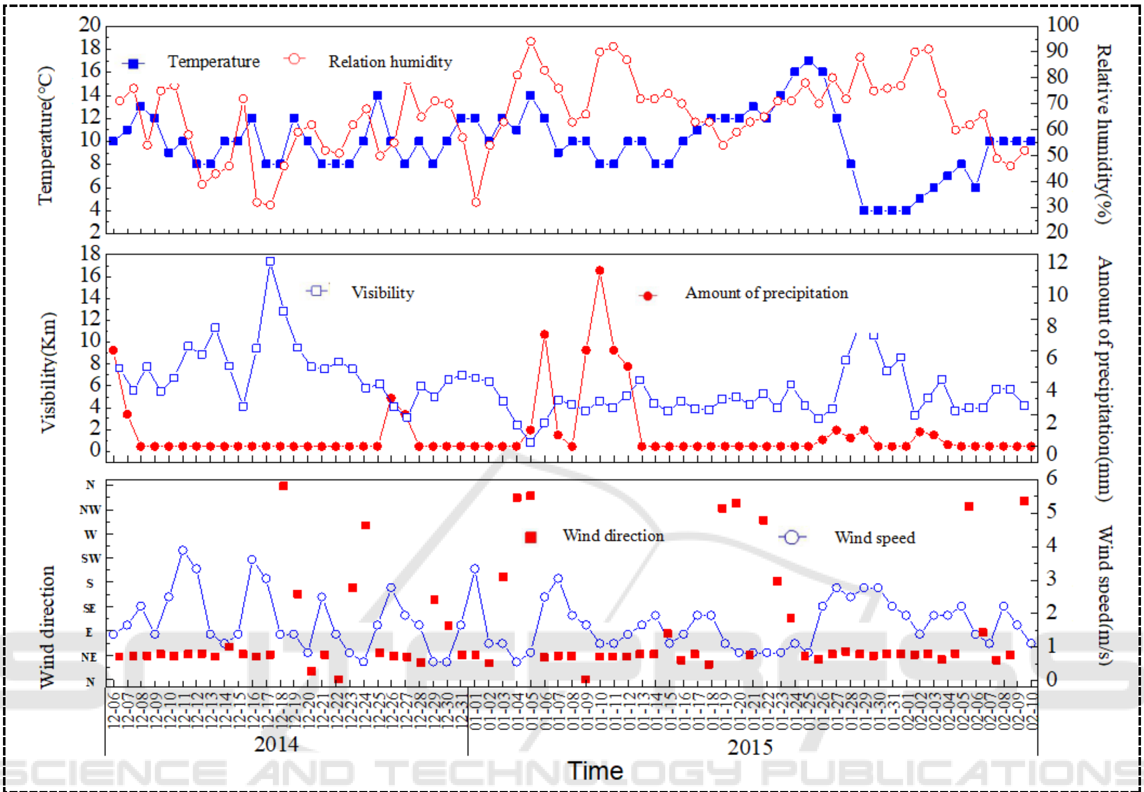

Figure 2. Daily change of meteorological conditions in Guilin during observation period.

Table 1. Classification of haze episodes.

Classification	*VR(km)*	RH(%)	*Weather*	Number
Non-haze	≥10	/	/	16
Mild haze	5～10	RH≤80, or when RH=80～95, PM_1≥65 μg m^{-3} or $PM_{2.5}$≥75 μg m^{-3}	Excluding bad weather, such as rain, snow and dust storms	17
Slight haze	3～5			16
Moderate haze	2～3			1
Serious Haze	<2			/

Observation and forecasting levels of haze (QX/T 113-2010) – National standard (China)

3.2. Water soluble ions in $PM_{2.5}$

Concentrations of water soluble ions in $PM_{2.5}$ during the observation period are shown in Figure 3 and Figure 4. In this study, the continuous period with mean daily $PM_{2.5}$ mass concentration over 75 μg/m^3 is defined as haze episode (Grade II National Ambient Air Quality Standard, GB3095-2012). According to this definition, three typical haze episodes were observed during the observation period, i.e., December 23-26, 2014; December 28, 2014 to January 5, 2015, and January 10-27, 2015. The mass concentration of $PM_{2.5}$ presented a characteristic saw-tooth pattern, indicating the repeatability and complexity of the haze pollution processes.

During the monitoring period, the changes of mass concentrations in NO_3^-, SO_4^{2-} and NH_4^+ were similar to the change of $PM_{2.5}$, exhibiting a saw-tooth pattern. Considering the meteorological factors obtained during December 23−26, 2014, the water absorption capabilities of NO_3^-, SO_4^{2-} and NH_4^+ increased due to the light rain on December 25, and their peak concentrations appeared. As the rainfall was heavier to 2−3 mm on December 26−27, the concentrations of NO_3^-, SO_4^{2-} and NH_4^+ decreased quickly and reached the peak-valley values. During sunny days on Jan 1−2, 2015, the levels of NO_3^- and SO_4^{2-} increased relatively quickly and accumulated in the presence of winter inversion layer. Their peak concentrations appeared on January 4, and the level of SO_4^{2-} reached 37.3 μg/m^3. In addition, the peak concentration of fine PM also achieved. Then, all these substances decreased due to the rainfall on January 5−6. However, the reduction was limited because the rainfall was light. Accumulation of these substances was rebuilt in the cloudy days on January 8−9 and decreased again to the peak-valley value in a rainy day on January 10. Nevertheless, these substances cannot be cleared continuously by rainfall, and were concentrated again in the serious pollution days, which lasted for a long period of 10 days from January 14 to 23. This heavy-polluted process did not end until the rainfall coming on January 27, and the concentrations of NO_3^-, SO_4^{2-} and NH_4^+ decreased correspondingly.

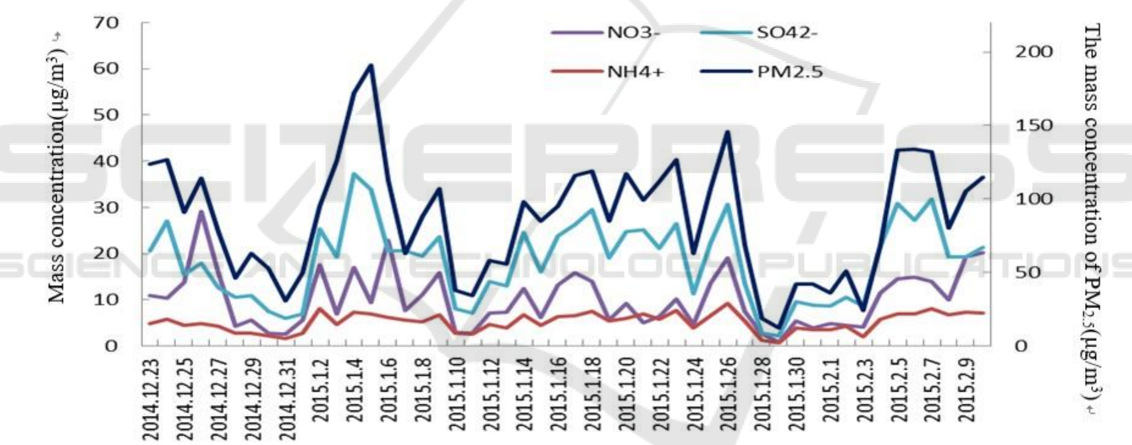

Figure 3. Variations of NO_3^-, SO_4^{2-}, NH_4^+ and $PM_{2.5}$ concentrations during the monitoring period.

The changes of mass concentrations in Cl^-, F^-, Na^+, K^+, Mg^{2+} and Ca^{2+} showed a positive relationship with the change in $PM_{2.5}$, presenting a saw-tooth pattern as well. These water-soluble ions were obviously affected by the weather conditions, especially the rainfall. The changing processes of these ions during the observation period had similar features in comparison with NO_3^- and SO_4^{2-}.

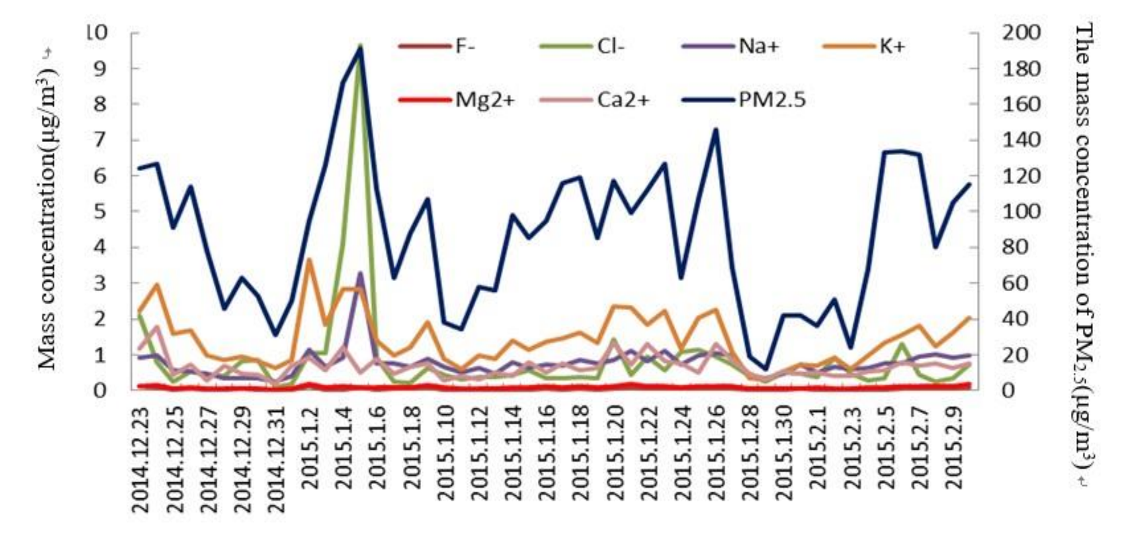

Figure 4. Varitions of Cl^-, F^-, Na^+, K^+, Mg^{2+}, Ca^{2+} and $PM_{2.5}$ concentrations during the monitoring period.

3.3. Effects of pollutant emissions and meteorological factors

The monitoring results showed that rainfall only had a temporary effect on the reduction of NO_3^-, SO_4^{2-} and NH_4^+. Therefore, the pollutant emissions may significantly affect $PM_{2.5}$ pollution. A lower pollutant emission intensity decreased $PM_{2.5}$ concentrations. In fact, a majority of SO_4^{2-} and NO_3^- in $PM_{2.5}$ are produced by oxidation of SO_2 and NO_2, respectively, while NH_4^+ is discharged from the poultry industry, agriculture and vegetation decay. These substances are inorganic PMs generated from the secondary reactions. Due to the Karst landscape in Guilin, the particulates normally contain high concentrations of Ca^{2+}, which has a catalytic effect on oxidation of SO_2 [6, 10]. Furthermore, the formation of SO_4^{2-} from SO_2 is promoted by the coexistence of NO_x on the surface of fine particles in the presence of Ca^{2+} [11]. The relatively higher SO_4^{2-} concentrations were found in aqueous phase of particulate aerosols than NO_3^- and NH_4^+ in this study. The results suggested that a catalytic oxidation pathway of SO_2 to SO_4^{2-} played an important role on the severe winter haze episodes in Guilin. As a result, the local authorities should prioritize the reduction of air pollutant emissions, particularly during the serious haze episodes. Once the generation of secondary inorganic aerosols was controlled, the impact on growth of air PMs could be mitigated.

4. Conclusions

In this work, we investigated the daily variations of $PM_{2.5}$ and water soluble ions along with the meteorological parameters during December 23, 2014 to February 10, 2015 in Guilin, and the factors affecting the formation of haze episodes were discussed. The results showed that 34 haze days occurred during the observation period. SO_4^{2-} was the main water soluble ion in aqueous phase of particulate aerosols in the typical three haze stages, suggesting that the emission of SO_2 significantly contribute to haze formation in winter season in Guilin.

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