Atmospheric Research 102 (2011) 110–119

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmos

Water-soluble ions in atmospheric aerosols measured in Xi'an, China: Seasonal variations and sources

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ARTICLE INFO

Article history:
Received 11 October 2010
Received in revised form 6 June 2011
Accepted 17 June 2011

Keywords:
Aerosols
Water-soluble ions
Seasonal variation
Source
Xi'an

ABSTRACT

Daily $PM_{2.5}$ and water-soluble inorganic ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}) were collected in Xi'an (34.23°N, 108.88°E), China from March 2006 to March 2007. $PM_{2.5}$ was collected using battery-powered mini-volume samplers. And the ions were determined by ion chromatography from the measured aerosol mass. The annual average mass concentration of $PM_{2.5}$ was found to be 194.1 ± 78.6 μg m^{-3}, which exceeded substantially the international guidelines for health concerns. The seasonal average mass concentration of $PM_{2.5}$ was highest in winter (266.8 μg m^{-3}) and lowest in summer (138.6 μg m^{-3}). The three highest abundant ions were SO_4^{2-}, NO_3^-, and NH_4^+, with average concentrations of 35.6 ± 19.5 μg m^{-3}, 16.4 ± 10.1 μg m^{-3}, and 11.4 ± 6.8 μg m^{-3}, which were accounted for 18.7%, 8.0%, and 5.7% of the $PM_{2.5}$ mass, respectively. The major ions were in the species of $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3, and their concentrations were highest in winter, due to high coal combustion. The concentrations of Ca^{2+} were higher in spring than other seasons, due to the higher mineral dust concentrations. Ca^{2+} was strongly correlated with CO_3^{2-}, which was calculated as the difference in the measured cations minus anions. Ion balance calculations indicate that the $PM_{2.5}$ was acidic, and this result is consistent with the measurement of pH values. Sulfur oxidation ratio was higher in summer and autumn, which implies that the formation of secondary sulfate-rich particles is favored by warm and relatively moist weather. Nitrogen oxidation ratio was highest in autumn.

1. Introduction

Atmospheric particulate matter (PM) is directly emitted into the air (primary PM) or generated in the atmosphere from precursor gasses (secondary PM). Particulate matter with aerodynamic diameters less than 2.5 μm ($PM_{2.5}$) causes air quality problems in urban areas, especially visibility reduction (Larson and Cass, 1989; Larson et al., 1989; Tie and Cao, 2009a) and health problems, such as asthma and even mortality (Dockery and Pope, 1994; Schwartz et al., 1996; Tie et al., 2009b). Water-soluble ions (ws-ions) are major components of the atmospheric aerosols, especially $PM_{2.5}$. They can compose up to 60–70% of the total mass of suspended particulate matter (Ali-Mohamed, 1991). Therefore, observations on the chemical composition of water-soluble fine aerosols would be valuable for understanding their physical/chemical characteristics, sources, and behavior and formation mechanism.

With increasing industrial development and urbanization, the contribution from anthropogenic sources to aerosol loadings has significantly increased, especially over urban/industrial

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doi:10.1016/j.atmosres.2011.06.014

locations (Safai et al., 2010). Aerosol ions have been studied extensively in China. Prior studies have shown that ws-ions accounted for one-third or more of the aerosol particles' mass in urban regions (He et al., 2001; Hu et al., 2002; Wang et al., 2002; Yao et al., 2002; Wang et al., 2006; Shen et al., 2009; Tan et al., 2009).

Xi'an, the site for our study, is located on the Guanzhong Plain, at the southern edge of the Loess Plateau, (33°29′ to 34°44′ N, 107°40′ to 109°49′ E, and 400 m above sea level). With a population of about 8 million, Xi'an is the largest city in northwestern China. Due to the rapid increase of motor vehicles and the growth in energy consumption over the past few decades, Xi'an is facing serious air quality problems, mainly due to the high aerosol loadings in the region (Zhang et al., 2002; Cao et al., 2005a, 2009a; Shen et al., 2008). Although there is an evidence that the air quality has begun to improve recently (Zhang et al., 2002; Shen et al., 2008), high loadings of aerosol particles (henceforth simply aerosols) are still a major problem for the city. In the present study, we conducted a one-year monitoring program to measure the loadings of the ws-ions in $PM_{2.5}$ and to investigate the temporal variations and possible sources for these species. This study can provide useful information for establishing control strategies of aerosol pollution.

2. Experiment

2.1. Sampling site

The site (34.23°N, 108.88°E) for the study was located ~15 km south of downtown Xi'an in an urban zone that is surrounded by a residential area (Chow et al., 2002), where there are no major industrial activities, nor local fugitive dust sources. The air sampler itself was deployed ~10 m above ground level on the rooftop of the building housing of the Institute of Earth Environment, Chinese Academy of Sciences. Based on local meteorological characteristics and the residential heating season (mid-November through mid-March), the period from 15 March to May was designated as spring, the period from June to August was designated as summer, the period from September to 14 November was designated as autumn, and the period from 15 November to 14 March was designated as winter.

2.2. Sample collection

Daily 24-hour $PM_{2.5}$ samples were collected from March 2006 to March 2007. These were collected with the use of battery-powered mini-volume samplers (Airmetrics, Oregon, USA) operating at flow rates of 5 L min^{-1} (Cao et al., 2005a). Samples were collected on 47-mm quartz microfiber filters (Whatman QM/A, Maidstone, UK) which were pre-combusted at 900 °C for 3-h before sampling to remove contaminants. After collection, the loaded filters were placed in clean polystyrene petri dishes and stored in a refrigerator at about 4 °C to prevent the evaporation of volatile components.

Each filter sample was used for gravimetric determinations of aerosol mass concentrations. For these determinations of PM mass, each filter aliquot was equilibrated for 24-h in a room with a controlled temperature (20 to 23 °C) and relative humidity (35 to 45%) (U.S. EPA, 1997) both before and after sampling. The filters were weighed twice on an MC5 electronic microbalance (Sartorius, GÖTTINGEN, Germany) which has a sensitivity of 1 μg. The precisions (based on replicate weighing) were less than 15 μg per filter before sampling and 20 μg after sampling. The filters were reweighed whenever the difference between replicate weighing was out of that range.

2.3. Ion analyses

The concentrations of three anions (Cl^-, NO_3^- and SO_4^{2-}) and five cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were determined in aqueous extracts of the sample filters. To extract the ws-ions from the quartz filters, the portions of the filters used for the gravimetric analysis were placed in a separate 15 mL vials containing 10 mL distilled–deionized water (18.2 MΩ resistivity). The vials were placed in an ultrasonic water bath and shaken with a mechanical shaker for 1 h to extract the ions. The extracts were filtered through 0.45 μm pore size microporous membranes, and the filtrates were stored at 4 °C in clean tubes before instrumental analysis.

A Dionex-600 Ion Chromatograph (Dionex Inc., Sunnyvale, CA, USA) was used for the determinations of both cations and anions in the aqueous extracts of the air filters. For the cation analyses, the instrument was equipped with an IonPacCS12A column (20 mM methanesulfonic acid as the eluent) while for anions an IonPac AS14A column (8 mM Na_2CO_3/1 mM $NaHCO_3$ as the eluent) was used. Detection limits (MDLs) were as follows: 4.6 mg L^{-1} for Na^+, 4.0 mg L^{-1} for NH_4^+, 10.0 mg L^{-1} for K^+, Mg^{2+} and Ca^{2+}, 0.5 mg L^{-1} for F^-, Cl^- and Br^-, 15 mg L^{-1} for NO_2^- and NO_3^-, and 20 mg L^{-1} for SO_4^{2-}. Standard reference materials produced by the National Research Center for Certified Reference Materials (Beijing, China), were analyzed for quality control and assurance purposes. All the reported ion concentrations were corrected for field blanks, i.e., filters brought to the field and installed in the samplers but which no air was pumped. The experimental uncertainties were ±0.04 for F^-, NO_3- and SO_4^{2-}, ±0.03 for Ca^{2+}, ±0.02 for Cl^- and Br^-, ± 0.01 for NO_2^-, NH_4^+, K^+ and Mg^{2+}, and ±0.004 for Na^+.

2.4. Measurement of pH

pH-values were determined for the portions of the aqueous extracts that remained after the ion determinations were made. A Mettler Toledo MPC 227 pH/Conductivity Meter (Columbus, OH, USA) equipped with a Mettler Toledo InLab Pure Pro electrode (pH 1–11) was used for the pH value analysis.

2.5. Meteorology in Xi'an

Meteorological parameters were recorded during the sampling period. Continuous hourly temperature, relative humidity (RH) and precipitation were obtained from a local weather station (15 km north of the sampling site). Wind speed was monitored within 20 m of sampling site, 10 m above the ground level using an HFY-IA wind speed/wind direction instrument (Changchun Institute of Metrological Instruments, Changchun, Jilin Province, China). The monthly mean temperature (°C), relative humidity (%), precipitation (mm) and wind speed (m/s) are presented in Fig. 1. The monthly average highest temperature was recorded as 28.9 °C during July 2006 and lowest was 2.4 °C during January 2007. March 2006 was recognized as the driest month (relative humidity of 44.9%) and October 2006 was the most humid (74.4%) in the whole sampling period. Moreover, the monthly highest wind speed (m/s) were observed as 1.9 m/s on April, May, July 2006 and March 2007 and the lowest was 1.2 m/s on October 2006. Monthly average precipitation was highest during September 2006 (129.9 mm) and lowest during January 2007 (1.9 mm).

3. Results and discussion

3.1. Aerosol mass and ionic concentrations

The 24-h average $PM_{2.5}$ mass concentrations varied from 31.4 to 577.3 μg m^{-3} (Fig. 2), with an overall average and standard deviation of 194.1 ± 78.6 μg m^{-3}. The average $PM_{2.5}$ mass was far higher than recommended in international guidelines, and this finding raises serious health concerns for local residents. The $PM_{2.5}$ mass during winter was nearly twice than that in summer. Monthly average $PM_{2.5}$ concentrations were highest during December (288.7 μg m^{-3}) and lowest during May (130.8 μg m^{-3}). Prior studies on aerosols from Xi'an (Cao et al., 2005a; Shen et al., 2008) and other sites in northern China (Yao et al., 2002; Wang et al., 2005) lead us to suggest that the high loadings of $PM_{2.5}$ in winter are caused by local anthropogenic emissions, primarily those from coal combustion. The pollution episode days defined as mass concentration exceed 2 standard deviation of the seasonal average.

Fig. 2 also shows that there were different characteristics for different ions during different seasons. For example, dust storm events (DS) occurred during the study; these were on 27 March, 31 March and 1 April (green shadowed areas in Fig. 2). The corresponding $PM_{2.5}$ loadings were 317.4, 395.8 and 313.5 μg m^{-3} during the 3 dust events, respectively. During the DS event, high Ca^{2+} (10–20 μg m^{-3}) was found. The daily average $PM_{2.5}$ mass concentrations were 299.7 μg m^{-3} on 10 June and 253.9 μg m^{-3} on 11 June, the concentration was over twice than average mass concentration in summer (red shadowed areas in Fig. 2). Compared with the dust event, the concentrations of K^+ and Cl^- were high, with peak values of about 30 μg m^{-3}. Because Xi'an is located in the center of China (far from oceans), the effect of marine air on the urban aerosol particles should be minimal, and therefore, the high K^+ and Cl^- are likely from straw combustion emission (Shen et al., 2009). This presents a typical straw combustion event. SO_4^{2-}, NO_3^-, and NH_4^+ were major pollution ions in autumn (yellow) and winter (blue), which is represented in Fig. 2. This presents a typical haze event.

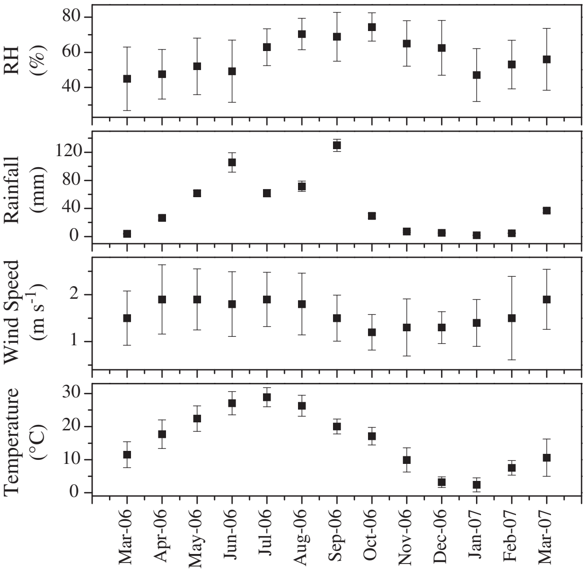

Fig. 1. Monthly average RH, rainfall, wind speed and ambient temperature in Xi'an. Vertical bars indicate ±1 standard deviation of the average.

In order to better understand the sources of measured ions, air mass back trajectories during the different pollution events defined in Fig. 2 (such as DS, straw combustion and haze) are given in Fig. 3. The HYSPLIT (NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory) model was applied with archive GDAS meteorological data to calculate 120 hour backward trajectories at our sampling location (34.23°N, 108.88°E) (Draxler and Rolph, 2003) during the different pollution events. The trajectory result shows that during the DS spring (27 March, 31 March and 1 April), air was predominantly from NW of the sampling site. Because there are mainly arid and semi-arid areas in NW of the sampling site, it indicates that dust events caused the high mass concentrations coupled with the high Ca^{2+} ions indicator.

Plots of the daily ion concentrations show some general similarities to the $PM_{2.5}$ mass but also some differences for the various ions (Fig. 2). SO_4^{2-}, NO_3^-, and NH_4^+ exhibited the highest concentrations of the ws-ions studied. The annual average concentration of SO_4^{2-} was 35.6 μg m^{-3}; and the highest daily loading of SO_4^{2-} (123.9 μg m^{-3}) occurred on October 13 and the lowest value (2.8 μg m^{-3}) on June 20. The NO_3^- concentrations varied from 0.1 μg m^{-3} to 66.7 μg m^{-3}, with the overall average of 16.4 μg m^{-3}. The concentrations of NH_4^+ ranged from 0.04 μg m^{-3} to 45.7 μg m^{-3}, and averaged 11.4 μg m^{-3} for the year. The maximum-to-minimum ratios for monthly average ion concentrations were 2.9 for SO_4^{2-}, (October/March), 3.6 for NO_3^- (February/May), and 5.6 for NH_4^+ (December/March), respectively.

On average, the three major soluble inorganic species (sulfate, nitrate and ammonium) accounted for 32.4% of the $PM_{2.5}$ mass and 82.0% of the total measured ws-ion concentration. The annual average concentrations of Cl^-, K^+, Na^+ and Ca^{2+} were 5.1 μg m^{-3}, 3.3 μg m^{-3}, 2.5 μg m^{-3} and 1.7 μg m^{-3}, and these four ions combined to account for 6.5% of the $PM_{2.5}$ mass and 16.2% of the measured ws-ions. The Mg^{2+} concentrations (on average of 0.5 μg m^{-3}) were generally lower than 1 μg m^{-3} during the year-long sampling period.

Sulfate is a major constituent of the $PM_{2.5}$ in Xi'an. Some fractions of the emitted SO_2, through the heterogeneous or homogeneous reaction, are oxidized to sulfate aerosols before dry or wet deposition (Cheng et al., 2000). Nitrate is also one of the major constituents of urban atmospheric aerosols. Particulate nitrate is transformed through the photo-oxidation of NO_2 derived from combustion of fossil fuels (Logan, 1983). Particulate ammonium mainly originates from ammonia vapor. Ammonium sulfate is the most stable while

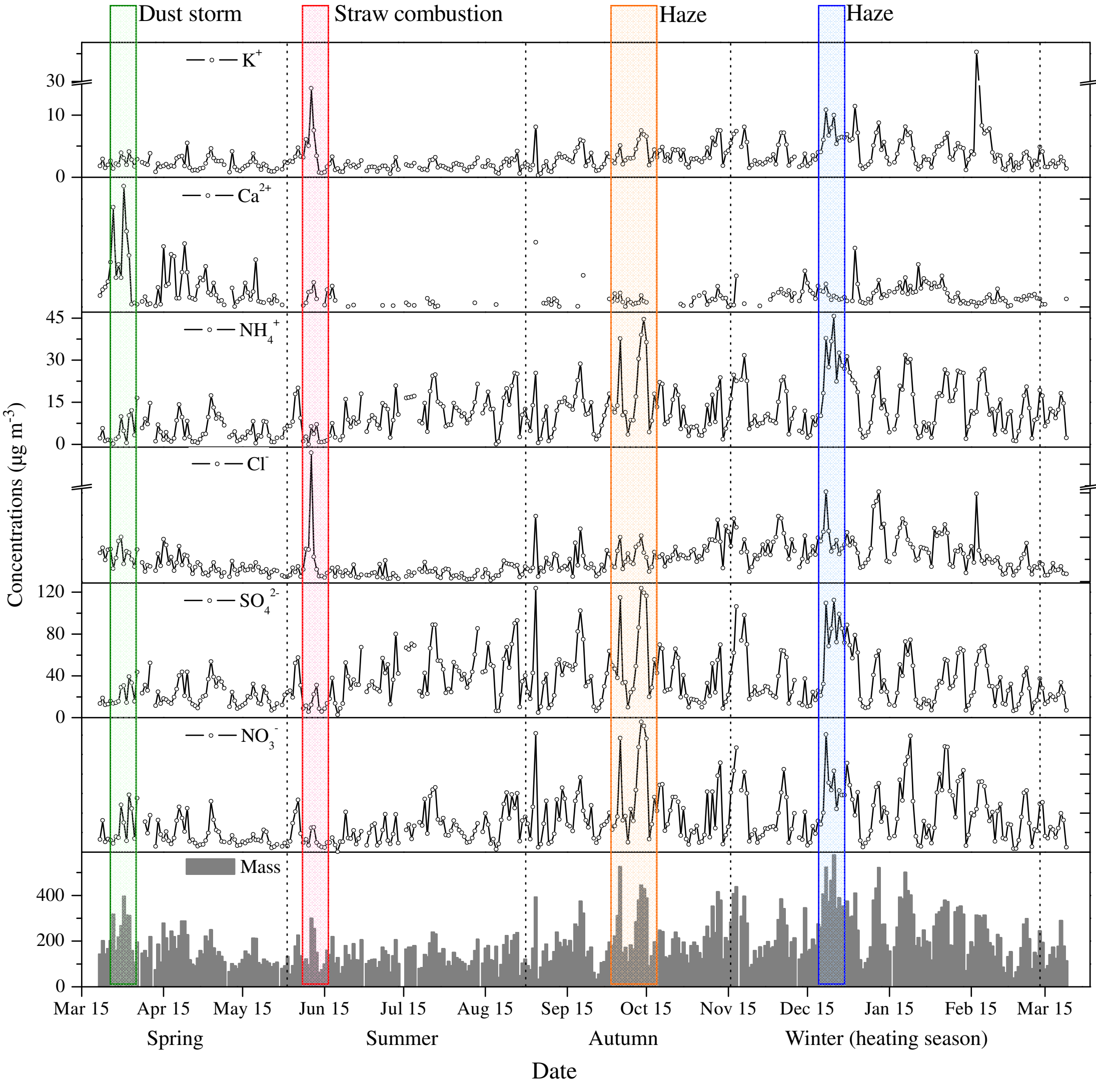

Fig. 2. Daily variations of PM2.5 mass concentrations and various ionic species. The shadowed areas show pollution episodes during all seasons.

ammonium chloride is the most volatile, hence ammonia prefers to react with sulfuric acid or sulfate. NH_4^+ and NO_3^- in the atmosphere are also the components of ammonium nitrate (NH_4NO_3), which is a product of gas-phase reactions between ammonia and nitric acid (Stelson and Seinfeld, 1982; Ho et al., 2003).

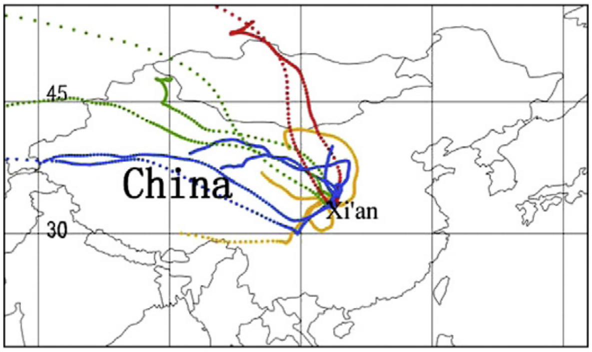

Fig. 3. Air mass back trajectories at Xi'an during March 2006–March 2007(NOAA Hysplit Model). Green: spring; red: summer; yellow: autumn; blue: winter.

The speciation of major ions in aerosol particles over Xi'an was investigated by examining the correlations among the ions. The abundances of SO_4^{2-} and NH_4^+ (equivalent units) in fine mode aerosols exhibit significant linear correlation ($[SO_4^{2-}]=0.5[NH_4^+]+0.06$, R = 0.93, P < 0.0001) over the study location, indicating the predominance of SO_4^{2-} as ammonium salt in the fine mode. The NH_4^+/SO_4^{2-} ratio (in equivalence units) was higher during winter months compared to those in spring, summer and autumn. The lower ratios during spring are associated with parallel increase of dust enriched in carbonate content and act as a substrate for efficient neutralization of SO_4^{2-} (Kumar and Sarin, 2010). Similarly, a strong correlation (R > 0.9) was observed for the molar concentration of NO_3^- and NH_4^+, with a relationship of $[NO_3^-]=0.39[NH_4^+]+0.02$. The concentrations of these major species can be calculated based on the individual ion concentrations and their mutual relationships (Wang et al., 2005, 2006). The strong correlation between NH_4^+ and SO_4^{2-} and NH_4^+ and NO_3^- suggests that these three major ions primarily existed as ammonium sulfate ($(NH_4)_2SO_4$), ammonium bisulfate (NH_4HSO_4) and ammonium nitrate (NH_4NO_3). NO_3^- and SO_4^{2-} were highly correlated with a correlation coefficient of 0.81. The high correlation suggested that the precursors of these species were released from similar emission sources such as coal burning, vehicle exhaust or industrial sectors. In addition to the sources, internal mixing and meteorological conditions might also play some roles for the high correlation.

3.2. Seasonal variations

The $PM_{2.5}$ mass was consistently higher in winter than in spring, summer and autumn (Fig. 2). The concentrations of SO_4^{2-} were highest in autumn (on average of 42.0 μg m^{-3}) during the whole sampling period (Table 1). The higher concentration of SO_4^{2-} was found in summer than in winter. The increased photochemical activity was one of the important reasons for the enhanced sulfate concentration during the period (Husain and Dutkiewicz, 1990). The seasonal NO_3^- concentration is presented in Table 1. Nitrate in autumn and winter was much higher than spring and summer. The relative low temperature (Fig. 1) and the high emissions of NO_x were favorable for the formation of NO_3^- aerosol and the reaction with NH_4^+ (Park et al., 2005; Mariani and Mello, 2007). NH_4^+ concentration was highest in winter, with an averaged value of 14.3 μg m^{-3}. The magnitude of the seasonal NH_4^+ concentration was found to be winter > autumn > summer > spring. The high NH_4^+ concentrations in Xi'an aerosols were most likely related to the use of fertilizers on the Guanzhong Plain as well as contributions from local sanitary wastes (Zhang et al., 2002). The conversion of NH_3 to NH_4^+ aerosol depends on the concentration of acids in the atmosphere, temperature, and water availability (Koerkamp et al., 1998; Kobara et al., 2007), as well as the flux rates of NH_3 (Nemitz et al., 2001). In winter, lower temperature and higher acid species such as sulfate and nitrate will favor the gas-particle reactions. In contrast, the higher temperatures in summer were not favorable for the conversion from NH_3 to NH_4^+. Previous studies also showed the higher NH_3 in summer while higher NH_4^+ in winter (Cao et al., 2009b). Cl^- showed seasonal variations similar to those of the two major ws-ions, indicating that emissions from coal combustion affected these ions as well (Yao et al., 2002). Unlike the other ions, Ca^{2+} was distinctly higher in spring than in the other seasons, and as the concentration of ws-Ca^{2+} is an indicator of mineral dust (Choi et al., 2001; Arimoto et al., 2004; Yin et al., 2005), this springtime peak in Ca^{2+} is most reasonably attributed to the well-known high concentrations of fugitive dust in spring (Cao et al., 2005a; Shen et al., 2008). Calcium, magnesium and sodium were all found mainly in the coarse mode indicating their crustal origin (Krivacsy and Molnar, 1998).

The secondary ion (SO_4^{2-}, NO_3^- and NH_4^+) concentrations in Xi'an were generally comparable to or slightly higher than those measured in other urban cities in China (Table 1). The SO_4^{2-} concentration in $PM_{2.5}$ at Xi'an was higher than what has been reported for Beijing (Wang et al., 2005), Shanghai (Wang et al., 2006), Nanjing (Wang et al., 2002), Qindao (Hu et al., 2002) and Hong Kong (Ho et al., 2003). NO_3^- concentrations at Xi'an were similar to those at Beijing (Wang et al., 2005) and Shanghai (Wang et al., 2006) in spring and

Table 1
Concentrations of SO_4^{2-}, NO_3^- and NH_4^+ in $PM_{2.5}$ from Xi'an and other Chinese cities.

Location	Period	Ion	Concentration (μg m^{-3})				Reference
			Spring	Summer	Autumn	Winter	
Xi'an	March 2006–March 2007	SO_4^{2-}	21.2	38.9	42.0	35.0	This study
		NO_3^-	9.6	11.8	20.6	20.2	
		NH_4^+	4.7	10.5	13.1	14.3	
Beijing	2001–2003	SO_4^{2-}	13.5	18.4	12.7	21.0	Wang et al., 2005
		NO_3^-	11.9	11.2	9.1	12.3	
		NH_4^+	6.5	10.1	6.3	10.6	
Shanghai	September 2003–January 2005	SO_4^{2-}	11.7	5.4	8.7	12.8	Wang et al., 2006
		NO_3^-	9.1	2.6	3.7	8.5	
		NH_4^+	4.1	2.4	3.6	4.4	
Nanjing	February 2001–May 2001	SO_4^{2-}	17.1				Wang et al., 2002
		NO_3^-	5.6				
		NH_4^+	9.6				
Qindao	1997–2000	SO_4^{2-}	11.9	12.3	11.6	16.1	Hu et al., 2002
		NO_3^-	3.4	2.6	3.1	9.0	
		NH_4^+	5.8	5.4	3.9	8.1	
Hong Kong	November 2000–February 2001	SO_4^{2-}				13.7	Ho et al., 2003
		NO_3^-				2.0	
		NH_4^+				2.6	

summer, but generally higher than at Nanjing (Wang et al., 2002), Qindao (Hu et al., 2002) and Hong Kong (Ho et al., 2003). The NH_4^+ concentrations were comparable to those at Beijing (Wang et al., 2005), Shanghai (Wang et al., 2006), Nanjing (Wang et al., 2002), Qindao (Hu et al., 2002) and Hong Kong (Ho et al., 2003).

The comparison among sites shows that the mixture of ws-ions in the $PM_{2.5}$ fraction at Xi'an is somewhat different from other Chinese cities, with a higher proportion of SO_4^{2-}.

3.3. Principal component analysis

A preliminary source identification study of the ws-ions was carried out by principal component analysis (PCA, SPSS version 13.0, SPSS Inc. 1988). PCA is a widely used statistical technique for data reduction and interpretation. In our application of PCA, a small number of latent factors (principal components or PCs) were extracted from the concentration data, and they were used to interpret the relationships among the measured variables (Han et al., 2006). If large differences exist in the standard deviations of variables, the PCA results will vary considerably depending on whether the covariance or correlation matrix is used (Farnham et al., 2003). The correlation matrix was used for the present study because the communality of these eight ws-ions was rather reasonable.

Furthermore, in this study all principal factors extracted with eigenvalues>1.0, were retained for interpretation as suggested by the Kaiser criterion (Kaiser, 1960). When the VARIMAX normalized rotation is used in PCA, as was the case in our study, each PC score contains information on correlations among all of the variables combined into a single number. The individual loading for each ion indicates its relative contribution each of the PC scores.

The two factor PCA model for the ws-ions in the $PM_{2.5}$ aerosol samples accounted for ~73.7% of the total variance in the concentration data (Table 2). Factor 1 account for ~49.0% of the total variance, and it was strongly loaded with SO_4^{2-}, NO_3^-, NH_4^+ and K^+, suggesting likely origins from anthropogenic sources, especially coal combustion, traffic emissions and biomass burning. Factor 2 is dominated by Na^+, Mg^{2+} and Ca^{2+}, and it accounted for ~24.7% of the total variance, suggesting their concentrations are affected by mineral dust from both natural and anthropogenic sources.

Table 2
Rotated component matrix for water-soluble ions in $PM_{2.5}$. (PCA loadings>0.6 are shown in bold).

Ion	Component		Communities
	1	2	
Na^+	0.26	**0.73**	0.61
NH_4^+	**0.97**	−0.03	0.94
K^+	**0.67**	0.46	0.65
Mg^{2+}	0.11	**0.85**	0.73
Ca^{2+}	−0.21	**0.80**	0.68
Cl^-	0.52	0.54	0.57
SO_4^{2-}	**0.92**	0.03	0.84
NO_3^-	**0.93**	0.11	0.88
Initial eigenvalue	3.92	1.98	
Variance explained	49.0%	24.7%	
Cumulative variance explained	49.0%	73.7%	

3.4. Ion balance calculations

Ion balance calculations are frequently used to investigate the acid–base balance of the ions in aerosol or other environmental samples. Equations (1) and (2) are used here to calculate the charge balance between cations and anions as follows:

$$\text{Cation equivalents} = \frac{Na^+}{23} + \frac{NH_4^+}{18} + \frac{K^+}{39} + \frac{Mg^{2+}}{12} + \frac{Ca^{2+}}{20}$$

$$\text{Anion equivalents} = \frac{SO_4^{2-}}{48} + \frac{NO_3^-}{62} + \frac{Cl^-}{35.5}.$$

The relationships between anions and cations are shown graphically in Fig. 4. The correlation coefficients for the anion vs. cation concentration data stratified by season all were higher than 0.94, and one simple explanation for this is that the ions share a common origin. The slope (anion/cation) of the linear regression for all $PM_{2.5}$ samples (Fig. 4) was close to 1.3. As most of the known major ions except hydrogen ions (H^+) were measured, the cation deficits are best explained by the presence of that ion. This result implies that the aerosol particles are acidic (Kerminen et al., 2001).

Dust storms are common atmospheric phenomenon in Xi'an, especially during the dry and windy spring (Zhang et al., 2002; Cao et al., 2005a; Shen et al., 2008). The anion/cation ratios, determined from the slopes of linear regressions for the seasonally stratified data followed the order summer (1.5)> autumn (1.4)>winter (1.2)>spring (0.8), and therefore in all seasons except spring, the $PM_{2.5}$ apparently was acidic. The low anion/cation ratio in spring suggests that the high concentrations of mineral dust particles buffered the aerosol acidity. The pH measurements of the sample solutions show a similar result, i.e., the samples were most acidic in winter (5.96) and least acidic in spring (6.17). Overall, the pH values varied from 4.71 to 6.87, with the annual average of 5.90.

In order to further understand the relationship between pH and major aerosol components, a statistical approach of multiple linear regression (MLR) was used to evaluate the

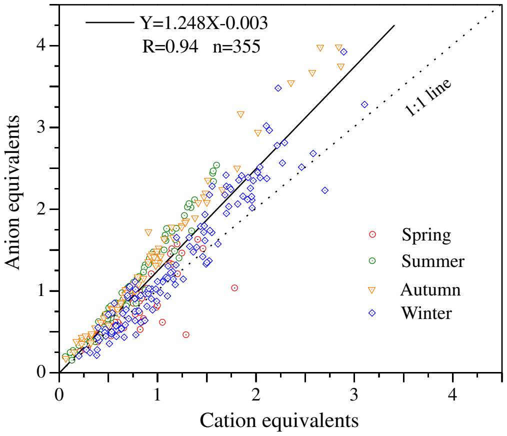

Fig. 4. Ion balance in $PM_{2.5}$.

correlation of the pH value with sulfate, calcium and potassium. The MLR formula is expressed by the following equations.

$$[\mathrm{pH}] = 6.26{-}0.09\left[\mathrm{SO_4^{2-}}\right] + 0.25\left[\mathrm{Ca^{2+}}\right]{-}0.09\left[\mathrm{K^{+}}\right] \qquad R = 0.78$$

The estimated regression coefficient in the above equations expressed the degree of pollutant contribution to pH value. Therefore, calcium was the main influencing factors on aerosol acidity. This may be partly due to the fact that northern China acid deposition was heavily modified by natural soil dust from desert and semiarid areas (Cao et al., 2005b).

3.5. Carbonate

CO_3^{2-} can affect atmospheric chemistry and aerosol characteristics because its alkalinity favors the uptake of SO_2 and NO_x and their conversion to SO_4^{2-} and NO_3^- on the surface, as well as removal of HNO_3 and H_2SO_4 from the gas phase (Dentener et al., 1996). The low anion to cation ratios observed in some of our springtime samples can be explained by the fact that carbonate ion was not measured. Mineral dust is the main source for aerosol carbonate (Claquin et al., 1999; Shen et al., 2007), and when relatively high concentrations of this ion are present, aerosol acidity can be buffered (Kerminen et al., 2001). Unfortunately, carbonate cannot be directly determined by our analytical methods because carbonate is contained in the chromatographic eluent. However, estimates of the carbonate concentration can be made based on the differences in the measured cations minus anions (in μg m^{-3}) as follows (Jankowski et al., 2008):

$$\mathrm{CO_3^{2-}} = \left(\mathrm{Na^+} + \mathrm{NH_4^+} + \mathrm{K^+} + \mathrm{Mg^{2+}} + \mathrm{Ca^{2+}}\right) - \left(\mathrm{Cl^-} + \mathrm{NO_3^-} + \mathrm{SO_4^{2-}}\right).$$

The calculated CO_3^{2-} mass concentration averaged 0.7 μg m^{-3} for the entire study, and this would account for only 0.4% of the total $PM_{2.5}$ mass, but in spring the CO_3^{2-} concentration (1.8 μg m^{-3}) was considerably higher, 1% of $PM_{2.5}$. The carbonate concentration in $PM_{2.5}$ at Xi'an was lower than what has been reported for Horqin sand land (Shen et al., 2007). The apparent carbonate mass fractions calculated in this study are lower than what has been seen in other samples at Xi'an. For example, Cao et al. (2005b) documented strong dust storm events at Xi'an and showed the CO_3^{2-} was 8% of the Asian dust mass in the $PM_{2.5}$ fraction (corresponding to 13% of carbonate minerals). The molar concentrations of Ca^{2+} were strongly correlated with those of the calculated CO_3^{2-} ($R=0.83$, $P<0.0001$, Fig. 5), and this implies that the two ions likely originated from the same source, most likely mineral dust. The slope of a linear regression between the two variables was slightly greater than unity, however (1.14), and this suggests that carbonates were not solely in the form of Ca_2CO_3, i.e., that CO_3^{2-} may have reacted to some extent with cations besides Ca^{2+}. While the weak correlation is observed between Ca^{2+} and SO_4^{2-} ($R=-0.03$), it indicates that Ca_2CO_3 was the major form for CO_3^{2-} in the aerosol samples.

Carbonate concentrations in the DS samples increased because of the large contribution of crustal matter. The peak concentrations of daily average calculated CO_3^{2-} reached 24.8 μg m^{-3} on 27 March, 22.4 μg m^{-3} on 31 March and 12.9 μg m^{-3} on 1 April. And the concentrations of CO_3^{2-} in $PM_{2.5}$ accounted for 7.8%, 5.7% and 4.1%, respectively. This result shows similar profiles with $PM_{2.5}$ mass concentrations analysis, the sample was highly influenced by transportation of Asian dust (the event marked in Fig. 2), an observation sustained also by the backward trajectory analysis. The carbonate concentration was found in order of, spring (1.8 μg m^{-3}) > winter (1.1 μg m^{-3}) > autumn (0.03 μg m^{-3}) > summer (0 μg m^{-3}). It was noticed that the order of seasonal average mass concentration of CO_3^{2-} was almost similar result with aerosol acidity analyzed. Therefore, airborne CO_3^{2-} may provide the important atmospheric alkaline component for buffering acid aerosol in northern China.

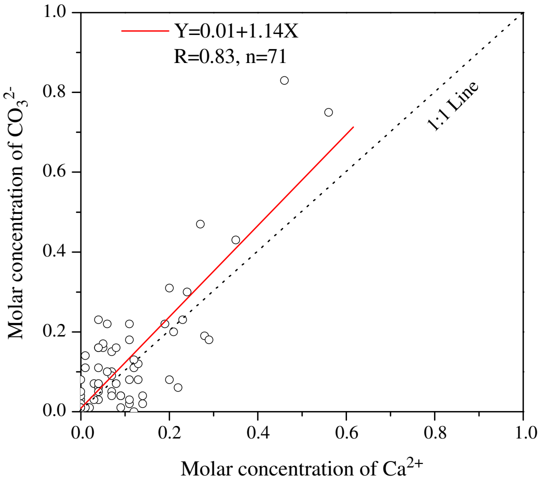

Fig. 5. Relationship between measured Ca^{2+} concentration and calculated CO_3^{2-} concentration.

3.6. Chemical conversions of species

Sulfate, nitrate and ammonium are typically the most abundant ions in the atmospheric aerosol, and this was the case in our study. To investigate the extent to which SO_2 is converted to SO_4^{2-} and NO_x is converted to NO_3^-, sulfur and nitrogen oxidation ratios (SOR and NOR, respectively) were calculated. These are defined as follows (Colbeck and Harrison, 1984; Ohta and Okita, 1990; Kaneyasu et al., 1999):

$$\mathrm{SOR} = \frac{n{-}\mathrm{SO_4^{2-}}}{\left(n{-}\mathrm{SO_4^{2-}} + \mathrm{SO_2}\right)}$$

$$\mathrm{NOR} = \frac{n{-}\mathrm{NO_3^{-}}}{\left(n{-}\mathrm{NO_3^{-}} + \mathrm{NO_2}\right)}.$$

Air Pollution Index (API) of SO_2 and NO_2 in Xi'an were collected from Xi'an Environmental Monitoring Station (http://www.xianemc.gov.cn/) and converted to concentrations. The formulas used for converting API to concentration is

$$C = C_{low} + \left[\left(I{-}I_{low}\right) / \left(I_{high}{-}I_{low}\right)\right] \times \left(C_{high}{-}C_{low}\right),$$

where C is the concentration and I is the API value. I_{high} and I_{low}, the two values most approaching to value I in the API grading limited value table, stand for the value larger and lower one than I, respectively; C_{high} and C_{low} represent the concentrations corresponding to I_{high} and I_{low}, respectively.

The SOR is a measure of the degree of oxidation of sulfur, and it is expressed in terms of the ratio of sulfate sulfur to "total" sulfur (as sulfate plus sulfur dioxide). Similarly, the NOR expresses the degree of oxidation of nitrogen in terms of the ratio of nitrate nitrogen to "total" nitrogen (as nitrate plus nitrogen dioxide). High SOR and NOR values imply that the photochemical oxidation of precursor gasses has led to the formation of large proportions of sulfate- and nitrate-containing secondary aerosol particles (Colbeck and Harrison, 1984; Ohta and Okita, 1990; Kaneyasu et al., 1995).

Monthly and seasonal variations in the SOR and NOR, along with changes in temperature, are plotted in Fig. 6, and peaks in the SOR are evident in summer and autumn. This result implies that the formation of secondary sulfate-rich particles is favored by the warm and relatively moist weather in summer and autumn. Further inspection of Fig. 6 shows that the NORs and SORs are at roughly the same level in autumn and winter, but in spring and summer the NOR is considerably lower than the SOR. This uncoupling of the two oxidation indices could be the result of differences in the ways in which sulfate- and nitrate-rich particles form and also by differences in their sources and removal.

The SORs were strongly related to NH_4^+ concentrations in summer (R = 0.93, Fig. 7.), and the strengths of the correlations between those variables were similar in spring (R = 0.87), autumn (R = 0.84) and winter (R = 0.86). Moreover, the SORs and temperature showed some similarities (R = 0.52), with both reaching their highest values during July. There are various mechanisms by which SO_4^{2-} forms from SO_2; these include gas-phase reactions involving SO_2 and OH radical, aqueous transformations (metal-catalyzed oxidation or H_2O_2/O_3 oxidation), and in-cloud processes, etc. The gas-phase oxidation of SO_2 to SO_4^{2-} by OH radical is a strong function of temperature (Seinfeld, 1986), and therefore, the positive correlation of SOR with temperature may provide some insight into the way in which SO_4^{2-} particles form. That is, a large proportion of the particles may form via the local gas-phase oxidation of SO_2 followed by condensation or sorption into the particle phase.

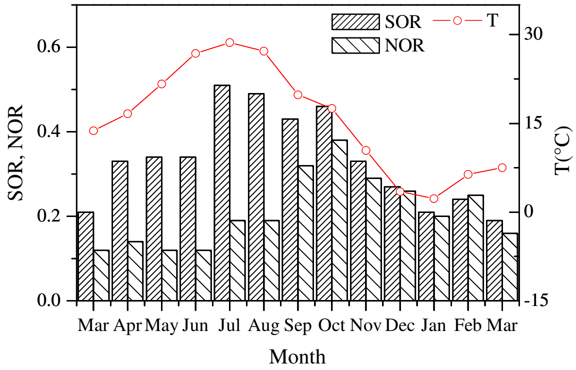

Fig. 6. Monthly average sulfur oxidation ratio (SOR), nitrogen oxidation ratio (NOR), and temperature.

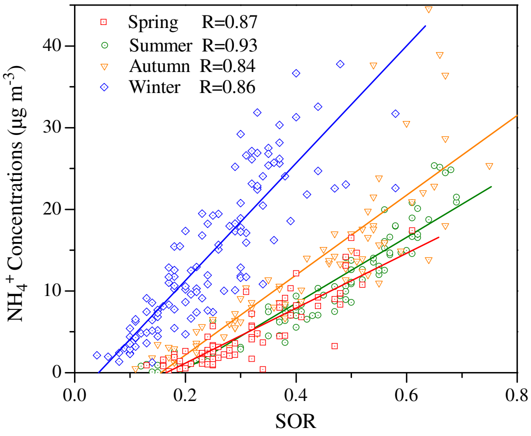

Fig. 7. Relationship between sulfur oxidation ratio (SOR) and NH_4^+ concentration.

Another factor that presumably affects the oxidation of SO_2 is the concentration of total ammonia (NH_3 and NH_4^+). In this study, gaseous NH_3 and NH_4^+ aerosol concentrations were only weakly correlated, implying that gas-particle reactions involving total ammonium can be influenced by many factors including sources, meteorology, removal, and so on. Prior studies by Cao et al. (2009b) have shown that NH_3 concentrations in Xi'an are high, and this likely to have a significant influence on atmospheric acidity and the formation of secondary aerosols. The positive correlation of SOR with NH_4^+ would suggest that $(NH_4)_2SO_4$ and NH_4HSO_4 might be the main chemical forms of SO_4^{2-}. The dominant controlling factors for the oxidation of SO_2 might be NH_4^+. Therefore, the control of NH_3, SO_2, and NO_2 emission could be an effective method to reduce PM levels and acid deposition in the near future.

5. Conclusions

The 24-h average mass concentration of $PM_{2.5}$ for a year-long study in Xi'an (194.1 μg m^{-3}) is high enough to raise health concerns over the air quality in the city. The three most abundant water-soluble ions were SO_4^{2-}, NO_3^- and NH_4^+, and they existed primarily as $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3. The analysis suggests that coal combustion is the main source for the three ions, especially in winter. Coal combustion is also an important source for NH_4^+ and K^+ and possibly Na^+ and Cl^- as well. The relative proportions of the major ions in Xi'an were somewhat different from those in other Chinese cities, e.g., with a higher proportion of SO_4^{2-} in Xi'an than in Beijing. Ion balance calculations indicate that $PM_{2.5}$ in summer, autumn and winter was acidic, while the aerosol was less acidic and possibly even alkaline in spring due to the buffering effects of mineral dust. The springtime dust storms are major source for Na^+, Mg^{2+} and Ca^{2+}. The observed low anion-to-cation ratios found in spring were ascribed to carbonate, which was not measured but is known to be another component of mineral dust. Indeed, a strong relationship between CO_3^{2-} and Ca^{2+} implies that Ca_2CO_3 was the major form for the aerosol carbonate. Seasonal patterns in the SOR indicate that the formation of secondary sulfate is favored by the warm moist weather in summer and autumn. A difference in the seasonality of the SOR vs. NOR can be explained by differences in the ways in which sufate- and nitrate-rich particles form but this also may reflect differences in their sources or removal. The control of NH_3 emission is important to the reduction of the atmospheric loading of secondary PM in Xi'an. PCA analyses were used to gain insight into the origins of different water-soluble ions in Xi'an. SO_4^{2-}, NO_3^-, NH_4^+ and K^+ are attributed to a main origin from anthropogenic sources. Furthermore, Na^+, Mg^{2+} and Ca^{2+} originate mainly from natural sources, which mainly buffered the acidity of $PM_{2.5}$ in spring.

Acknowledgments

This work was supported by the Natural Science Foundation of China (NSFC40925009, NSFC41073102), projects from the Chinese Academy of Sciences (no. O929011018, KZCX2-YW-BR-10, KZCX2-YW-148) and the Ministry of Science & Technology (2009IM030100). The National Center for Atmospheric Research is sponsored by the National Science Foundation.

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