Characteristics of the water-soluble components of aerosol particles in Hefei, China

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ABSTRACT

Size-classified daily aerosol mass concentrations and concentrations of water-soluble inorganic ions were measured in Hefei, China, in four representative months between September 2012 and August 2013. An annual average mass concentration of 169.09 $\mu g/m^3$ for total suspended particulate (TSP) was measured using an Andersen Mark-II cascade impactor. The seasonal average mass concentration was highest in winter (234.73 $\mu g/m^3$) and lowest in summer (91.71 $\mu g/m^3$). Water-soluble ions accounted for 59.49%, 32.90%, 48.62% and 37.08% of the aerosol mass concentration in winter, spring, summer, and fall, respectively, which indicated that ionic species were the primary constituents of the atmospheric aerosols. The four most abundant ions were NO_3^-, SO_4^{2-}, Ca^{2+} and NH_4^+. With the exception of Ca^{2+}, the mass concentrations of water-soluble ions were in an intermediate range compared with the levels for other Chinese cities. Sulfate, nitrate, and ammonium were the dominant fine-particle species, which were bimodally distributed in spring, summer and fall; however, the size distribution became unimodal in winter, with a peak at 1.1–2.1 μm. The Ca^{2+} peak occurred at approximately 4.7–5.8 μm in all seasons. The cation to anion ratio was close to 1.4, which suggested that the aerosol particles were alkalescent in Hefei. The average NO_3^-/SO_4^{2-} mass ratio was 1.10 in Hefei, which indicated that mobile source emissions were predominant. Significant positive correlation coefficients between the concentrations of NH_4^+ and SO_4^{2-}, NH_4^+ and NO_3^-, SO_4^{2-} and NO_3^-, and Mg^{2+} and Ca^{2+} were also indicated, suggesting that aerosol particles may be present as $(NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3.

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Introduction

Aerosols, which comprise suspended particulate matter in air with diverse physical and chemical attributes, are a major factor in global climatic fluctuations and air pollution.

Aerosols can also have an impact on the climate through the absorption and scattering of solar radiation (Penner et al., 1994), altering the radiation budget and affecting radiative forcing (Alpert et al., 1998; Satheesh and Moorthy, 2005). In addition, aerosols change the size and density of cloud

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droplets, thus modifying cloud albedo and lifetime, and precipitation (Twomey et al., 1984; Kaufman and Nakajima, 1993). Because of their role in light extinction, aerosol particles are responsible for a reduction in visibility that can affect traffic (National Research Council, 1993). The exact effects of aerosols depend strongly on their size distribution, chemical composition, and mass concentration, which are related to the complex sources of aerosol, including local primary aerosols, secondary aerosols and remote transport. Thus, detailed information on aerosol chemical and physical properties is important for aerosol studies.

Atmospheric aerosols contain water-soluble inorganic compounds, organic carbon, elemental carbon and metals. Among these components, water-soluble components, such as sulfate, nitrate, ammonium, and chloride, are of great concern in the urban atmosphere because they control the degree of acidity of the aerosols and the impact on environmental acidification. Nitrate, sulfate, and ammonium are the primary compounds that define secondary aerosols (Kadowaki, 1976; Hara et al., 1983). To investigate the effect of air pollutants on the natural environment and ecological systems, we must measure the dry deposition of particles and analyze their water-soluble components, which are related to the formation, growth and evolution of aerosol particles (Wang et al., 2006a,2006b; Du et al., 2011). Many studies have focused on the characteristics of water-soluble components. Chemical species and the size distribution of water-soluble ions in atmospheric aerosols have been investigated in various countries, including Japan (Takeuchi et al., 2004), Egypt (Khoder and Hassan, 2008), Korea (Park et al., 2013) and Italy (Contini et al., 2014). In China, research on water-soluble components of aerosol particles began in the early 1990s (Wu and Chen, 1994; Wu et al., 1994; Wu, 1995). More recently, because of the deterioration of air quality in China, the characteristics of water-soluble components of the atmospheric aerosols have been studied in many Chinese cities (Wang et al., 2003, 2012, 2014a,2014b; Lai et al., 2007; Xiao and Liu, 2004; Hu et al., 2014; Fan et al., 2014; Cheng et al., 2014; Wu et al., 2006).

Hefei City, the capital of Anhui Province, is located in the upper reaches of the Yangtze Delta in China. The city has a population of 4.86 million and covers an area of 11,408 km^2. Anhui Province is located in the transitional region between the temperate and subtropical zones of China and is one of the most important agricultural provinces in the country. The recent rapid increase in agricultural activity and urbanization has had a substantial impact on the atmospheric aerosol and air quality in Anhui, especially in Hefei. Many studies have focused on Hefei City to determine the mechanisms influencing the atmospheric aerosol concentrations. Previous studies have indicated that the number of foggy days have decreased, although the duration of fog events has increased in Hefei (Shi et al., 2008; Wei et al., 2012). Furthermore, the extent of haze and aerosol has expanded considerably in the last 10 years (Zhang et al., 2010; Deng et al., 2012), and the acidity of rain has also increased in Hefei (Qiu et al., 2009). The chemical composition of precipitation in Hefei was previously investigated from April to September in 2010; the major ions were found to be SO_4^{2-}, NH_4^+, and Ca^{2+} (Tang et al., 2012). Due to the variety of sources, atmospheric aerosol particles are highly dynamic. However, little information is available with regard to aerosol chemical characteristics and size distributions in Hefei.

In this study, the aerosol size distributions and mass concentrations were examined. Additionally, the concentrations of water-soluble ions (NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-}, and NO_2^-) were evaluated. A period of approximately 1 week in each season was selected for aerosol sampling between September 2012 and August 2013. The objectives of this study were to characterize both the size distributions of aerosols and the concentrations of water-soluble species in the capital of Anhui Province in China.

1. Materials and methods

1.1. Sampling site

The sampling site was located on the roof of an office building of the Anhui Meteorological Bureau (31.87°N, 117.23°E, 82 m asl) (Fig. 1). The site was located 10 km west of the downtown area of Hefei City and was surrounded by residential areas (i.e., no industry). An Andersen Mark-II cascade impactor (FA-3 model, Kangjie Company, China) was installed on the top-floor balcony of the Yunshui building (15 m agl). The observation period was between September 2012 and August 2013. During this period, we selected a period of approximately 1 week for aerosol sampling in each season. A total of 38 samples were collected. Only 24 samples were saved after a quality assurance review. The other samples were discarded on the basis of the observation records, including the sampler condition, flow rate of the pump, and the appearance of the membrane. Sampling dates and weather conditions, as provided by the Hefei Meteorological Bureau, are listed in Table 1.

1.2. Sampling methods

The aerosol mass concentrations were measured using an Andersen Mark-II cascade impactor (FA-3 model, Kangjie
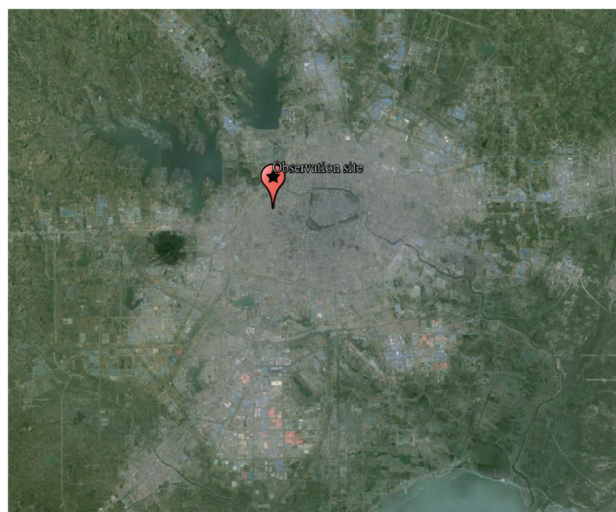

Fig. 1 – Map showing the location of the observation site in Hefei City.

Table 1 – Sampling dates and weather conditions.

Number	Date	Weather phenomenon	Mean visibility (km)	Mean relative humidity (%)
1	Sep. 27, 2012	Mist, haze,	7.00	75.75
2	Oct. 10, 2012	Mist, haze	4.50	58.00
3	Oct. 18, 2012	Mist, haze	7.00	68.25
4	Oct. 19, 2013	Haze	8.50	55.75
5	Jan. 14, 2013	Fog, mist	1.03	97.50
6	Jan. 16, 2013	Mist	3.25	76.00
7	Jan. 17, 2013	Mist, haze	3.50	75.50
8	Jan. 18, 2013	Mist	8.50	70.25
9	Jan. 19, 2013	Mist, haze	6.50	66.75
10	Apr. 09, 2013	Clear	12.00	29.25
11	Apr. 10, 2013	Clear	12.25	40.00
12	Apr. 11, 2013	Clear	13.00	41.75
13	Apr. 12, 2013	Mist, haze	10.75	53.75
14	Apr. 14, 2013	Clear	11.00	58.25
15	Apr. 16, 2013	Clear	12.25	61.25
16	Jun. 15, 2013	Mist, haze	6.75	82.50
17	Jun. 16, 2013	Mist, haze	9.00	81.25
18	Jul. 09, 2013	Clear	12.75	76.50
19	Jul. 10, 2013	Clear	15.25	74.00
20	Jul. 11, 2013	Clear	14.00	73.50
21	Jul. 12, 2013	Clear	12.25	74.50
22	Aug. 05, 2013	Clear	12.50	74.25
23	Aug. 06, 2013	Clear	14.00	64.75
24	Aug. 07, 2013	Clear	14.00	63.75

company, China). The principles of operation for the instrument have been reported in the literature (Wang et al., 2010). The Andersen Mark-II cascade impactor collected aerosol particles in nine size bins; the mass concentration of each level was determined using Teflon membranes. The aerodynamic cutoff points at a flow rate of 28.3 L/min were as follows: ≥9.0, 9.0–5.8, 5.8–4.7, 4.7–3.3, 3.3–2.1, 2.1–1.1, 1.1–0.65, 0.65–0.43, and ≤0.43 μm. The aerosols were continuously collected over a 24-hr period from 8:00 am to 8:00 am the following day. The membranes were weighed using a MX-5 microbalance (MX-5 microbalance, Mettler Toledo, Switzerland) following a constant temperature and humidity treatment both before and after sampling. The microbalance was calibrated using standard weights. The weight difference before and after sampling was considered to represent the particle weight. The membranes were refrigerated and stored in the dark prior to analyzing the water-soluble ion contents of the particles.

1.3. Analytical methods for water-soluble ions

Water-soluble ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, and NO_2^-) were measured using a 850 ion chromatograph (850 ion chromatograph, Metrohm, Switzerland). The chromatograph includes a column oven, a conductivity detector and an 858

auto-injector with a soft workstation employing MagIC Net software (Metrohm, Switzerland). The columns included a Metrosep C 4 150/4.0 separation column and a Metrosep A Supp 5 150/4.0 separation column. The eluent was 3.2 mmol/L Na_2CO_3 + 1.0 mmol/L $NaHCO_3$ for anions and 1.7 mmol/L HNO_3 + 0.7 mmol/L pyridine carboxylic acid for cations. The column temperature was 30 °C, the flow rate was 1.0 mL/min, and the injection volume was 20 μL. Solution preparation and dilution used ultra-pure water with a resistivity of 18.2 MΩ.

2. Results and discussion

2.1. Ionic concentrations in total suspended particulate

The ion concentrations measured in the sampled aerosol particles in Hefei are presented in Table 2. The annual average total suspended particulate (TSP) mass concentration was 169.09 μg/m³, and the seasonal average mass concentration was highest in winter (234.73 μg/m³) and lowest in summer (91.71 μg/m³). Water-soluble ions accounted for 45.41% of the average aerosol mass concentration, with seasonal values of 59.49% (winter), 32.90% (spring), 48.62% (summer) and 37.08%

Table 2 – Ion concentrations in total suspended particulate (TSP) during all four seasons in Hefei (unit: μg/m³).

	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Aerosol mass
Winter	1.17	21.35	1.92	15.79	1.00	3.62	0.55	50.58	40.10	234.73
Spring	1.29	5.13	1.16	13.96	0.82	1.77	0.43	11.51	13.78	162.42
Summer	1.09	4.36	0.77	11.31	0.56	1.54	0.62	8.09	12.65	91.71
Fall	1.34	8.12	1.73	13.62	0.78	1.95	0.52	21.59	16.54	187.50
Mean	1.22	9.74	1.40	13.67	0.79	2.22	0.53	22.94	20.77	169.09

(fall). By contrast, the total water-soluble ions in PM_{10} contributed a mean mass fraction of 37.85% in the cities of the Pearl River Delta (Lai et al., 2007), 30% in Yokohama (Takeuchi et al., 2004), and 16.03% in Lanzhou (Fan et al., 2014). Therefore, the mass fraction of water-soluble ions in Hefei was substantially greater than in these other cities, because water-soluble ionic species are the primary constituents of the atmospheric aerosol particles in Hefei.

The mean concentrations of water-soluble ions decreased in the following order: $NO_3^- > SO_4^{2-} > Ca^{2+} > NH_4^+ > Cl^- > K^+ > Na^+ > Mg^{2+} > NO_2^-$. Our results confirmed that NO_3^-, SO_4^{2-}, Ca^{2+}, and NH_4^+ were the major ionic species. The mean concentrations of NO_3^-, SO_4^{2-}, Ca^{2+}, and NH_4^+ were 22.94, 20.77, 13.67 and 9.74 $\mu g/m^3$, respectively, and the maximum contribution of these four ions to the total water-soluble ions was 87.40%. The mass concentrations of the other five ions (Na^+, K^+, Mg^{2+}, Cl^-, and NO_2^-) were lower (each by approximately 1 $\mu g/m^3$), accounting for only 12.60% of the total water-soluble ions. The seasonal variations in the ionic concentrations were also notable. The highest concentrations of all ions (except Na^+ and NO_2^-) were recorded in winter, and the lowest concentrations were recorded in summer (except Cl^-).

Nitrate and sulfate were the most important water-soluble ions in the atmospheric aerosol particles sampled in Hefei. Nitrate ions exhibited the highest annual mean concentration during our study. The concentration was highest in winter, followed by fall and spring, while the lowest value occurred in summer, because relatively low temperatures and high NO_x concentrations are favorable for the formation of NO_3^- aerosol (Park et al., 2005). The detected nitrate concentrations exceeded the sulfate concentrations in winter and fall in Hefei, which may be related to anthropogenic emissions. Based on the Anhui Environment Protection Bureau data, the NO_2 concentration was higher than the SO_2 concentration during most months in Hefei. Particulate-related nitrate is formed primarily by the oxidation of nitrogen oxides (NO_x) to nitric acid, which then forms particles through reactions with sodium chloride or ammonia (Clase and Gysels, 1998). In urban areas, NO_x is derived primarily from anthropogenic sources, such as vehicular and industrial emissions. The high concentrations of nitrate detected in each city suggest that there was a large contribution of NO_x from motor vehicle emissions.

The ionic species with the second highest annual mean concentration during our study was sulfate. The sulfate concentration was also higher in winter and lower in spring and summer. Furthermore, the sulfate concentration was higher than the nitrate concentration in spring and summer, although it was lower than the nitrate concentration in winter and fall. Anthropogenic emissions account for approximately 75% of the total sulfur emissions in the Northern Hemisphere (Seinfeld and Pandis, 1998). In urban areas, most sulfate is formed via the oxidation of sulfur dioxide, which is produced primarily by fossil fuel combustion and some biogenic gases (Wang and Shooter, 2001). The Anhui Environment Protection Bureau data indicated that sulfate was one of the most abundant ionic species throughout the year. In Hefei, the SO_2 concentration was higher in winter, which may result in seasonal variations in sulfate loadings.

The ammonium concentration detected in Hefei was highest in winter, with an average of 21.35 $\mu g/m^3$. The seasonal ammonium concentrations exhibited the following order in Hefei: winter > autumn > spring > summer. Previous work has suggested that ammonium is most likely related to the use of fertilizers and local sanitary wastes (Zhang et al., 2002). The conversion of NH_3 to NH_4^+ depends on the concentration of acids in the atmosphere, temperature and water availability (Koerkamp et al., 1998; Kobara et al., 2007). In winter, the lower temperature and higher concentrations of acid species, such as sulfate and nitrate, were favorable for gas-particle reactions. By contrast, the higher temperatures in summer were not favorable for the conversion from NH_3 to NH_4^+.

The calcium concentration did not differ markedly among the four seasons during our study. The concentration in winter was slightly higher than in the other seasons. Calcium is found primarily in the coarse mode, making its concentration a useful indicator of mineral dust (Yin et al., 2005). A great deal of city infrastructure has recently been constructed in Hefei, which has produced large amounts of dust. Therefore, the primary source of calcium in Hefei is dust from building sites. Furthermore, dust emissions are constant throughout the year; thus, seasonal changes in calcium concentrations are related primarily to weather conditions, e.g., rainfall and wind.

2.2. Ion concentrations in $PM_{2.5}$

$PM_{2.5}$ refers to aerosol particles with an aerodynamic diameter that is equal to or less than 2.5 μm. These fine mode particles influence visibility and human health and have been the focus of many recent studies. Table 3 shows the concentrations of water-soluble ions in $PM_{2.5}$ during the four seasons in Hefei. The Andersen Mark-II cascade impactor used in this study does not have a 2.5-μm size bin; thus, $PM_{2.1}$ was used for the analysis, although we refer to these values as $PM_{2.5}$. As shown in Table 3, the $PM_{2.5}$ concentration accounted for 51.03% of the TSP on average, indicating that the pollution was dominated by fine particles. The proportion of $PM_{2.5}$ in TSP in Hefei was less than in Nanjing (63%–77%), Beijing (70%) and Huangshan (75%, in summer) (Wang et al., 2002; Sun et al., 2014; Wen et al., 2013). The water-soluble ion

Table 3 – Ion concentrations in $PM_{2.5}$ during all four seasons in Hefei (unit: $\mu g/m^3$).										
	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	$PM_{2.5}$	$PM_{2.5}$/TSP
Winter	0.49	17.71	1.42	6.39	0.43	2.42	0.16	39.33	30.75	145.05	61.79%
Spring	0.48	4.25	0.69	4.28	0.23	0.83	0.17	5.64	9.85	68.16	41.97%
Summer	0.51	3.38	0.47	5.37	0.29	0.72	0.31	4.19	9.42	49.22	53.67%
Fall	0.45	5.95	1.23	4.93	0.25	0.86	0.24	11.41	12.22	82.74	44.13%
Mean	0.48	7.82	0.96	5.24	0.30	1.21	0.22	15.14	15.56	86.29	51.03%

Table 4 – Ion concentrations in PM$_{2.5}$ in several Chinese cities (unit: μg/m^3).

	Sampling time	SO$_4^{-2}$	NO$_3^-$	Cl$^-$	NH$_4^+$	Na$^+$	Ca^{2+}	Mg^{2+}	K$^+$	Remark
Hefei	Sep. 2012–Nov. 2013	15.56	15.14	1.21	7.82	0.48	5.24	0.30	0.96	This study
Shanghai	2003–2005	10.39	6.23	3.00	3.78	0.57	1.28	0.95	1.37	Wang et al., 2006b
Beijing	2009–2010	19.10	20.50	2.90	6.40	0.50	1.50	0.20	1.70	Zhao et al., 2011
Jinan	Oct. 2007–Dec. 2008	38.30	15.80	4.20	21.30	1.20	0.80	0.10	2.40	Gao et al., 2011
Mount Huang	Jun. 2011–Aug. 2011	5.72	0.55	0.21	1.77	0.19	0.73	0.02	0.23	Wen et al., 2013

concentrations in PM$_{2.5}$ followed an order similar to TSP: SO$_4^{2-}$ > NO$_3^-$ > NH$_4^+$ > Ca^{2+} > Cl$^-$ > K$^+$ > Na$^+$ > Mg^{2+} > NO$_2^-$. The major ions were also SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, and Ca^{2+}. The mass concentration of Ca^{2+} in PM$_{2.5}$ was lower than in TSP, indicating that Ca^{2+} was primarily in coarse mode particles. In addition, the ion with the highest concentration in our study was SO$_4^{2-}$, and 75% of the total SO$_4^{2-}$ was found in PM$_{2.5}$. The fraction of NO$_3^-$ in PM$_{2.5}$ was only 66%. The PM$_{2.5}$ levels in Hefei were consistently higher in winter than in spring, summer and autumn. The peak concentrations for most of the water-soluble ions in PM$_{2.5}$, including SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Ca^{2+}, Cl$^-$, K$^+$, and Mg^{2+}, were recorded in winter. The minimum concentrations of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Cl$^-$, and K$^+$ in PM$_{2.5}$ were recorded in summer, which may be related to local meteorological conditions. Similar variations were previously reported in Guiyang (Xiao & Liu, 2004).

The concentrations of the dominant water-soluble ions were compared to those recently reported at various sites in China (Table 4). Considering the rapid changes in Chinese emissions that have occurred, only results for the last 10 years are included. As shown in Table 4, the mean sulfate concentration in Hefei was higher than in Shanghai (10.39 μg/m^3) and Mount Huang (5.72 μg/m^3) and lower than in Beijing (19.10 μg/m^3) and Jinan (38.30 μg/m^3). Sulfate originates primarily from industrial emissions. However, Anhui Province is a large agricultural province, and the study site in Hefei was located in a residential area with no influences from industrial activities; thus, the observed sulfate concentrations were low. In summer, the sulfate concentrations in Hefei and Mount Huang were 9.42 and 5.72 μg/m^3, respectively, which is indicative of widespread regional sulfate pollution. The order of nitrate concentrations was identical to that of the sulfate concentrations. The nitrate concentrations in Hefei were the third highest among the five cities listed in Table 4 and were comparatively high (15.14 μg/m^3). The high nitrate concentrations in Hefei were due to the site's location near a roadway with heavy traffic and exposure to automobile exhaust. The nitrate concentrations were closely linked to the concentrations of nitrogen dioxide. Since 2006, nitrogen dioxide concentrations have noticeably increased in east China (Shi et al., 2010), which explains the low nitrate concentrations in Shanghai between 2003 and 2005. Generally, soil is considered to be the primary source of Ca^{2+}, Mg^{2+}, and K$^+$. The average Ca^{2+} concentrations in Hefei were the highest among the assessed cities (Table 4), which was possibly due to the large-scale construction of city infrastructure in Hefei. Several large construction sites are located within a 5-km radius around the sampling site, including Hefei Metro Line 2 and a residential community. These construction activities may have resulted in the observed high calcium concentrations. The concentrations of K$^+$, Na$^+$,

and Cl$^-$ in Hefei were relatively low compared to the other cities listed in Table 4 except for Mount Huang; these ions primarily originate from biomass combustion and sea salt. The ammonium concentrations in Hefei were only one-third those in Jinan, although they were higher than in the other three cities. Generally, the mass concentrations of water-soluble ions detected in Hefei were moderate compared to the five sites and were less than in the more economically developed area (Jinan).

2.3. Size distribution of water-soluble ions

The Andersen Mark-II cascade impactor has nine uneven aerosol particle size bins. Thus, the measured mass concentration of each level is not a precise determination of the aerosol size distribution. To objectively analyze aerosol characteristics, a distribution function of the mass concentration (q) is used (Kong et al., 2010; Xu et al., 2012a):

$$q = \frac{dC}{d \lg D_p} \tag{1}$$

where, dC is the observed mass concentration of each level, and $d \lg D_p$ is the logarithmic difference between the maximum and the minimum aerosol diameter of each level. The mass median aerodynamic diameters (MMADs), which represent the central tendency, are used as metrics to compare the size distribution data.

Fig. 2 shows the seasonal size distributions of water-soluble ions in Hefei. Most of the inorganic species exhibited bimodal distributions. The most important water-soluble ions, i.e., NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$, had similar sizes. These species were bimodally distributed in spring, summer and fall, with one mode peaking at 0.43–0.65 μm and another peaking at 2.1–5.8 μm, which was similar to the size range measured at the Linan Station (Xu et al., 2012a). However, the three water-soluble ions (i.e., NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$) exhibited a single mode that peaked at about approximately 0.43–1.1 μm in Beijing (Xu et al., 2007). In winter, the size distributions were unimodal, peaking at 1.1–2.1 μm, possibly due to high-humidity conditions, which was previously observed in Hong Kong (Zhuang et al., 1999). The mass concentrations of sulfate, nitrate and ammonium were predominantly in the fine mode, with low MMADs of 1, 1.32 and 0.95 μm, respectively. The mass concentrations in winter were noticeably higher than in the other seasons, with the lowest concentrations occurring in summer. The peak size range for calcium was approximately 4.7–5.8 μm, and the ratio of the fine mode to coarse mode was high. The largest MMAD was approximately 3.31 μm, because calcium originated primarily from the coarse-grained sand used in city construction. Kong et al. (2010) and Geng et al. (2010) also obtained a similar size
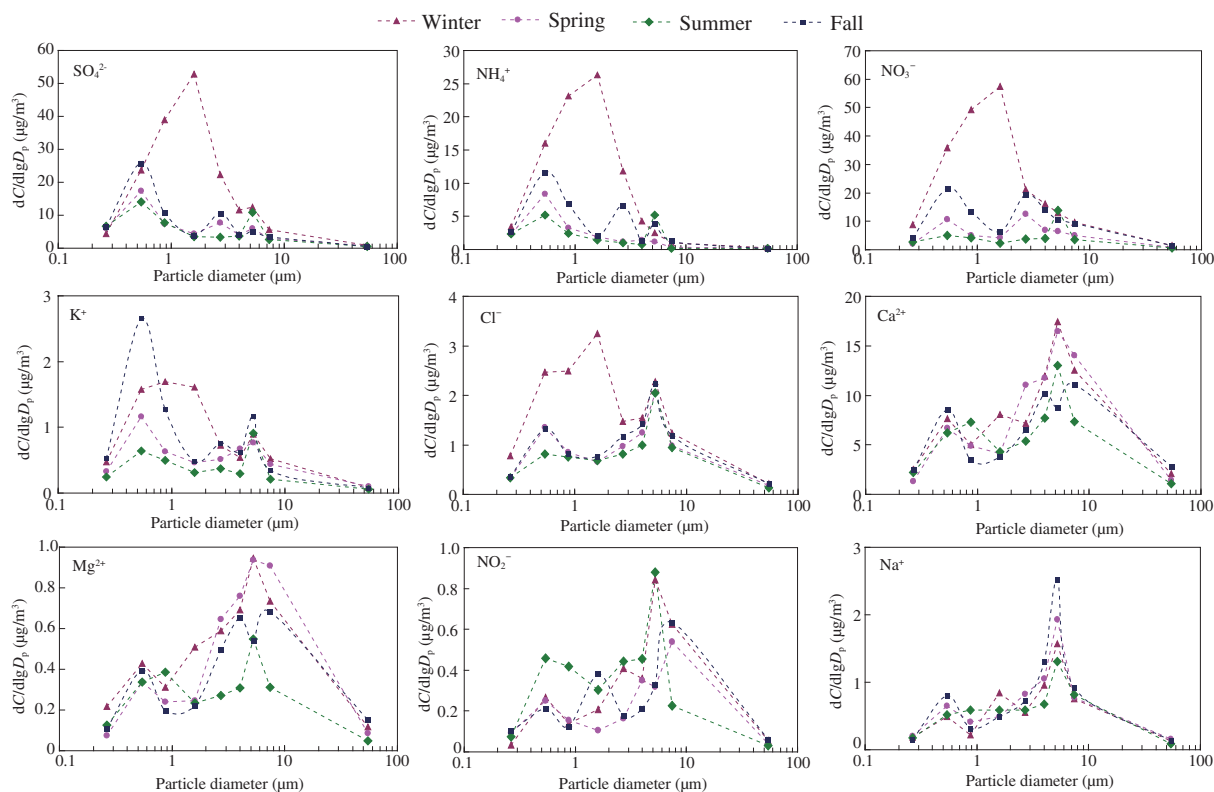
Fig. 2 – Particle size distributions (dC/dlgD$_p$) of the water-soluble ions in the atmospheric aerosol in the four seasons in Hefei.

distribution for calcium in Nanjin and Shanghai, respectively. Furthermore, the mass concentration of calcium in Hefei was higher in winter and spring. The mass concentrations of the other five ions in Hefei were lower than the mass concentrations of the four primary ions discussed above. The maximum mass concentrations of chlorine (MMAD, 1.82 μm), sodium (MMAD, 3.12 μm), nitrite (MMAD, 2.82 μm), and magnesium (MMAD, 3.18 μm) ions were found to be in the coarse size range (4.7–5.8 μm), and similar size distributions were also observed in Beijing (Huang et al., 2013). Their seasonal mass concentration changes were not substantial, with the exception of chlorine. In winter, chlorine was observed in the fine mode, together with sulfate and nitrate. However, the size distribution of potassium was similar to that of sulfate. A bimodal structure was apparent, with a larger fine mode than coarse mode. In winter, there was a unimodal size distribution, with a peak at 0.43–2.1 μm, although the potassium concentration was low.

The size distributions of the water-soluble ions in winter, especially sulfate, nitrate, ammonium, and chloride, were different from the size distributions for these ions in the other seasons. The sampling day for winter (i.e., 14 January, 2013) was a foggy day with very high relative humidity, as shown in Table 1. The hygroscopic growth of water-soluble ions may be the primary reason for their large sizes. For example, the diameter of ammonium sulfate under conditions of 80% relative humidity is twice the diameter under dry conditions. Therefore, the high relative humidity may have contributed to the observed size distribution characteristics for the measured water-soluble ions in winter.

2.4. Cation and anion balance

The equivalent concentrations of cations (ΣCation) and anions (ΣAnion) were calculated using the following equations:

$$\sum \text{Cation} = \frac{[\text{Na}^+]}{23} + \frac{[\text{NH}_4^+]}{18} + \frac{[\text{K}^+]}{39} + \frac{[\text{Mg}^{2+}]}{12} + \frac{[\text{Ca}^{2+}]}{20} \qquad (2)$$

$$\sum \text{Anion} = \frac{[\text{Cl}^-]}{35.5} + \frac{[\text{NO}_2^-]}{46} + \frac{[\text{NO}_3^-]}{62} + \frac{[\text{SO}_4^{2-}]}{48} \qquad (3)$$
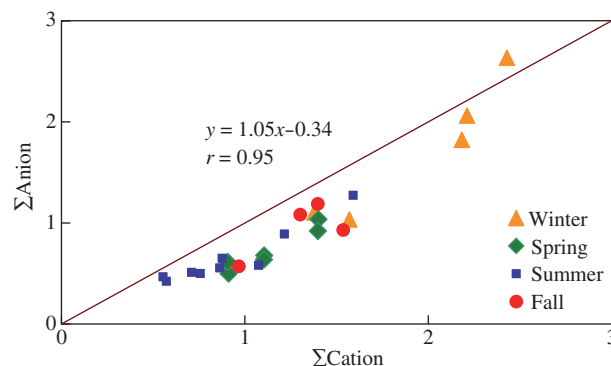

Fig. 3 – Equivalence between the concentrations of cations (ΣCation) and anions (ΣAnion) in the atmospheric aerosol measured in Hefei.

where, $[Na^+]$, $[NH_4^+]$, $[K^+]$, $[Mg^{2+}]$, $[Ca^+]$, $[Cl^-]$, $[NO_2^-]$, $[NO_3^-]$, and $[SO_4^{2-}]$ denoted as the concentration of different ions.

The correlations between the equivalent concentrations of cations and anions are shown in Fig. 3. Good correlations ($R = 0.95$) between the cation and anion concentrations were found, which suggested that the measured cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) and anions (Cl^-, NO_3^-, SO_4^{2-}, and NO_2^-) maintained a constant neutralization relationship during the four seasons (Lai et al., 2007). The ratio of cations to anions is a good indicator of the acidity of aerosol particles. Based on the measurements, this ratio was close to 1.4 (see Fig. 3). Because most of the known major ions were measured, the anion deficits are best explained by the presence of carbonate. The presence of carbonate implies that the aerosol particles are alkalescent. Similar results have also been reported for other Chinese cities, *e.g.*, Shanghai (Geng et al., 2010) and Beijing (Cai et al., 2011).

2.5. Source identification using the NO_3^-/SO_4^{2-} ratio

Nitrogen oxide emissions from mobile sources are an important contributor to particulate NO_3^- in the atmosphere. Therefore, the NO_3^-/SO_4^{2-} mass ratio has been used as an indicator of the relative importance of stationary *vs.* mobile sources of sulfur and nitrogen in the atmosphere (Xiao and Liu, 2004). Arimoto et al. (1996) ascribed a high NO_3^-/SO_4^{2-} mass ratio to the predominance of mobile over stationary pollutant sources. In this study, the average NO_3^-/SO_4^{2-} mass ratio was 1.10 in Hefei. The average mass ratio in Hefei was greater than the NO_3^-/SO_4^{2-} ratios determined for Tianjing (0.86; Zhao et al., 2011), Shijiazhuang from 2009 to 2010 (0.80; Zhao et al., 2011), and Nanjing in 2008 (0.80; Xu et al., 2012b) and less than the mass ratio reported in Beijing from 2009 to 2010 (1.13; Zhao et al., 2011). The high NO_3^-/SO_4^{2-} mass ratios in Hefei were likely due to the high traffic density and the site location. Generally, the NO_3^-/SO_4^{2-} mass ratio was >1, suggesting that mobile source emissions were dominant.

The average NO_3^-/SO_4^{2-} mass ratios also exhibited seasonal variations in Hefei; the ratios for the four seasons were 1.26 (winter), 0.84 (spring), 0.64 (summer), and 1.31 (fall). The data indicate that the mass ratios in summer were the lowest. The high temperatures in summer lowered the stability of NH_4NO_3, decreasing the rate of NO_3^- formation. The NO_3^-/SO_4^{2-} mass ratios in the summer were lower than in the other seasons. In winter and fall, the NO_3^-/SO_4^{2-} mass ratios were

high, which may have been due to two factors. First, based on the Anhui Environment Protection Bureau data, the NO_2 concentrations were higher than the SO_2 concentrations in winter and fall in Hefei. Second, low temperatures can increase the rate of NO_3^- formation.

2.6. Correlations between ionic species

Calculating the inter-correlations between ions in aerosol samples is a simple means of investigating their possible sources and the associations between them in aerosol particles. Correlation coefficients for the relationships between the ionic concentrations in Hefei are presented in Table 5. Significant positive correlation coefficients were found between NH_4^+ and SO_4^{2-} (0.95), NH_4^+ and NO_3^- (0.95), SO_4^{2-} and NO_3^- (0.86), and Mg^{2+} and Ca^{2+} (0.91). As reported in Tang et al. (2012), these ions also exhibit strong relationships with precipitation in Hefei, with correlation coefficients of 0.77, 0.75, 0.87, and 0.84 for NH_4^+ and SO_4^{2-}, NH_4^+ and NO_3^-, SO_4^{2-} and NO_3^-, and Mg^{2+} and Ca^{2+}, respectively.

A significant positive correlation was found between SO_4^{2-} and NH_4^+ in Hefei (Table 5), which suggested neutralization by ammonia gas. A strong positive correlation coefficient (0.95) for the relationship between SO_4^{2-} and NH_4^+ indicated that SO_4^{2-} was present as $(NH_4)_2SO_4$ and/or NH_4HSO_4. The linear fit to the data can be described by $SO_4^{2-} = 0.75\ NH_4^+ + 0.05$ (μeq *vs.* μeq). Because the equivalent ratios of SO_4^{2-} to NH_4^+ for $(NH_4)_2SO_4$ and NH_4HSO_4 are 2 and 1, respectively, the slope of 0.75 indicates the incomplete neutralization of SO_4^{2-} by NH_4^+, and NH_4HSO_4 is the primary chemical form. There was also a strong correlation coefficient (0.95) for the relationship between NH_4^+ and NO_3^- in Hefei, which confirms the existence of NH_4NO_3 in the fine mode aerosol particles. NO_3^- can react with Ca^{2+} and Mg^{2+} in the coarse mode.

The strong correlation for the relationship between Mg^{2+} and Ca^{2+} suggests they have a common source. In the coarse mode, they may originate from soil particles. In addition to soil, sea salt is also a source of Mg^{2+}. Normally, the ratio of Mg^{2+}/Na^+ is approximately 0.12 in sea salt aerosol (Xu et al., 2012b), whereas the ratio was 0.64 in this study. Thus, the contribution of the soil source to Mg^{2+} was larger than that of sea salt in Hefei. Calcium generally originates from local soil and dust transported from the desert during storms. The Mg^{2+}/Ca^+ ratio is 0.17 in the desert region (Xu et al.,

Table 5 – Correlation coefficients among the ionic concentrations in Hefei.									
	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
Na^+	1.00								
NH_4^+	−0.01	1.00							
K^+	0.35	0.61[**]	1.00						
Ca^{2+}	0.08	0.32	0.34	1.00					
Mg^{2+}	0.15	0.47[*]	0.54[**]	0.91[***]	1.00				
Cl^-	0.18	0.69[***]	0.62[**]	0.53[*]	0.63[**]	1.00			
NO_2^-	0.03	0.18	0.09	−0.35	−0.31	−0.01	1.00		
NO_3^-	0.03	0.95[***]	0.65[***]	0.47[*]	0.56[**]	0.79[***]	0.06	1.00	
SO_4^{2-}	0.06	0.95[***]	0.53[*]	0.31	0.44[*]	0.52[*]	0.17	0.86[***]	1.00

[*] Significant ($p < 0.05$).
[**] Significant ($p < 0.01$).
[***] Significant ($p < 0.001$).

2012a,2012b), whereas it was only 0.06 in Hefei, which suggests that Ca^+ in Hefei is mainly generated from local soil sources.

3. Conclusions

This study determined size-classified daily aerosol mass concentrations of aerosol particles and concentrations of water-soluble inorganic ions (i.e., NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-}, and NO_2^-) in Hefei, China, using an Andersen Mark-II cascade impactor. The main conclusions were as follows.

Water-soluble ions were the primary fraction of the atmospheric aerosols in Hefei, accounting for 59.49% (winter), 32.90% (spring), 48.62% (summer) and 37.08% (fall) of the total aerosol concentrations. The four most abundant water-soluble ions were NO_3^-, SO_4^{2-}, Ca^{2+}, and NH_4^+, and the maximum contribution of the four ions to the total concentrations in the water-soluble ions was 87.40%. The seasonal variability in the water-soluble ions was noteworthy. For most of the ions, the concentrations were highest in winter and lowest in summer. Compared with other Chinese cities, the water-soluble ion mass concentrations in Hefei (except for Ca^{2+}) were in the intermediate range. The size distribution of water-soluble ions was found to depend on local sources, reaction conditions, and long-range transport. In Hefei, sulfate, nitrate, and ammonium were the dominant fine-mode species, which were bimodally distributed; however, in winter, these species exhibited unimodal distributions. The calcium peak was in the coarse mode (4.7–5.8 μm) in all seasons. The ratio of cations to anions can be used to indicate the acidity of aerosols; this ratio was found to be 1.4 in Hefei, indicating that the aerosol particles were alkalescent. The NO_3^-/SO_4^{2-} ratio indicated that mobile sources had a considerable contribution to the observed urban aerosol. The average NO_3^-/SO_4^{2-} mass ratio was 1.10 (i.e., greater than 1) in Hefei, which indicated that mobile source emissions were dominant. Significant positive correlation coefficients were also confirmed between the concentrations of NH_4^+ and SO_4^{2-}, NH_4^+ and NO_3^-, SO_4^{2-} and NO_3^-, and Mg^{2+} and Ca^{2+}, which indicated that aerosol particles may consist of $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3.

Acknowledgments

REFERENCES

Alpert, P., Kaufman, Y.J., Shay-El, Y., Tanre, D., da Silva, A., Schubert, S., et al., 1998. Quantification of dust-forced heating of the lower atmosphere. Nature 395 (6700), 367–370.

Arimoto, R., Duce, R.A., Savoie, D.L., Prospero, J.M., Talbot, R., Cullen, J.D., et al., 1996. Relationships among aerosol constituents from Asia and the North Pacific during PEM-West A. J. Geophys. Res. 101 (D1), 2011–2023.

Cai, Y.Y., Yang, F.M., He, K.B., Ma, Y.L., Okuda, T., Tanaka, S., 2011. Characteristics of water-soluble ions in dry deposition in urban Beijing. China Environ. Sci. 31 (7), 1071–1076.

Cheng, H.R., Gong, W., Wang, Z.W., Zhang, F., Wang, X.M., Lv, X.P., et al., 2014. Ionic composition of submicron particles ($PM_{1.0}$) during the long-lasting haze period in January 2013 in Wuhan, central China. J. Environ. Sci. 26 (4), 810–817.

Clase, M., Gysels, K., 1998. IUPAC Series on Analytical and Physical Chemistry of Environmental Systems. Wiley, New York, pp. 141–145.

Contini, D., Cesari, D., Genga, A., Siciliano, M., Ielpo, P., Guascito, M.R., et al., 2014. Source apportionment of size-segregated atmospheric particles based on the major water-soluble components in Lecce (Italy). Sci. Total Environ. 472, 248–261.

Deng, X.L., Shi, C.E., Wu, B.W., Chen, Z.H., Nie, S.P., He, D.Y., et al., 2012. Analysis of aerosol characteristics and their relationships with meteorological parameters over Anhui province in China. Atmos. Res. 109–110, 52–63.

Du, H.H., Kong, L.D., Cheng, T.T., Chen, J.M., Du, J.F., Li, L., et al., 2011. Insights into summertime haze pollution events over Shanghai based on online water-soluble ionic composition of aerosols. Atmos. Environ. 45 (29), 5131–5137.

Fan, J., Yue, X.Y., Jing, Y., Chen, Q., Wang, S.G., 2014. Online monitoring of water-soluble ionic composition of PM_{10} during early summer over Lanzhou City. J. Environ. Sci. 26 (2), 353–361.

Gao, X.M., Yang, L.X., Cheng, S.H., Gao, R., Zhou, Y., Xue, L.K., et al., 2011. Semi-continuous measurement of water-soluble ions in $PM_{2.5}$ in Jinan, China: Temporal variations and source apportionments. Atmos. Environ. 45 (33), 6048–6056.

Geng, Y.H., Liu, W., Shan, J., Yao, J., Fan, X.B., Wei, N.N., et al., 2010. Characterization of major water-soluble ions in size-fractionated particulate matters in Shanghai. China Environ. Sci. 30 (12), 1585–1589.

Hara, H., Honda, K., Nagara, K., Goto, A., 1983. Seasonal variation in particle-size distribution of chloride and nitrate in the ambient air. Nippon Kagaku Kaishi 1983 (8), 1221–1225.

Hu, G.Y., Zhang, Y.M., Sun, J.Y., Zhang, L.M., Shen, X.J., Lin, W.L., et al., 2014. Variability, formation and acidity of water-soluble ions in $PM_{2.5}$ in Beijing based on the semi-continuous observations. Atmos. Res. 145–146, 1–11.

Huang, Y.M., Liu, Z.R., Chen, H., Wang, Y.S., 2013. Characteristics of mass size distributions of water-soluble inorganic ions during summer and winter haze days of Beijing. Environ. Sci. 34 (4), 1236–1244.

Kadowaki, S., 1976. Size distribution of atmospheric total aerosols, sulfate, ammonium and nitrate particulates in the Nagoya area. Atmos. Environ. 10 (1), 39–43.

Kaufman, Y.J., Nakajima, T., 1993. Effect of Amazon smoke on cloud microphysics and albedo–analysis from satellite imagery. J. Appl. Meteorol. 32 (4), 729–744.

Khoder, M.I., Hassan, S.K., 2008. Weekday/weekend differences in ambient aerosol level and chemical characteristics of water-soluble components in the city centre. Atmos. Environ. 42 (32), 7483–7493.

Kobara, H., Takeuchi, K., Ibusuki, T., 2007. Effect of relative humidity on aerosol generation through experiments at low concentrations of gaseous nitric acid and ammonia. Aerosol Air Qual. Res. 7 (2), 193–204.

Koerkamp, P.W.G.G., Metz, J.H.M., Uenk, G.H., Phillips, V.R., Holden, M.R., Sneath, R.W., et al., 1998. Concentrations and emissions of ammonia in livestock buildings in Northern Europe. J. Agric. Eng. Res. 70 (1), 79–95.

Kong, C.X., Guo, S.L., Tang, L.L., 2010. Size distribution of water soluble ions in aerosol and its variation with height in Nanjing. Trans. Atmos. Sci. 33 (6), 757–761.

Lai, S.C., Zou, S.C., Cao, J.J., Lee, S.C., Ho, K.F., 2007. Characterizing ionic species in $PM_{2.5}$ and PM_{10} in four Pearl River Delta cities, South China. J. Environ. Sci. 19 (8), 939–947.

National Research Council, 1993. Protecting Visibility in National Parks and Wilderness Areas. National Academy Press, Washington, DC.

Park, S.S., Sim, S.Y., Bae, M.S., Schauer, J.J., 2013. Size distribution of water-soluble components in particulate matter emitted from biomass burning. Atmos. Environ. 73, 62–72.

Park, S.S., Ondov, J.M., Harrison, D., Nair, N.P., 2005. Seasonal and shorter-term variations in particulate atmospheric nitrate in Baltimore. Atmos. Environ. 39 (11), 2011–2020.

Penner, J.E., Charlson, R.J., Laulainen, N.S., Leifer, R., Novakov, T., Ogren, J., et al., 1994. Quantifying and minimizing uncertainty of climate forcing by anthropogenic aerosols. Bull. Am. Meteorol. Soc. 75 (3), 375–400.

Qiu, M.Y., Shi, C.E., Zhang, H., Zhang, P., Zhou, S.X., 2009. Marked changes of acid rain in Hefei and their causes. Acta Sci. Circumst. 29 (6), 1329–1338.

Satheesh, S.K., Moorthy, K.K., 2005. Radiative effects of natural aerosols: a review. Atmos. Environ. 39 (11), 2089–2110.

Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. John Wiley & Sons, Inc., New York.

Shi, C.E., Roth, M., Zhang, H., Li, Z.H., 2008. Impacts of urbanization on long-term fog variation in Anhui Province, China. Atmos. Environ. 42 (36), 8484–8492.

Shi, C.E., Qiu, M.Y., Zhang, A.M., Zhang, H., Zhang, S., Wang, Z.F., 2010. Spatiotemporal trends and the impact factors of acid rain in Anhui Province. Environ. Sci. 31 (6), 1676–1681.

Sun, K., Qu, Y., Wu, Q., Han, T.T., Gu, J.W., Zhao, J.J., et al., 2014. Chemical characteristics of size-resolved aerosols in winter in Beijing. J. Environ. Sci. 26 (8), 1641–1650.

Takeuchi, M., Okochi, H., Igawa, M., 2004. Characteristics of water-soluble components of atmospheric aerosols in Yokohama and Mt. Oyama, Japan from 1990 to 2001. Atmos. Environ. 38 (28), 4701–4708.

Tang, R., Wang, T.J., Shi, C.E., Deng, X.L., Chen, R.L., 2012. Analysis on the chemical composition of precipitation in Hefei. J. Meteorol. Sci. 32 (4), 459–465.

Twomey, S.A., Piepgrass, M., Wolfe, T.L., 1984. An assessment of the impact of pollution on the global albedo. Tellus B 36B (5), 356–366.

Wang, G.H., Huang, L.M., Gao, S.X., Gao, S.T., Wang, L.S., 2002. Characterization of water-soluble species of PM_{10} and $PM_{2.5}$ aerosols in urban area in Nanjing, China. Atmos. Environ. 36 (8), 1299–1307.

Wang, G.H., Wang, H., Yu, Y.J., Gao, S.X., Feng, J.F., Gao, S.T., et al., 2003. Chemical characterization of water-soluble components of PM_{10} and $PM_{2.5}$ atmospheric aerosols in five locations of Nanjing, China. Atmos. Environ. 37 (21), 2893–2902.

Wang, H.B., Shooter, D., 2001. Water soluble ions of atmospheric aerosols in three New Zealand cities: seasonal changes and sources. Atmos. Environ. 35 (34), 6031–6040.

Wang, H.L., Zhu, B., Ma, L.C., Chen, S., Chen, C., Wang, P., 2010. Analysis of aerosol pollution characteristics in summer in various functional areas of Nanjing. J. Nanjing Univ. Inf. Sci. Technol. (Nat. Sci. Ed.) 2 (3), 221–229.

Wang, H.L., Zhu, B., Shen, L.J., Kang, H.Q., 2012. Size distributions of aerosol and water-soluble ions in Nanjing during a crop residual burning event. J. Environ. Sci. 24 (8), 1457–1465.

Wang, H.L., An, J.L., Shen, L.J., Zhu, B., Pan, C., Liu, Z.R., et al., 2014a. Mechanism for the formation and microphysical characteristics of submicron aerosol during heavy haze

pollution episode in the Yangtze River Delta, China. Sci. Total Environ. 490, 501–508.

Wang, Y., Zhuang, G.S., Sun, Y.L., An, Z.S., 2006a. The variation of characteristics and formation mechanisms of aerosols in dust, haze, and clear days in Beijing. Atmos. Environ. 40 (34), 6579–6591.

Wang, Y., Zhuang, G.S., Zhang, X.Y., Huang, K., Xu, C., Tang, A.H., et al., 2006b. The ion chemistry, seasonal cycle, and sources of $PM_{2.5}$ and TSP aerosol in Shanghai. Atmos. Environ. 40 (16), 2935–2952.

Wang, Y.S., Yao, L., Wang, L.L., Liu, Z.R., Ji, D.S., Tang, G.Q., et al., 2014b. Mechanism for the formation of the January 2013 heavy haze pollution episode over central and eastern China. Sci. China Earth Sci. 57 (1), 14–25.

Wei, W.H., Wang, T.J., Shi, C.E., Zhang, H., 2012. Analysis of weather conditions for fog in Hefei. J. Meteorol. Sci. 32 (4), 437–442.

Wen, B., Yin, Y., Qing, Y.S., Chen, K., 2013. Chemical characteristics of water-soluble components of aerosol particles at different altitudes of the Mount Huang in the summer. Environ. Sci. 34 (5), 1973–1981.

Wu, D., 1995. The distribution characteristics of water-soluble composition of atmospheric aerosol over north of the South China Sea. Sci. Atmos. Sin. 19 (5), 615–622.

Wu, D., Chen, W.C., 1994. Intra-annual variation features of mass distribution and water soluble composition distribution of atmospheric aerosol over Guangzhou. Acta Meteorol. Sin. 52 (4), 499–505.

Wu, D., Chen, W.C., Chang, Y.D., Xiang, P.Y., Mao, J.T., Qin, Y., 1994. A primary study of the size-distribution and water soluble composition distribution of atmospheric aerosols over South China. J. Trop. Meteorol. 10 (1), 85–96.

Wu, D., Tie, X.X., Deng, X.J., 2006. Chemical characterizations of soluble aerosols in southern China. Chemosphere 64 (5), 749–757.

Xiao, H.Y., Liu, C.Q., 2004. Chemical characteristics of water-soluble components in TSP over Guiyang, SW China, 2003. Atmos. Environ. 38 (37), 6297–6306.

Xu, H.H., Liu, J., Wang, Y.S., Mao, M.J., Pu, J.J., 2012a. Variation pattern of water-soluble ions in atmospheric at Lin'an regional background station. Environ. Chem. 31 (6), 796–802.

Xu, H.H., Wang, Y.S., Wen, T.X., He, X.X., 2007. Size distributions and vertical distributions of water soluble ions of atmospheric aerosol in Beijing. Environ. Sci. 28 (1), 14–19.

Xu, M.J., Wang, Y.H., Tang, L.L., Zhang, X.Z., Tang, L., Li, X.W., et al., 2012b. Study on characteristics of water-soluble ions in PM_{10} in autumn in Nanjing. Environ. Eng. 30 (5), 108–113.

Yin, J., Allen, A.G., Harrison, R.M., Jennings, S.G., Wright, E., Fitzpatrick, M., et al., 2005. Major component composition of urban PM_{10} and $PM_{2.5}$ in Ireland. Atmos. Res. 78 (3-4), 149–165.

Zhang, X.Y., Cao, J.J., Li, L.M., Arimoto, R., Cheng, Y., Huebert, B., et al., 2002. Characterization of atmospheric aerosol over Xi'an in the south margin of the Loess Plateau, China. Atmos. Environ. 36 (26), 4189–4199.

Zhuang, H., Chan, C.K., Fang, M., Wexler, A.S., 1999. Size distributions of particulate sulfate, nitrate, and ammonium at a coastal site in Hong Kong. Atmos. Environ. 33 (6), 843–853.

Zhang, H., Shi, C.E., Qiu, M.Y., Xie, W., 2010. Long-term variation of haze phenomena in Hefei and its impact factors. Acta Sci. Circumst. 30 (4), 714–721.

Zhao, P.S., Zhang, X.L., Meng, W., Yang, B.Y., Fan, W.Y., Liu, H.Y., 2011. Characteristics of inorganic water-soluble ions from aerosols in Beijing–Tianjin–Hebei area. Environ. Sci. 32 (6), 1546–1549.