



Ionic composition of TSP and PM_{2.5} during dust storms and air pollution episodes at Xi'an, China

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ARTICLE INFO

Article history:

Received 13 September 2008

Received in revised form

14 February 2009

Accepted 5 March 2009

Keywords:

TSP

PM_{2.5}

Water-soluble ions

Pollution episodes

ABSTRACT

TSP and PM_{2.5} samples were collected at Xi'an, China during dust storms (DSs) and several types of pollution events, including haze, biomass burning, and firework displays. Aerosol mass concentrations were up to 2 times higher during the particulate matter (PM) events than on normal days (NDs), and all types of PM led to decreased visibility. Water-soluble ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, F⁻, Cl⁻, NO₃⁻, and SO₄²⁻) were major aerosol components during the pollution episodes, but their concentrations were lower during DSs. NH₄⁺, K⁺, F⁻, Cl⁻, NO₃⁻, and SO₄²⁻ were more abundant in PM_{2.5} than TSP but the opposite was true for Mg²⁺ and Ca²⁺. PM collected on hazy days was enriched with secondary species (NH₄⁺, NO₃⁻, and SO₄²⁻) while PM from straw combustion showed high K⁺ and Cl⁻. Firework displays caused increases in K⁺ and also enrichments of NO₃⁻ relative to SO₄²⁻. During DSs, the concentrations of secondary aerosol components were low, but Ca²⁺ was abundant. Ion balance calculations indicate that PM from haze and straw combustion was acidic while the DSs samples were alkaline and the fireworks' PM was close to neutral. Ion ratios (SO₄²⁻/K⁺, NO₃⁻/SO₄²⁻, and Cl⁻/K⁺) proved effective as indicators for different pollution episodes.

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1. Introduction

The composition of the atmospheric aerosol is important relative to its effects on biogeochemical cycles, human health, and visibility (Horvath, 1996; Yadav et al., 2003; Schichtel et al., 2001; Tsai and Cheng, 1999; Tsai et al., 2003; Lee et al., 2005; Ho et al., 2006a,b; Yuan et al., 2004, 2006). Prior studies showed that water-soluble ions accounted for one-third or more of the aerosol particles' mass in Chinese urban regions (He et al., 2001; Hu et al., 2002; Wang et al., 2002, 2006). Furthermore, the relative abundances of water-soluble ions, such as sulfate, nitrate, ammonium, and other species play an important role in determining the hygroscopicity of atmospheric aerosols (Tang et al., 1995); and their tendency to absorb water at high relative humidities (RHs) can exacerbate visibility impairment (Dougle et al., 1996; Lee et al., 2005; Yuan et al., 2006). In addition, detailed information on particle-size

distributions of water-soluble ions has been obtained (Kadowaki, 1976; Wall et al., 1988; Kerminen et al., 2001; Venkataraman et al., 2001; Tsai et al., 2003; Shen et al., 2008), and it has been shown that the size distributions of the ions can vary significantly with season and geographic location (Fitzgerald, 1991).

Xi'an (area = 1066 km², population = 5.1 million), located on the Guanzhong Plain on the southern edge of the Loess Plateau, is the largest city in northwestern China. Along with a rapid increase in motor vehicle traffic and energy consumption during the past few decades, Xi'an is facing long-term air quality problems, with aerosol particles (hereinafter aerosols) being a major concern (Zhang et al., 2002; Cao et al., 2005a; Shen et al., 2008). Although the air quality has improved recently (Zhang et al., 2002; Shen et al., 2008), high loadings of aerosols are still the major problem for the city. Dust storms (DSs) and pollution in the form of haze and smoke from straw burning and firework displays are considered as the main reasons for the episodes of poor air quality in Xi'an and other cities like Beijing in China (Cao et al., 2005a; Wang et al., 2006, 2007). Investigations of these sources are important because they also cause high aerosol loadings at other cities in Asia.

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Haze, which is defined as a condition in which the atmospheric visibility is less than 10 km by China Meteorological Agency (http://www.cma.gov.cn/zcfg/qxbz/bzzqyj/index_5.html), has been frequently observed in Xi'an. Most of the haze, which is most common in winter and spring, results from excess PM emitted by anthropogenic sources and particles produced via gas-to-particle conversion (Watson, 2002). Dust storms are another atmospheric phenomenon in Xi'an, and they are most common in the dry springtime. Cao et al. (2005b) reported that a heavy DS in Xi'an led to extremely high PM_{2.5} levels (740 µg m⁻³). Straw combustion in suburban areas, which is most prevalent during the summer and fall harvests, also causes serious air pollution in Xi'an. The burning of agricultural residues, mainly rice and wheat straw, is a common method for waste disposal after the crops are harvested (Haleh and Lowell, 2007). Although this source is sporadic, the combustion of straw may release pollutants such as NO_x, SO₂, CO, and produce PM with a very high content of K⁺ and Cl⁻ 40–80%(w/w) (Jacobs et al., 1997; Katsumi et al., 2000). Moreover, there are increased risks for bronchial asthma in children who live near the areas where the straw was burned (Jacobs et al., 1997; Katsumi et al., 2000). Firework displays are common during Chinese traditional Spring Festivals, and they can also lead to the impairment of air quality. Fireworks contain chemicals such as potassium nitrate, potassium chlorate, potassium perchlorate, charcoal, sulfur, manganese, sodium oxalate, aluminum, and iron dust powder, strontium nitrate, and barium nitrate, etc. (Mclain, 1980). The composition of PM produced from fireworks includes trace metals and organic compounds which may pose a threat to human health (Ravindra et al., 2001). Furthermore, firework displays can generate ground-level ozone, which may put people at risk for respiratory disease (Attri et al., 2001).

Information on water-soluble ions in samples collected during PM episodes is needed to: (1) create speciated emission inventories for use in source-oriented models, (2) evaluate possible effects on human health, and (3) improve pollution control strategies. As the potential effects of these pollution episodes on the environment and human health have been recognized, several studies have focused on one or two aspects of these four PM sources (Okada et al., 2001; Schichtel et al., 2001; Yadav et al., 2003; Kang et al., 2004; Wang et al., 2006, 2007), but none has considered all four simultaneously. Here, aerosol particles were collected to investigate the effects of the four PM sources on the major ion composition of two types of PM, that is PM_{2.5} (particle size smaller than 2.5 µm) and TSP (Total Suspended Particulates).

2. Experimental

2.1. Aerosol sample collection

The TSP and PM_{2.5} samples were collected simultaneously on 47-mm diameter cellulose nitrate membranes (0.8 µm pore size, AAWP04700, Millipore Corp.) from the roof of a 15-m high building. The sampling site is located in the southeastern part of downtown Xi'an, only about 100 m from the South Second Ring Road (Fig. 1). North and east of the sampling site are residential areas and the campus of Xi'an Jiaotong University, while to the south and west are the South Second Ring and Xingqin Roads, where the traffic is always heavy. During the sampling periods, meteorological data, including ambient temperature, relative humidity (RH), dew point, wind speed, wind direction, visibility, and rainfall were recorded by the Shaanxi meteorological agency.

Twenty-four hour TSP and PM_{2.5} (10:00 am to 10:00 am, local time) samples were obtained simultaneously every third day from 1 October 2006 to 30 September 2007 using a dual-channel low-

volume sampler (Tokyo Dylec Corp., Japan) operating at a flow rate of 5 l min⁻¹. A total of 227 aerosol samples was collected, and these include 14 pairs of haze samples, 5 sets of DSs samples, 2 pairs of straw combustion samples, 5 PM_{2.5} firework burning samples (no TSP samples were collected for the latter due to a failure of the volume measurements for the TSP channel), and 90 pairs of samples collected on normal days (NDs). Of the fourteen haze samples, two were collected during autumn; one was in spring, and others were in winter. DSs samples were collected in spring exclusively; the straw combustion filters were sampled in early June, and during that time the peasants had just finished harvesting the wheat and burning the straw residues. Firework display samples were collected during the Chinese Spring Festival (sampling from 17 to 21 in Feb 2007). Field blank filters were also collected each month by exposing filters in the sampler but not drawing air through them; these were used to account for any artifacts introduced during the sample handling procedure. The exposed filters were stored in a refrigerator at ~4 °C until analysis to minimize the evaporation of volatile components.

Aerosol mass loadings were determined gravimetrically with the use of a Sartorius MC5 electronic microbalance (±1 µg sensitivity, Sartorius, Göttingen, Germany). Before weighing, the filters were equilibrated for 24 h at 20–23 °C and a relative humidity between 35% and 45% (USEPA, 1997). Each filter was weighed at least three times before and after sampling following the 24 h equilibration period. The mean net mass for each filter was obtained by subtracting the pre-deployment weight from the average of the post-sampling readings.

2.2. Water-soluble ions analysis

One-fourth of each filter sample was used to determine the aerosol ion mass concentrations. Six anions (SO₄²⁻, NO₃⁻, Cl⁻, and F⁻) and five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) in aqueous extracts of the filters were determined by an ion chromatography (IC, Dionex 500, Dionex Corp, Sunnyvale, CA). To extract the water-soluble species from the cellulose nitrate filters, one-fourth of each filter was put into a separate 20 ml vial containing 10 ml distilled-deionized water (a resistivity of 18 MΩ), and then placed in ultrasonic water bath for 60 min. The samples were shaken two times using a mechanical shaker for 1 h each time to completely extract the ionic compounds. The extracts were filtered with a 0.45 µm pore size microporous membrane, and the filtrates were stored at 4 °C in a clean tube before analysis.

Cation (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) concentrations were determined with the use of a CS12A column (Dionex Corp.), using 20 mM methanesulfonate as an eluent. Anions (SO₄²⁻, NO₃⁻, Cl⁻, and F⁻) were separated by an AS11-HC column (Dionex Corp.), using 20 mM KOH as the eluent. The method detection limits (MDLs) were 4.6 µg L⁻¹ for Na⁺, 4.0 µg L⁻¹ for NH₄⁺, 10.0 µg L⁻¹ for K⁺, Mg²⁺ and Ca²⁺, 0.5 µg L⁻¹ for F⁻ and Cl⁻, 15 µg L⁻¹ for NO₃⁻, and 20 µg L⁻¹ for SO₄²⁻. Standard Reference Materials produced by the National Research Center for Certified Reference Materials, China were analyzed for quality assurance purposes. Blank values were subtracted from sample concentrations.

3. Results and discussion

3.1. Mass concentrations of aerosol particles during four PM episodes

TSP and PM_{2.5} mass concentrations for the DSs, pollution events, and NDs are given in Fig. 2. The average TSP mass concentration during haze, DSs, and straw combustion were 677.3 µg m⁻³, 631.2 µg m⁻³, and 622.6 µg m⁻³, respectively, and all were more

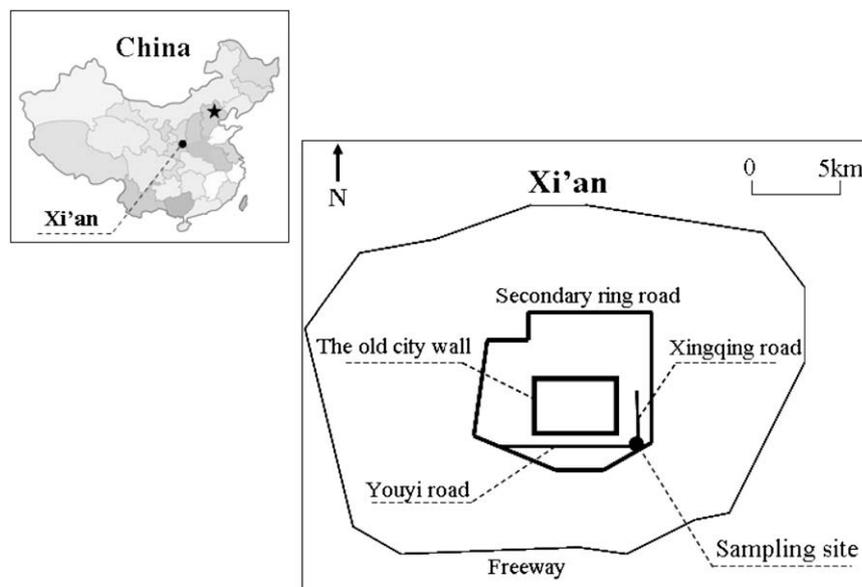


Fig. 1. Location of sampling site.

than double what was measured on NDs. These high mass loadings exceed the Chinese Class 2 TSP standard (24-h mean value of $300 \mu\text{g m}^{-3}$) and the yearly standard, that is, a mean value of $200 \mu\text{g m}^{-3}$. Compared with the TSP mass, the variation of $\text{PM}_{2.5}$ concentrations for DSs and three pollution episodes showed some differences, exhibiting a decreasing order as follows: straw burning ($404.1 \mu\text{g m}^{-3}$) > haze ($351.2 \mu\text{g m}^{-3}$) > fireworks ($298.8 \mu\text{g m}^{-3}$) > DSs ($137.6 \mu\text{g m}^{-3}$). Among the four PM types, DSs showed a relatively low $\text{PM}_{2.5}$ mass, closest to the NDs mean value of $130.0 \mu\text{g m}^{-3}$, while the $\text{PM}_{2.5}$ concentrations for haze, straw burning, and fireworks increased by 2- to 3-fold over NDs. The $\text{PM}_{2.5}$ concentrations for these pollution events also exceeded the 24-h American air quality standard of $35 \mu\text{g m}^{-3}$ and yearly mean value of $15 \mu\text{g m}^{-3}$ (EPA, 2006). China currently has no National $\text{PM}_{2.5}$ standard, but this comparison illustrates the seriousness of the fine particle pollution in Xi'an.

Previous studies have shown that aerosol loadings are one of the factors most responsible for visibility reduction (Sequeira and Lai, 1998; Watson, 2002; Lee et al., 2005). One would expect the high PM loadings at Xi'an to impair visibility, and so we examined the data for relationships between aerosol mass and visibility. The

meteorological records show that the mean ambient visibilities on NDs averaged 13.1 km, but they were reduced to 10.4 km for DSs days, 5.3 km for haze events, 8.5 km for straw combustion, and 11.8 km for fireworks shows, respectively. Furthermore, the reduction in visibility was strongly related to $\text{PM}_{2.5}$ mass (the correlation coefficient $R = 0.71$, not shown), but the relationship between visibility and TSP was much weaker ($R = 0.34$). These preliminary results suggest that fine-particles are especially important for visibility reduction, but there are additional factors (such as meteorological variable) that need to be evaluated, and a detailed analysis of PM and visibility is beyond the scope of this paper.

The ratios of $\text{PM}_{2.5}$ to TSP mass concentrations for DSs, haze, straw, and NDs were 21.0%, 51.8%, 64.9%, and 49.0%, respectively, and therefore the dust storms had the greatest proportion of coarse particles. Wang et al. (2006) reported a similar result; in their studies, which were conducted in Beijing, the $\text{PM}_{2.5}/\text{TSP}$ mass ratios during dust storm events were 22%. For the pollution events, $\text{PM}_{2.5}$ composed more than half of TSP mass, and this demonstrates the major contribution of fine-particles to aerosol pollution.

3.2. Concentration and variation of ionic species during pollution episodes and NDs

For comparison with the episodes of elevated PM, the major ion composition for NDs is summarized in Table 1. The total ion concentrations on NDs for TSP and $\text{PM}_{2.5}$ were $80.1 \mu\text{g m}^{-3}$ and $56.5 \mu\text{g m}^{-3}$, amounting to 32.9% of TSP and 49.1% of $\text{PM}_{2.5}$ mass. The TSP ion masses were in the order $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Ca}^{2+} > \text{NH}_4^+ > \text{Cl}^- > \text{K}^+$ while for $\text{PM}_{2.5}$ the order was slightly different $\text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+ > \text{Cl}^- > \text{K}^+ > \text{Ca}^{2+}$. Total ion masses on NDs were much lower than those in the PM from the pollution sources, but actually higher than on DS days. In general, the percentage of the total aerosol mass contributed by the ions was higher in $\text{PM}_{2.5}$ than in TSP, showing that water-soluble ions were more concentrated in the finer-sized particle.

During the haze periods, the ions in TSP samples followed this decreasing order: $\text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+ > \text{Ca}^{2+} > \text{Cl}^- > \text{K}^+ > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+}$. The total ion mass concentration was $266.1 \mu\text{g m}^{-3}$ on average during haze, and this accounted for 39.0% of the TSP mass. For $\text{PM}_{2.5}$, the concentrations followed the order $\text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+ >$

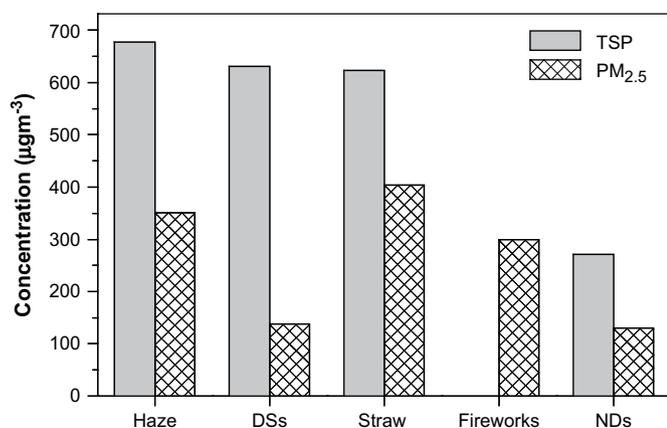


Fig. 2. TSP and $\text{PM}_{2.5}$ mass concentration for dust storms (DSs), pollution events, and normal days (NDs).

Table 1
Concentrations for aerosol particles and ionic species.

Pollution events			Concentration ($\mu\text{g m}^{-3}$) and standard deviation (S.D.)									
			mass	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Haze	TSP (n = 14)	Average	677.3	2.5	30.1	6.6	2.3	22.2	3.2	18.3	70.0	110.9
		S.D.	144.9	0.9	14.1	1.9	0.6	7.6	1.2	6.2	35.2	52.1
	PM _{2.5} (n = 14)	Average	351.2	1.8	28.8	6.0	0.5	2.7	1.5	15.2	56.2	93.6
		S.D.	89.6	0.6	11.6	1.5	0.2	1.4	0.8	6.1	23.7	39.0
Dust Storms	TSP (n = 5)	Average	631.2	3.7	2.7	1.3	1.0	18.6	1.0	2.9	5.3	16.7
		S.D.	343.2	2.5	2.6	0.5	0.5	6.6	0.2	1.6	2.2	9.7
	PM _{2.5} (n = 5)	Average	137.6	1.1	1.4	1.1	0.2	4.3	0.7	2.2	3.1	11.7
		S.D.	26.4	0.4	0.9	0.6	0.2	2.5	0.1	0.6	1.6	9.1
Straw Combustion	TSP (n = 2)	Average	622.6	2.4	18.2	15.1	1.3	13.4	0.9	15.5	33.1	65.1
		S.D.	24.7	0.3	1.0	0.8	0.1	5.7	0.4	11.5	6.9	24.8
	PM _{2.5} (n = 2)	Average	404.1	0.6	14.4	14.3	0.3	1.3	0.8	14.6	29.3	62.7
		S.D.	12.8	0.4	2.9	3.6	0.0	0.2	0.4	7.2	4.7	6.6
Fireworks Displays	PM _{2.5} (n = 5)	Average	298.8	2.9	21.1	14.7	1.4	0.8	0.8	8.3	59.9	30.2
		S.D.	26.7	0.4	6.4	12.0	1.3	0.6	0.1	6.5	8.9	7.0
Normal Days	TSP (n = 90)	Average	270.8	1.4	8.3	2.3	0.9	11.4	0.9	4.9	16.1	34.0
		S.D.	110.5	0.9	5.9	1.4	0.5	6.7	0.7	3.0	10.9	21.9
	PM _{2.5} (n = 90)	Average	130.0	0.9	7.6	1.9	0.2	1.3	0.5	4.2	12.0	27.9
		S.D.	63.9	1.0	5.8	1.3	0.1	1.0	0.4	2.8	9.1	19.3

Cl⁻ > K⁺ > Ca²⁺ > Na⁺ > F⁻ > Mg²⁺. The Ca²⁺ concentrations differed by nearly ten-fold between TSP and PM_{2.5}, from 22.2 $\mu\text{g m}^{-3}$ in TSP to 2.7 $\mu\text{g m}^{-3}$ in PM_{2.5}. The results showed that SO₄²⁻, NO₃⁻, NH₄⁺, Cl⁻, and K⁺ were enriched in fine particles during the haze episodes, while Ca²⁺ and Mg²⁺ were more concentrated in the coarse particle fraction. The average total ion concentration in PM_{2.5} during haze was 206.3 $\mu\text{g m}^{-3}$; this is equal to 58.7% of the PM_{2.5} mass and shows that water-soluble ions were abundant in PM_{2.5} during haze episodes. In the haze samples, the three secondary aerosol species, that is, sulfate, nitrate, and ammonium were the most abundant of the ions studied; they accounted for 79.3% of the total TSP and 86.6% of the total PM_{2.5} ion concentrations. Our results are consistent with those of haze studies conducted in Beijing by Wang et al. (2006).

The major ion composition of TSP and PM_{2.5} ions during DSs differed strong from that during haze. During DSs, the total TSP and PM_{2.5} ion mass concentrations (51.6 and 27.3 $\mu\text{g m}^{-3}$, respectively) were the lowest of the four types of PM events. In the TSP samples, Ca²⁺, SO₄²⁻, and NO₃⁻ were the most abundant ions, and Ca²⁺ alone accounted for 35.0% of TSP mass, ranking at the top of the ions. Prior studies have similarly shown that high Ca²⁺ occurs during dust storms (Cao et al., 2005b; Choi et al., 2001; Arimoto et al., 2004; Shen et al., 2007). The secondary ions' concentrations during the DSs were at the lowest levels of the PM episodes, and perhaps more interestingly, lower also than on NDs. That is, SO₄²⁻, NO₃⁻, and NH₄⁺ concentrations during DSs were 16.7 $\mu\text{g m}^{-3}$, 5.3 $\mu\text{g m}^{-3}$, and 2.7 $\mu\text{g m}^{-3}$, respectively, which were only 8–17% of those during haze events. The Ca²⁺ concentration in PM_{2.5} was less than one-quarter of that in TSP, again showing that Ca²⁺ is more abundant in coarse particles. The total water-soluble ions only accounted for 8.7% of the TSP mass and 18.9% of the PM_{2.5} mass, with much of the remainder most likely attributable to mineral dust.

Wheat straw and maize stalks are burned for cooking year round in suburban areas of Xi'an, and they are also burned for heat during winter and early spring. The TSP ions in the straw combustion samples ranked in the order SO₄²⁻ > NO₃⁻ > NH₄⁺ > Cl⁻ > K⁺ > Ca²⁺ > Na⁺ > Mg²⁺ > F⁻. The PM_{2.5} ion abundances were nearly in the same order as for TSP except for Ca²⁺, which proved relatively more abundant in TSP. Compared with haze and DSs samples, the chemical profiles for straw combustion were strongly enriched with K⁺ and Cl⁻, which together made up ~20% of the water-soluble ions. The K⁺/Cl⁻ mass ratio was

close to the unity for both TSP and PM_{2.5}. As Xi'an is far inland, marine influences on the urban aerosol particles should be minimal, and therefore, the high K⁺ and Cl⁻ are more likely from straw combustion emission.

Prior studies have shown that soluble K⁺ can be enriched in the aerosol as a result of biomass burning (Andreae, 1983; Duan et al., 2004; Chow et al., 2004; Jacobs et al., 1997; Katsumi et al., 2000; Ikegami et al., 2001). High K⁺ and Cl⁻ also have been measured in source profile studies of burning vegetation and residential wood combustion (Yamasoe et al., 2000; Watson et al., 2001), and their ratios in those studies were close to the unity as was the case in our samples from Xi'an. Total ion concentrations for the TSP and PM_{2.5} straw combustion samples were similar (160.2 $\mu\text{g m}^{-3}$ and 143.3 $\mu\text{g m}^{-3}$, respectively), and they accounted for 25.6% and 35.5% of TSP and PM_{2.5} mass. One would presume carbonaceous particles to be a major contributor to the undetermined mass for the PM from straw combustion (Watson et al., 2001).

Although there were no TSP firework samples available for analysis, the PM_{2.5} samples provide some insights into the composition of PM from fireworks. The mass concentrations of the PM_{2.5} ions followed the order NO₃⁻ > SO₄²⁻ > NH₄⁺ > K⁺ > Cl⁻. Interestingly, K⁺ was at a level comparable to that during the straw combustion events, but Cl⁻ was slightly lower. Further, the NO₃⁻ concentrations exceeded SO₄²⁻, and this is remarkably different compared with the DSs, haze, straw burning, or NDs samples. Some investigators have used NO₃⁻/SO₄²⁻ mass ratios to evaluate the influences of mobile versus stationary pollution sources (Arimoto et al., 1996; Hu et al., 2002; Yao et al., 2002; Ye et al., 2003). Several of those studies indicate that high NO₃⁻/SO₄²⁻ ratios occur when the influences of motor vehicle emissions exceed those from the coal combustion, but the high levels of K⁺ observed in the fireworks samples cannot be attributed to motor vehicle exhaust, and therefore, NO₃⁻/SO₄²⁻ ratios greater than unity combined with high levels of K⁺ may be a tracer of PM from fireworks. The chemical profile of the fireworks' PM is also quite consistent with the composition of fireworks (McLain, 1980). The average total ion concentration for the fireworks PM_{2.5} samples was 140.1 $\mu\text{g m}^{-3}$, and this accounted for 46.8% of the mass.

We noted that K⁺ and Cl⁻ were at high levels in both the fireworks and haze samples, but they were still less abundant than either sulfate or nitrate. To further investigate the characteristics of

Table 2Ratios of $\text{SO}_4^{2-}/\text{K}^+$, $\text{NO}_3^-/\text{SO}_4^{2-}$, and Cl^-/K^+ in dust storms (DSs), pollution events, and normal days (NDs).

Events	$\text{SO}_4^{2-}/\text{K}^+$				$\text{NO}_3^-/\text{SO}_4^{2-}$				Cl^-/K^+			
	TSP		$\text{PM}_{2.5}$		TSP		$\text{PM}_{2.5}$		TSP		$\text{PM}_{2.5}$	
	mean	ranges	mean	ranges	mean	ranges	mean	ranges	mean	ranges	mean	ranges
Haze	16.6	12.4–25.0	15.2	11.1–25.2	0.7	0.3–1.0	0.7	0.3–1.0	2.8	1.6–4.9	2.7	1.2–4.3
DSs	14.2	11.6–21.8	7.9	4.6–12.1	0.4	0.2–0.4	0.3	0.2–0.5	2.4	0.9–3.0	1.8	1.2–2.7
Straw Combustion	4.4	3.0–5.7	4.6	3.4–5.7	0.5	0.5–0.6	0.5	0.4–0.6	1.0	0.7–1.3	1.0	0.6–1.4
Fireworks Displays			3.3	2.1–4.8			2	1.8–2.1			0.6	0.5–0.8
NDs	16.3	3.2–40.3	17.1	4.6–59.6	0.5	0.2–0.9	0.4	0.2–0.8	2.8	0.7–17.6	2.9	0.9–18.1

the four types of PM, several ion ratios were calculated and compared. As shown in Table 2, the concentration ratio of SO_4^{2-} to K^+ in $\text{PM}_{2.5}$ was 4.6 in straw-combustion PM and 3.3 in fireworks PM, but much higher in DSs (7.9) and especially in haze (15.2). A similar pattern was also found for the TSP samples, suggesting that low $\text{SO}_4^{2-}/\text{K}^+$ ratios may be useful for distinguishing straw combustion and fireworks burning from other PM events. As noted above and also shown in Table 2, the $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio was remarkably different in the firework samples compared with other types of PM. Moreover, Cl^-/K^+ ratios varied considerably among PM events: the Cl^-/K^+ ratio in haze was over twice that during straw combustion; while in firework burnings, it was about half of that during straw combustion. The variations in the ion ratios tended to be consistent for both TSP and $\text{PM}_{2.5}$, and this further attests to their potential usefulness in source identification.

Comparisons of the ion profiles for the four types of PM showed some clear and characteristic differences, and these are graphically

presented in Fig. 3 which shows the mass contributions of the water-soluble ions for the different types of PM. The ions we analyzed accounted for at least one-third of the aerosol particle mass in the haze, straw combustion, and firework samples, but they were at a much lower level during DSs. To briefly summarize, our results indicate that secondary aerosol species were comparatively abundant during haze events; DSs PM was rich in Ca^{2+} ; straw combustion was marked by high levels of K^+ and Cl^- ; and $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios greater combined with high K^+ level may be a useful indicator of PM from fireworks.

3.3. Acidity of aerosol particles during the four types of PM events

Ion balance calculations are commonly used to evaluate the acid–base balance of aerosol particles. To calculate the cation/anion balance of TSP and $\text{PM}_{2.5}$, we converted the ions' mass

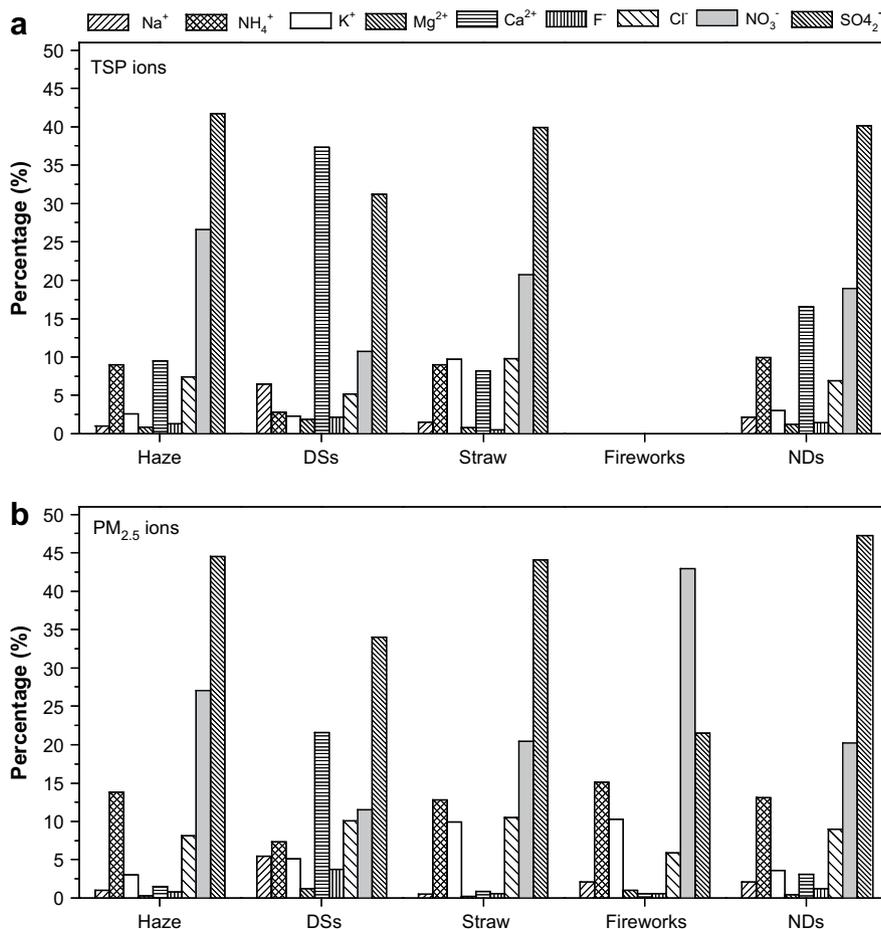


Fig. 3. Mass balance of water-soluble ions in dust storms (DSs), pollution events, and normal days (NDs): (a) TSP, (b) $\text{PM}_{2.5}$.

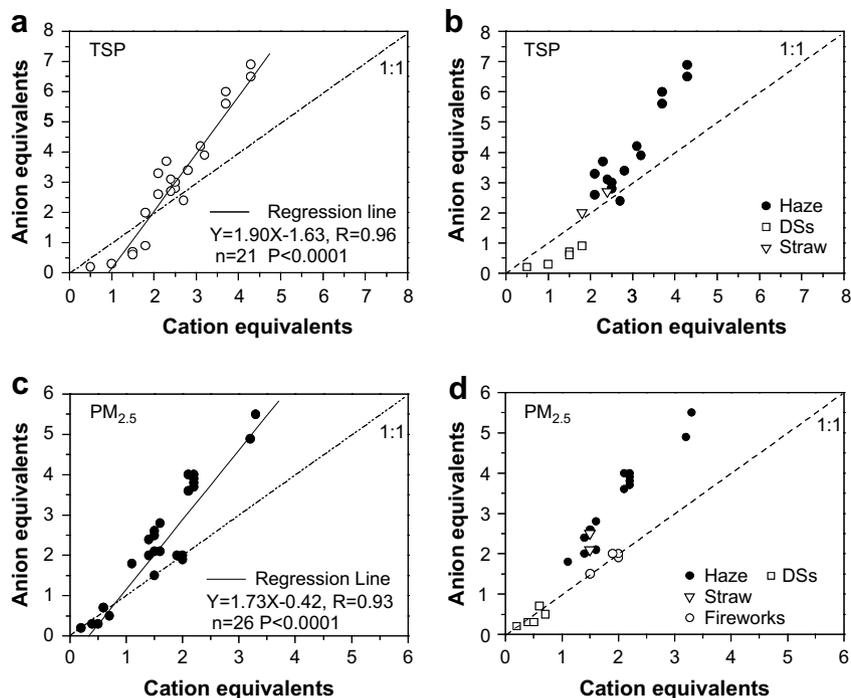


Fig. 4. Total cation microequivalents versus total anion microequivalents: (a) and (b) TSP, (c) and (d) PM_{2.5}.

concentrations into microequivalents. The cation and anion microequivalents in the four types of PM samples were calculated as follows:

$$C(\text{cation microequivalents}) = \text{Na}^+ / 23 + \text{NH}_4^+ / 18 + \text{K}^+ / 39 + \text{Mg}^{2+} / 12 + \text{Ca}^{2+} / 20 \quad (1)$$

$$A(\text{anion microequivalents}) = \text{F}^- / 19 + \text{Cl}^- / 35.5 + \text{NO}_3^- / 62 + \text{SO}_4^{2-} / 48 \quad (2)$$

The A/C ratios were the highest for the TSP from haze (1.4), and they decreased from the straw combustion samples (1.1) to the NDs samples (0.9) to DSs (0.6). For PM_{2.5}, the A/C ratios followed the order of haze (1.7) > straw combustion (1.5) > NDs (1.3) > fireworks (1.0) > DSs (0.8). These results thus indicate that PM from haze and straw combustion was more acidic than that from NDs. Furthermore, the A/C ratio for PM_{2.5} from fireworks is ~1.0, which indicates that those particles were nearly neutral. The DSs samples alone were alkaline, and the A/C ratios for the DSs TSP samples (0.6) were lower than those for PM_{2.5} (0.8), indicating that coarse DSs particles were more basic than fine ones.

Strong correlations between cation and anion equivalents in all of the TSP and PM_{2.5} samples were observed (Fig. 4, left), but we noted that the overall slopes of the orthogonal regression lines for both TSP and PM_{2.5} are higher than the unity, which implies cation deficiencies. However, the ion balance calculations stratified by PM event (Fig. 4 right) showed that most of the DSs samples, both TSP and PM_{2.5}, plotted near or below the 1:1 anion:cation line, again showing that the DSs samples were alkaline. The buffering of acidity by the DSs' PM is undoubtedly due to the high mineral-dust loadings (Zhang et al., 2002; Cao et al., 2005b; Yuan et al., 2004; Shen et al., 2008). Plumes of dust can affect the atmospheric sulphur and nitrogen cycles because reactions with the alkaline particles not only neutralize the acidity, but also alter the pathways that lead to formation of particles. Indeed, during spring, aerosol particles from cities in Northern China often are alkaline due to the

high dust loadings (Wang et al., 2006; Cao et al., 2005b; Shen et al., 2008).

The ion balances for the haze and straw combustion samples differed as a function of particle size; that is, the TSP samples plotted near or slightly over the 1:1 A:C line whereas the PM_{2.5} samples were farther above it, and so the haze and straw combustion samples were acidic, especially the finer-size particles. The mean A/C ratios for TSP from haze and straw combustion were 1.4 and 1.1 compared with 1.7 and 1.5 for the PM_{2.5} samples. The ion concentrations for the five PM_{2.5} firework samples plotted on or very close to the unity line, indicating again that the PM from the firework shows was nearly neutral. Although high levels of acidic materials such as nitrate and sulfate were found in fireworks samples, the trace elements in the fireworks apparently can neutralise much of the acidity (Ravindra et al., 2001).

4. Conclusions

High concentrations of aerosol particles during DSs, firework shows, haze, and straw burning events, caused a strong reduction in visibility over Xi'an. The water-soluble ion concentrations of TSP and PM_{2.5} were strongly elevated during all of the PM events except the DSs. Moreover, the proportions of the water-soluble ions varied in the four types of PM, and these differences may be characteristic of the types of particles that are produced from the different PM sources. Secondary ions (NO₃⁻, SO₄²⁻, and NH₄⁺) were most abundant in the haze events; high Ca²⁺ occurred during dust outbreaks; straw burning was associated with high loadings of K⁺ and Cl⁻; and an excess of NO₃⁻ relative to SO₄²⁻ combined with an enrichment of K⁺ was observed in fireworks samples. Of the ions studied, all except Ca²⁺ and Mg²⁺, were more concentrated in PM_{2.5} than TSP. Ion balance calculations indicate that the PM from haze and straw combustion is more acidic than that on NDs, but dust particles, especially coarse ones are alkaline. PM_{2.5} from fireworks was close to neutral. Carbonaceous particles are another important constituent of the aerosol population at Xi'an and many other large Asian

cities, and therefore, future studies also should include investigations of organic materials during PM events.

Acknowledgements

We thank two anonymous reviewers for their constructive suggestions and comments. This work was supported in part by the Natural Science Foundation of China (grants 40875089 and 40675081), the Chinese National Key Project of Basic Research (grant G2004CB720200), the SKLLQG, Chinese Academy of Sciences (grant SKLLQG0811), National Science Foundation of the United States (grant ATM 0404944), The Ministry of Education, Culture, Sports, Science and Technology of Japan (grants 13480160, 14048220, 16030209, 16404002, 16710008, and 18710014), Steel Industry Foundation for the Advancement of Environmental Protection Technology, the Iwatani Naoji Foundation's Research Grant, and Heiwa Nakajima Foundation, Japan. Any opinions, findings, and conclusions or recommendations expressed in this paper are those of the authors and do not necessarily reflect the views of the sponsors.

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