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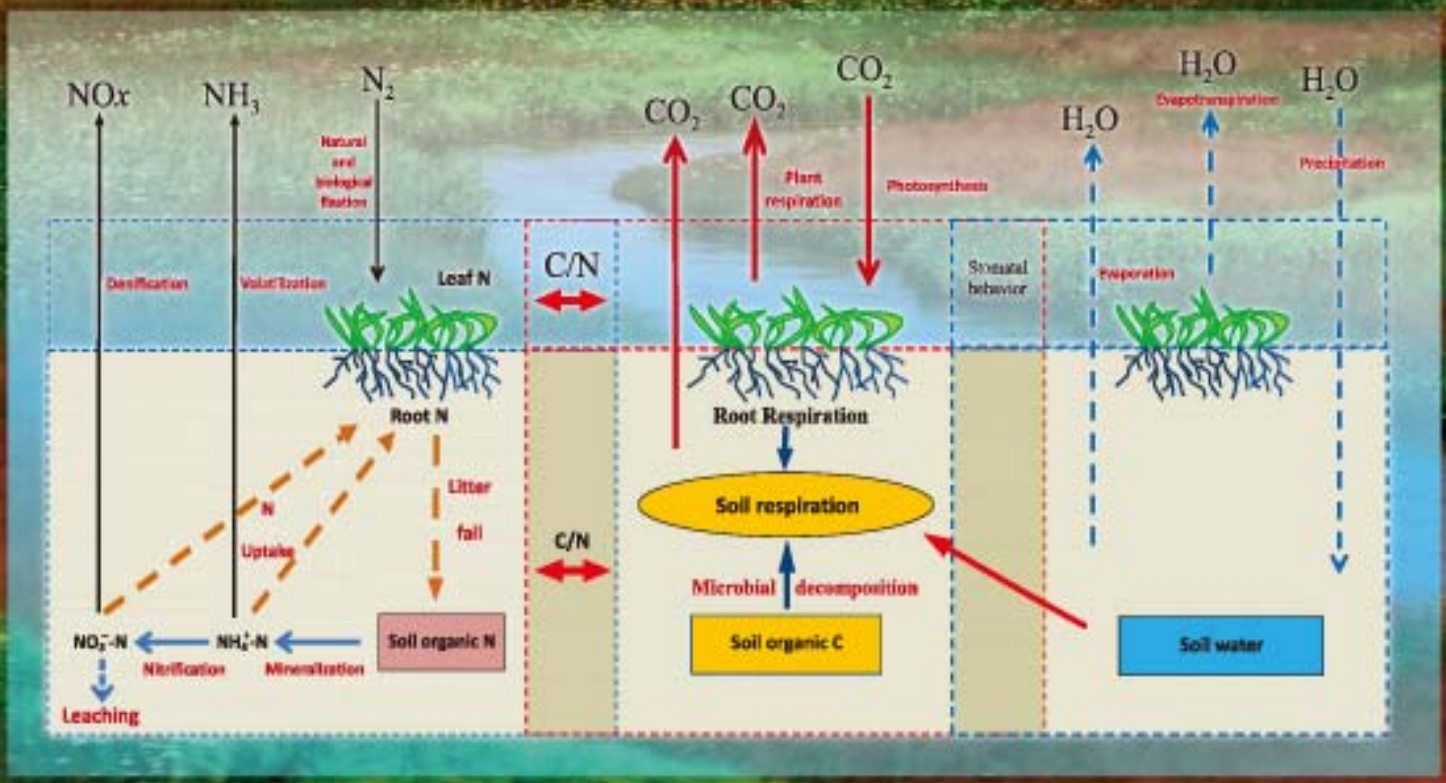


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# CONTENTS

## Aquatic environment



## Atmospheric environment



## Terrestrial environment



## Environmental biology

## Environmental health and toxicology



## Environmental analytical methods



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# Ionic composition of submicron particles ($PM_{1.0}$) during the long-lasting haze period in January 2013 in Wuhan, central China

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ABSTRACT

In January 2013, a long-lasting severe haze episode occurred in Northern and Central China; at its maximum, it covered a land area of approximately 1.4 million $km^2$. In Wuhan, the largest city in Central China, this event was the most severe haze episode in the 21st century. Aerosol samples of submicron particles ($PM_{1.0}$) were collected during the long-lasting haze episode at an urban site and a suburban site in Wuhan to investigate the ion characteristics of $PM_{1.0}$ in this area. The mass concentrations of $PM_{1.0}$ and its water-soluble inorganic ions (WSIIs) were almost at the same levels at two sites, which indicates that $PM_{1.0}$ pollution occurs on a regional scale in Wuhan. WSIIs ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $NO_3^-$ and $SO_4^{2-}$) were the dominant chemical species and constituted up to 48.4% and 47.4% of $PM_{1.0}$ at WD and TH, respectively. The concentrations of $PM_{1.0}$ and WSIIs on haze days were approximately two times higher than on normal days. The ion balance calculations indicate that the particles were more acidic on haze days than on normal days. The results of the back trajectory analysis imply that the high concentrations of $PM_{1.0}$ and its water-soluble inorganic ions may be caused by stagnant weather conditions in Wuhan.

## Introduction

Haze, which is defined by the China Meteorological Agency as a weather phenomenon that leads to visibility < 10 km, is formed by a combination of moisture, dust, smoke, and vapor in the atmosphere. It has attracted much attention in recent years due to its adverse impacts on visibility, human health, and global climate (Chameides et al., 1999; Schichtel et al., 2001; Watson, 2002; Yadav et al., 2003). The formation of haze is often related to stagnant weather conditions and high levels of airborne particles, especially fine particles such as $PM_{2.5}$ and $PM_{1.0}$.

Airborne particles contain a large proportion of water-soluble inorganic ions (WSIIs). WSIIs play an important role in the earth's radiation balance and are also related to particle formation, growth and evolution processes (Wang et al., 2006; Du et al., 2011). Previous studies reported that WSIIs accounted for one-third or more of $PM_{2.5}$ or $PM_{1.0}$ mass in China's urban regions (He et al., 2001; Hu et al. 2002; Shen et al., 2009a). Many studies have been carried out aiming to investigate the ion characteristics of atmospheric particles during haze episodes around the world (Schichtel et al., 2001; Yao et al., 2002; Kang et al., 2004; Sun et al., 2006; Fu et al., 2008; Shen et al., 2009b; Tan et al., 2009; Huang et al., 2011; Yin et al., 2012; Zhang et al., 2012). For example, Kang et al. (2004) found that the highest contributors to the $PM_{2.5}$ mass during a haze

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event in Seoul were major ionic species including $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$. Sun et al. (2006) investigated the chemical characteristics of $PM_{2.5}$ and $PM_{10}$ in several haze-fog episodes in Beijing, China. The air quality during haze-fog episodes was much worse than that during non-haze-fog days. The concentrations of water-soluble ions ($K^+$, $SO_4^{2-}$, and $NO_3^-$) were more than 10 times higher during haze-fog episodes than during non-haze-fog days. Zhang et al. (2012) reported that secondary pollutants ($SO_4^{2-}$, $NO_3^-$, $NH_4^+$, and OC) were the major chemical components of $PM_{2.5}$ in Fuzhou, China, accounting for 69.0%, 55.1%, 63.4%, and 64.9% of the $PM_{2.5}$ mass in summer normal, summer haze, winter normal, and winter haze conditions, respectively.

Particles with different aerodynamic diameters have different impacts on human health because fine particles can penetrate more deeply into the respiratory tract than coarser ones. $PM_{1.0}$ can even penetrate deep into the alveolar regions of the lungs. Furthermore, fine particles contain higher levels of toxic substances, such as lead (Pb), cadmium (Cd), and nickel (Ni), and are more strongly associated with health problems than coarse particles (Lin et al., 2005; Tao et al., 2012). An abundance of research has focused on the chemical components of ambient $PM_{2.5}$ and $PM_{10}$ (Wei et al., 1999; Marcazzan et al., 2001; Cheng et al., 2006; Cao et al., 2009; Tiwari et al., 2009; Wang et al., 2009; Choi et al., 2012). In comparison, much less information has been reported for $PM_{1.0}$ in China (Lee et al., 2006; Shen et al., 2009b; Tao et al., 2012), and even less work has been done to investigate the chemical characteristics of $PM_{1.0}$ during haze episodes. Concerning light scattering and visibility, $PM_{1.0}$ also plays a key role. For example, in a study in Guangzhou, China, it was estimated that $PM_{1.0}$ contributed an average of 76%, 85%, 94% and 93% to light extinction in spring, summer, autumn and winter, respectively (Lin et al., 2013).

Wuhan, the capital of Hubei Province, with an area of 8494 $km^2$ and a population of over 10 million, is the largest city in central China. The study area has a subtropical moist monsoon climate with four distinct seasons. The city is very hot in the summer and is cold in the winter. Because of rapid economic development and urbanization, Wuhan faces serious particulate pollution, and haze days have occurred frequently in recent years because of rapid increases in vehicular traffic, high coal consumption, and intensive steel manufacturing. However, to the best of our knowledge, very limited studies have been conducted to investigate the chemical characteristics of the particles in the atmosphere around Wuhan (Wei et al., 1999; Querol et al., 2006; Qian et al., 2007). No investigation of $PM_{1.0}$ during haze episodes has been done in this area so far. Hence, it is crucial to study the chemical characteristics of $PM_{1.0}$ during haze days in Wuhan to develop effective haze control strategies.

In this study, a field measurement study of $PM_{1.0}$ was carried out simultaneously from January 9 to February 6, 2013, at an urban site and a suburban site in Wuhan City. A long-lasting haze episode, which had not been experienced in this area in the 21st century, was observed during this period. The main objective of this study is to investigate the ion characteristics of $PM_{1.0}$ during a typical haze episode in Wuhan. Here, we first characterize the water-soluble inorganic ions of $PM_{1.0}$ during the typical haze episode and then compare the chemical differences between haze episodes and non-haze days. Finally, we identify the possible causes of the long-lasting haze episode.

## 1 Materials and methods

### 1.1 Sampling sites and sample collection

Air samples were collected at two typical sampling sites, namely, Wu Da and Tian Hong in Wuhan City (**Fig. 1**). The distance between the two sites is approximately 9 km. Wu Da site (30°30′N, 114°21′E) is situated in the Wu-chang district, which represents a commercial-traffic mixed area surrounded by shopping malls, schools, hotels and roads. The sampling was conducted on the rooftop of a building at Wuhan University, approximately 16 m above ground level. Tian Hong site (30°27′N, 114°23′E) is situated at the Environmental Monitoring Station of the Hong-shan District, which is a suburban area. The sampling was carried out on the rooftop of a building at Wuhan Tianhong Instruments Co. Ltd., approximately 15 m above ground level.

The 24 hr air samples were collected almost simultaneously at both sites during an intensive period from 9 January to 6 February, 2013, using a High Volume Cascade Impactor manufactured by BGI Incorporated at a flow rate of 0.9 $m^3$/min at Wu Da site and a High Volume Flow Rate Aerosol and Airborne Dust Sampler (KS-303)

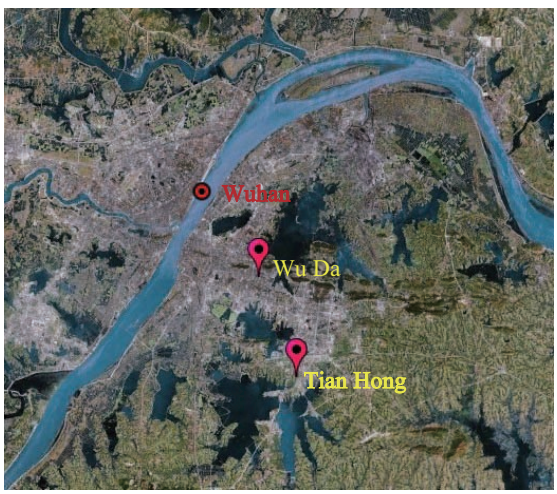


**Fig. 1** Location of sampling sites in Wuhan, China.

manufactured by KÁLMÁN System Ltd. at a flow rate of 0.4 $m^3$/min at Tian Hong site. A total of 54 samples were collected at the two sites. All the samples were collected on quartz fiber filters (QFFs). All QFFs were pre-baked at 450°C for 4 hr to remove residual ions before sampling. Before and after sampling, all filters were weighed gravimetrically using an analytical balance (Mettler Toledo) with a reading precision of 10 μg after stabilizing at constant temperature ((20 ± 1)°C) and humidity (40% ± 1%) for 24 hr. All samples were stored in a refrigerator at –20°C for subsequent analysis.

### 1.2 Chemical analysis and quality control

All filters were cut into four parts after sampling. One quarter of each filter was used to analyze water-soluble inorganic species. A punch (5.06 $cm^2$) of quartz filter was extracted twice with 10 mL ultrapure Milli-Q water (18.2 MΩ·cm) and sonicated for 15 min in an ultrasonic ice-water bath. The total water extracts (20 mL) were filtered through a 0.22 μm pore size filter and then stored in a pre-cleaned HDPE bottle. The cations ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$) and anions ($Cl^-$, $NO_3^-$, and $SO_4^{2-}$) were analyzed by an ion-chromatograph (Metrohm, 883 Basic IC plus). Cations were measured using a Metrosep C4-100 (Metrohm) column with 2 mmol/L sulphuric acid as the eluent. Anions were measured using a Metrosep A supp5-150 (Metrohm) column equipped with a suppressor. The anion eluent was a solution of 3.2 mmol/L $Na_2CO_3$ and 1.0 mmol/L $NaHCO_3$. The detection limits (MDLs) of $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $NO_3^-$ and $SO_4^2$ were 0.01, 0.05, 0.02, 0.04, 0.02, 0.03, 0.02 and 0.02 μg/$m^3$, respectively.

### 1.3 Meteorological data

Hourly meteorological data, including wind speed, temperature, relative humidity, dew point, pressure, and visibility, were collected from Weather Underground (http://www.wunderground.com/).

### 1.4 Back trajectories

Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4), offered by the National Oceanic and Atmospheric Administration (NOAA), was used to calculate trajectories. Trajectories tracing back 3 days (72 hr) were calculated four times a day (0, 6, 12, 18 UTC). Each trajectory was estimated at 100 m above ground level and was cross-checked at 500 m and 1000 m above ground level. To determine the pollutant sources, all the air mass back trajectories were clustered into three types by HYSPLIT 4.8.

## 2 Results and discussion

### 2.1 Haze episodes and meteorological conditions

Central China, Jing-Jin-Ji (Beijing-Tianjin-Hebei), and East China were blanketed by haze in most days of January 2013. During this period, Wuhan suffered a long-lasting haze episode from January 6 to 30, 2013. The Air Quality Index (AQI), ranged from 127 to 414 with a mean value of 215, which is nearly 2 times greater than the limit of China's Air Quality Standards Grade II (100). The primary pollutant during this period was $PM_{2.5}$.

**Figure 2** shows the hourly meteorological parameters, including visibility, relative humidity (RH), temperature, surface wind direction and wind speed, in Wuhan from January 1 to February 6, 2013. The air quality was good on the normal days between January 1 and January 6. The AQI ranged from 52 to 127, which indicates good or light air pollution. The visibility was above 10 km, along with

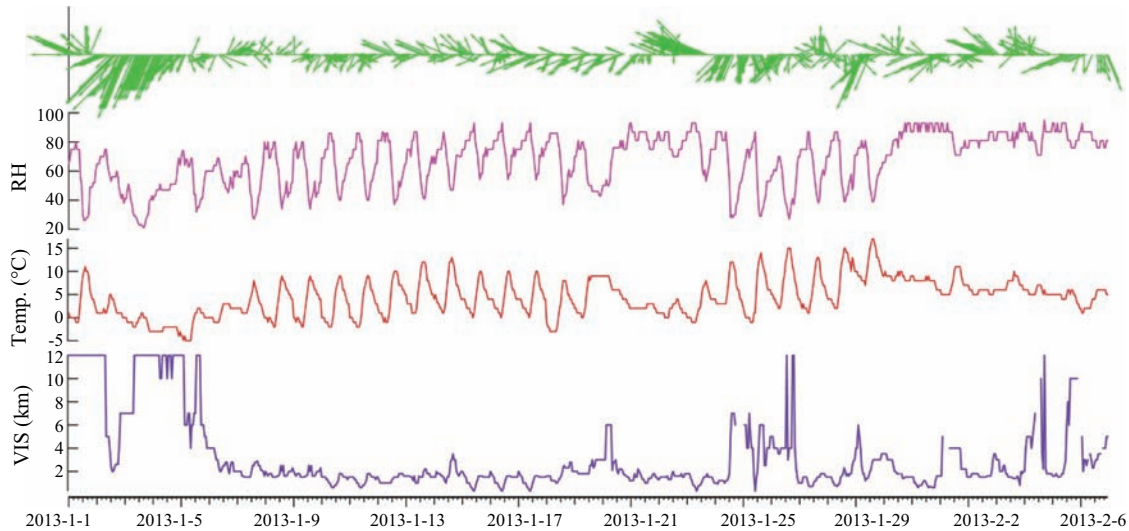


**Fig. 2** Hourly meteorological parameters, including visibility (VIS), relative humidity (RH), temperature, surface wind direction and wind speed in Wuhan from January 1 to February 6, 2013.

relatively low temperatures. The dominant wind direction was northeast with high wind speeds during this period. From January 6 to January 30, the AQIs were between 127 and 414 with a mean value of 241, indicating severe or hazardous air pollution. We defined these days as haze days. The visibility quickly decreased below 10 km, and even reduced to 300 m on January 15, 16, 17, 23 and 25. The wind speeds were light and in the southeast and northeast directions. The mean hourly wind speeds were 2 m/sec on most of the days, which produced unfavorable conditions for dispersing air pollutants horizontally. From the night of January 30, it began to rain occasionally in Wuhan. Because the light rain could not clear out the particulate matter immediately, the visibility was still relatively low on January 31. From January 31 to February 6, the AQI decreased gradually from 156 to 50. We defined these days as normal days. The visibility increased above 10 km on January 4 and 5. The temperature decreased in comparison to haze days. The dominant wind directions changed to southeast and more northeast with high wind speeds.

### 2.2 Ionic concentrations and composition

**Table 1** presents the average mass concentrations of $PM_{1.0}$ and its major ion compositions on all days, haze days and normal days at the sampling sites. The average $PM_{1.0}$ mass concentrations were 117.20 ± 49.36 (Wu Da) and 123.14 ± 44.77 μg/m$^3$ (Tian Hong), which exceeds the 24-hour China NAAQS for $PM_{2.5}$ (75 μg/m$^3$), and WSIIs were 56.70 ± 23.20 and 58.32 ± 23.95 μg/m$^3$ at Wu Da and Tian Hong, respectively, on all sampling days. WSIIs accounted for 48.4% and 47.4% of $PM_{1.0}$ mass at Wu Da and Tian Hong, respectively. The results indicated that WSIIs were the major components of $PM_{1.0}$ in Wuhan. Previous studies showed that WSIIs accounted for one third or more of the $PM_{2.5}$ or $PM_{1.0}$ mass in Chinese urban regions (He et al., 2001; Hu et al., 2002; Wang et al., 2006; Shen et al., 2009a). The average concentrations of WSIIs decreased in the order $SO_4^{2-} > NO_3^- > NH_4^+ > Cl^- > K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ at both sites. Our observation results demonstrated that $SO_4^{2-}$, $NO_3^-$, $NH_4^+$ and $Cl^-$ were the major ionic species, while the $Ca^{2+}$ and $Mg^{2+}$ concentrations exhibited the lowest concentrations in $PM_{1.0}$, suggesting that $Ca^{2+}$ and $Mg^{2+}$ are only abundant in coarse particles. It is worth noting that the mass concentrations of $PM_{1.0}$ and its major ion components were at the same level at both sites, which supports the idea of widespread, regional pollution of fine particles.

At Wu Da, the concentrations of $PM_{1.0}$ were 138.82 ± 36.53 μg/m$^3$ on haze days and 55.44 ± 18.02 μg/m$^3$ on normal days. The total detected concentrations of WSIIs were 64.57 ± 21.32 μg/m$^3$ on haze days and 34.23 ± 9.87 μg/m$^3$ on normal days. The concentrations of $PM_{1.0}$ and WSIIs on haze days were approximately two times higher than on normal days, suggesting that the chemical formation of $PM_{1.0}$ and WSIIs may enhance the accumulation of pollutants under unfavorable weather condition on the haze days. For the individual ionic species, the mean concentrations for five cations, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$, were 1.42 ± 0.30, 11.68 ± 0.39, 1.53 ± 0.58, 0.05 ± 0.03, and 0.17 ± 0.012 μg/m$^3$ on haze days, which is 1.14–5.42 times higher than those on normal days. The mean concentrations for three anions, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$, were 1.93 ± 0.88, 23.97 ± 9.82, and 24.11 ± 6.92 μg/m$^3$ on haze days, 1.67–2.15 times higher than those on normal days. Our observation results demonstrated that $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$ were the three major species in $PM_{1.0}$, contributing 92.5% and 89.1% of the total WSIIs on haze days and normal days, respectively.

Like Wu Da site, the average mass concentrations of $PM_{1.0}$ and its major ion composition showed the same characteristics at the Tian Hong site, and exhibited much higher concentrations in haze days than those in normal days. The concentrations of $PM_{1.0}$ were 140.26 ± 36.85 μg/m$^3$ during haze days, increased by a factor of approximately 1.79 compared to those on normal days. The

**Table 1** Average mass concentrations of $PM_{1.0}$, and its major ion composition in all days, haze days and normal days at sampling sites (unit: μg/m$^3$)

| Site | Sampling day | | $PM_{1.0}$ | $Na^+$ | $NH_4^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Wu Da | All days ($n$ = 27)[a] | mean | 117.20 | 1.30 | 9.96 | 1.39 | 0.05 | 0.14 | 1.72 | 20.65 | 21.61 |
| | | SD[b] | 49.36 | 0.30 | 4.58 | 0.58 | 0.03 | 0.13 | 0.88 | 10.34 | 7.57 |
| | Haze days ($n$ = 20) | mean | 138.82 | 1.42 | 11.68 | 1.53 | 0.05 | 0.17 | 1.93 | 23.97 | 24.11 |
| | | SD | 36.53 | 0.30 | 3.90 | 0.58 | 0.03 | 0.12 | 0.88 | 9.82 | 6.92 |
| | Normal days ($n$ = 7) | mean | 55.44 | 1.25 | 5.02 | 0.99 | 0.03 | 0.03 | 1.12 | 11.16 | 14.47 |
| | | SD | 18.02 | 0.29 | 2.10 | 0.41 | 0.01 | 0.04 | 0.56 | 4.06 | 4.02 |
| Tian Hong | All days ($n$ = 27) | mean | 123.14 | 0.33 | 11.65 | 1.34 | 0.05 | 0.30 | 1.76 | 21.59 | 21.29 |
| | | SD | 44.77 | 0.17 | 4.72 | 0.49 | 0.02 | 0.52 | 0.76 | 10.45 | 8.45 |
| | Haze days ($n$ = 20) | mean | 140.26 | 0.38 | 13.42 | 1.47 | 0.06 | 0.33 | 1.84 | 24.34 | 23.90 |
| | | SD | 36.85 | 0.15 | 4.05 | 0.41 | 0.02 | 0.33 | 0.78 | 9.78 | 7.10 |
| | Normal days ($n$ = 7) | mean | 78.22 | 0.22 | 6.84 | 0.99 | 0.03 | 0.03 | 1.38 | 14.07 | 14.95 |
| | | SD | 33.29 | 0.13 | 3.06 | 0.58 | 0.02 | 0.01 | 0.52 | 9.71 | 8.74 |

SD: standard deviation for Arithmetic mean.

total concentrations of WSIIs detected were 65.78 ± 21.22 μg/m$^3$ on haze days and 38.83 ± 22.12 μg/m$^3$ on normal days. For each ionic species, the mean concentrations of $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$ were 0.38 ± 0.15, 13.42 ± 4.05, 1.47 ± 0.41, 0.06 ± 0.02, and 0.33 ± 0.33 μg/m$^3$ on haze days, and 0.22 ± 0.13, 6.84 ± 3.06, 0.99 ± 0.58, 0.03 ± 0.02, and 0.03 ± 0.01 μg/m$^3$ on normal days, respectively. The mean concentrations for $Cl^-$, $NO_3^-$, and $SO_4^{2-}$ were 1.84 ± 0.78, 24.34 ± 9.78, and 23.90 ± 7.10 μg/m$^3$ on haze days, and 1.38 ± 0.52, 14.07 ± 0.91, and 14.95 ± 8.75 μg/m$^3$ on normal days. The results showed that $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$ were the most abundant ions in $PM_{1.0}$, accounting for 93.7% and 92.8% of the total WSIIs on haze days and normal days, respectively.

### 2.3 Acidity of $PM_{1.0}$

The validity of the WSIIs could be verified through anion (*A*) and cation (*C*) balances (Chow et al., 1994). The anion and cation microequivalents for the $PM_{1.0}$ samples were calculated as follows:

$$A_{(\text{anion microequivalents})} = Cl^-/35.5 + SO_4^{2-}/48 + NO_3^-/62 \quad (1)$$

$$C_{(\text{cation microequivalents})} = Na^+/23 + NH_4^+/18 + K^+/39 + Mg^{2+}/12 + Ca^{2+}/20 + NH_4^+/18 \quad (2)$$

The average ratios of molar equivalents (eq/m$^3$) of anions ($Cl^-$, $SO_4^{2-}$, and $NO_3^-$) to cations ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$) (*A/C*) were 1.31 ± 0.10 and 1.20 ± 0.24 at Wu Da and Tian Hong, respectively. The average *A/C* ratios were close to 1 and strong correlations between anion and cation equivalents were observed at both sites, indicating that the eight ionic species were the major ions in $PM_1$. We noted that the *A/C* ratios were also greater than 1, which may be due to a deficiency of $H^+$ in the calculation and/or to $NH_4^+$ being converted into the gaseous phase.

The *A/C* ratio is also a good indicator for studying the acidity of the aerosols. **Figure 3** shows a strong correlation between the anion and cation equivalents during haze days and normal days at Wu Da and Tian Hong, indicating that the relationship between measured cations and anions remained constant during neutralization (Lee and Hieu, 2013). At Wu Da the slope of the regression equation on haze days was higher (1.26) than on normal days (1.15). Comparatively, the slope of the regression equation on haze days was also higher (1.22) than on normal days (0.99) at Tian Hong, which implies that the particles were more acidic on haze days than on normal days.

### 2.4 Sources of WSIIs

#### 2.4.1 Source identification by chemical species/ratios

$SO_4^{2-}$, $NO_3^-$, and $NH_4^+$ represent secondary pollution, which results from the transformation of their precursors $SO_2$, $NO_2$, and $NH_3$, respectively. $Na^+$, $Mg^{2+}$, and $Ca^{2+}$ mainly originate from crustal sources, such as re-suspended road dust, soil dust, and construction dust. $Cl^-$ is usually considered to be from coal combustion, and $K^+$ comes from biomass burning (He et al., 2001; Duan et al., 2004; Wang et al., 2005). According to the different sources of WSIIs, these WSIIs were classified into 4 groups, which were representative of crust ($Na^+$, $Mg^{2+}$, and $Ca^{2+}$), secondary sources ($SO_4^{2-}$, $NO_3^-$, and $NH_4^+$), coal combustion ($Cl^-$), and biomass burning ($K^+$). The relative contributions of secondary sources ($Na^+$, $Mg^{2+}$, and $Ca^{2+}$), crust ($Na^+$, $Mg^{2+}$, and $Ca^{2+}$), coal combustion ($Cl^-$), and biomass burning ($K^+$) to $PM_{1.0}$ were 47.08%, 1.53%, 1.56%, and 1.30% at Wu Da, respectively, and 45.53%, 0.58%, 1.55%, and 0.58% at Tian Hong, respectively. The results indicated that secondary pollution played an important role in $PM_{1.0}$ at both sites in Wuhan.

$NO_2$ emissions from vehicle exhaust are the main precursor to $NO_3^-$, while $SO_2$ released from coal combustion is a large contributor to $SO_4^{2-}$ in the atmosphere. Therefore, the ratio of $NO_3^-/SO_4^{2-}$ has been used as an indicator of the relative contribution of mobile versus stationary sources of nitrogen and sulphur in the atmosphere. Previous studies showed that high $NO_3^-/SO_4^{2-}$ ratios (> 1) occurred when

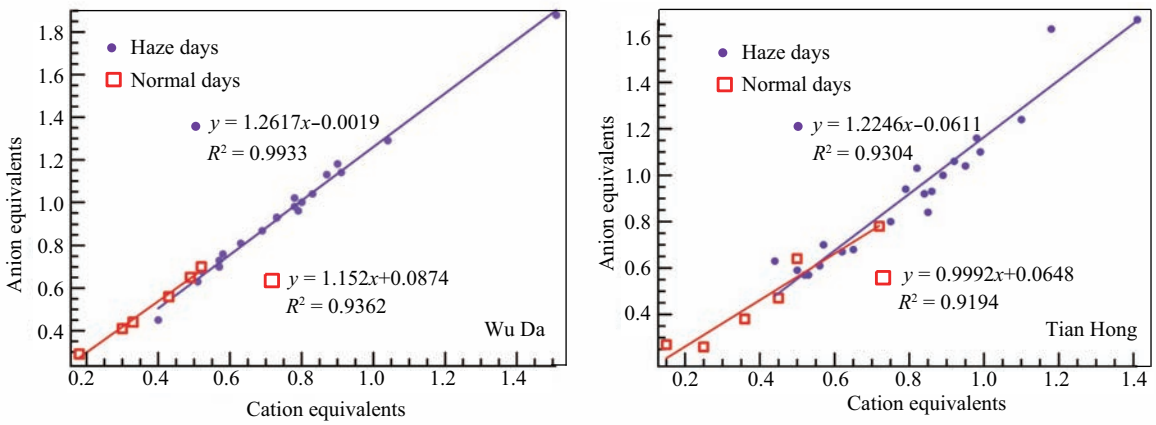


**Fig. 3** Correlations between the anion and cation equivalents during haze days and normal days at Wu Da and Tian Hong, respectively.

the influence of motor vehicle emissions exceeds that from coal combustion (Arimoto et al., 1996). The ratios of $NO_3^-/SO_4^{2-}$ were almost at the same at Wu Da and Tian Hong. The ratio was 0.98 on haze days and 0.78 on normal days at Wu Da and was 1.01 on haze days on 0.91 on normal days at Tian Hong. Compared to other cities, the ratio of $NO_3^-/SO_4^{2-}$ was much higher than in Guiyang City (0.15), an important industrial base in China (Xiao and Liu, 2004), much lower than in Southern California (where no coal was used) (2.0–5.0) (Kim et al., 2000), and comparable to Guangzhou during haze days (0.79) (Tan et al., 2009). The relatively low $NO_3^-/SO_4^{2-}$ ratio (< 1) in the atmosphere of Wuhan suggests that stationary sources (coal combustion) are still the dominant sources of pollutants in Wuhan. However, the influence of vehicle exhaust should not be neglected due to the rapid increase in the number of motor vehicles in Wuhan.

### 2.4.2 Air mass parcels and potential source regions

To identify the transport pathways of air masses from different potential source regions, backward air trajectory analysis was carried out using the HYSPLIT 4.8 model. Three typical types of trajectories were classified using the Hierarchical Clustering Method (Ward, 1963; Stohl, 1998) **(Fig. 4)**. The typical air mass patterns at Wu Da and Tian Hong were the same because the distance between the two sites is only 9 km. The proportions of air masses associated with each track and the corresponding concentrations of air pollutants are shown in **Table 2**.

The E-type trajectory, which prevailed from January 11 to 22 and January 27 to 30, 2013, cycled around Hubei Province with very low transport speeds, and 60% of the air masses came from this trajectory (**Fig. 4**). $PM_{1.0}$ and its component ions showed high concentrations. For example, the concentrations of $PM_{1.0}$, $SO_4^{2-}$, and $NO_3^-$ were 135.53, 23.11, and 23.0 μg/m$^3$ at Wu Da site, and 137.70, 23.61, and 25.29 μg/m$^3$ at Tian Hong site. During this period, stagnant weather conditions dominated in Wuhan, which was unfavorable for the dispersion of air pollutants.

The NW-type (January 22 to 26), accounting for 16% of all trajectories, initiated from Shanxi Province, and travelled across Henan Province prior to reaching Wuhan **(Fig. 4)**. $PM_{1.0}$ and its component ions also exhibited relatively high concentrations. For example, the concentrations of $PM_{1.0}$, $SO_4^{2-}$, and $Cl^-$ were 135.35, 25.73, and 1.93 μg/m$^3$ at the WD site and 125.59, 22.04, and 1.58 μg/m$^3$ at the Tian Hong site. Shanxi Province is the most important energy (such as coal and coke) and industrial (such as steel) base in China and has provided abundant coal and electronic power to ensure economic development in China (Zhang et al., 2009). The high concentrations of $PM_{1.0}$ and its ions may be influenced by Shanxi Province.

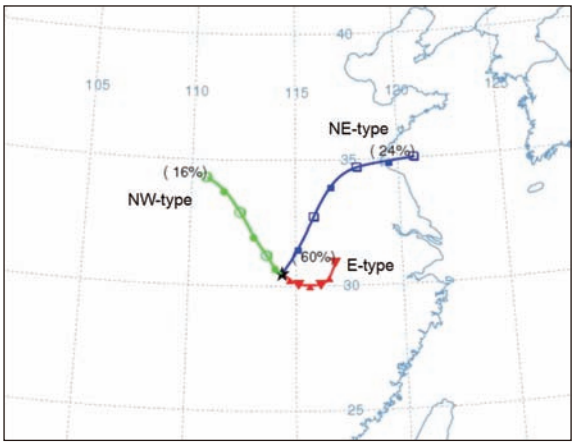


**Fig. 4** Three typical back trajectories at Wu Da site from January 9 to February 6, 2013.

The NE-type trajectory (February 1 to 6), accounting for 24% of all trajectories, originated from the Yellow Sea, where relatively few anthropogenic activities exist, passing over Jiangsu and Anhui Provinces with high transport speed **(Fig. 4)**. $PM_{1.0}$ and its component ions exhibited the lowest concentrations, which may be due to the high speed air from the Yellow Sea. The air mass with high speed would dilute the air pollutants in Wuhan. Furthermore, it rained occasionally during this period, which can wash particles from the atmosphere.

## 3 Conclusions

In this study, the water-soluble ionic compositions of $PM_{1.0}$ were identified during a long-lasting haze period in January 2003 and on normal days in February 2003 at Wu Da and Tian Hong in Wuhan. The concentration

**Table 2** Proportion of air masses associated with each typical trajectory and the corresponding concentrations of $PM_{1.0}$ and its ionic species (unit: μg/m$^3$)

| Site | Air mass (proportion) | $PM_{1.0}$ | $Na^+$ | $NH_4^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Wu Da | E-type (60%) | 135.53 | 1.26 | 11.10 | 1.56 | 0.05 | 0.16 | 1.94 | 23.00 | 23.11 |
| | NW-type (16%) | 135.35 | 1.20 | 12.07 | 1.41 | 0.06 | 0.20 | 1.93 | 24.09 | 25.73 |
| | NE-type (24%) | 53.20 | 1.47 | 5.14 | 0.91 | 0.03 | 0.03 | 0.98 | 11.50 | 14.16 |
| Tian Hong | E-type (60%) | 137.70 | 0.39 | 13.07 | 1.56 | 0.06 | 0.44 | 2.02 | 25.29 | 23.61 |
| | NW-type (16%) | 125.59 | 0.30 | 11.45 | 1.15 | 0.06 | 0.23 | 1.58 | 18.73 | 22.04 |
| | NE-type (24%) | 84.31 | 0.20 | 8.13 | 0.90 | 0.02 | 0.03 | 1.20 | 13.72 | 14.92 |

levels of $PM_{1.0}$ and its ions were similar at the two sites, demonstrating regional-level pollution of $PM_{1.0}$. WSIIs ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $NO_3^-$ and $SO_4^{2-}$) were the dominant chemical species and constituted up to 48.4% and 47.4% of $PM_{1.0}$ at Wu Da and Tian Hong, respectively. The concentrations of $PM_{1.0}$ and its ionic species were higher on haze days than on normal days, indicating that air pollution is very serious on haze days. The average *A/C* ratios were close to 1 and strong correlations between anion and cation equivalents were observed at both sites, indicating that the eight ionic species were the major ions in PM1. Ion balance calculations indicated that the particles were more acidic on haze days compared to normal days. The ratios of $NO_3^-/SO_4^{2-}$ indicated that mobile sources, such as vehicle emissions, were more important on haze days than normal days. Back trajectory analysis results implied that the high concentrations of $PM_{1.0}$ and its ions may result from stagnant weather conditions in Wuhan.

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