A Typical Formation Mechanism of Heavy Haze-Fog Induced by Coal Combustion in an Inland City in North-Western China

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ABSTRACT

$PM_{2.5}$, TSP, and the pollutant gases over Urumqi, an inland city near the Asian dust source region in north-western China, were measured for an entire year from March, 2008 to February, 2009. The chemical compositions of all these samples with daily visibilities were investigated for the sources and formation mechanisms of aerosol and the relationship of the optical property with various components in aerosols. The sources of the air pollutants that caused severe haze in Urumqi were clarified. It was found that the concentrations of SO_4^{2-}, Cl^-, NH_4^+, and Na^+ in $PM_{2.5}$ in the heating period were more than 9 times of those in the non-heating period. The concentrations of total water soluble inorganic ions (TWSII) in $PM_{2.5}$ and TSP in the heating period were 7.5 and 5.5 times of those in the non-heating period. The enrichment factors of the pollution elements, e.g., S, Cd, As, Zn, Pb, Cu, Cr, and Na in $PM_{2.5}$ in the heating period were 3–13 times of those in the non-heating period. The formation mechanism of the severe haze and the micro-mechanism of the visibility reduction in Urumqi in the heating period, especially in winter, were quantitatively revealed. SNA (the three secondary inorganic ions, SO_4^{2-}, NO_3^-, and NH_4^+), organic matter (OM), and chloride (Cl^-) in $PM_{2.5}$ were the three main components to cause aerosol extinction in Urumqi. The contributions of SNA, OM, and Cl^- to aerosol extinction, i.e., to visibility reduction, were 57%, 20%, and 12% during the heating period from October 15 to April 15, and 67%, 17%, and 12% in winter, respectively. It was evident that the major source of the air pollutants that caused severe haze in Urumqi was from coal combustion, for most of these ions and pollution elements in aerosols were emitted from coal burning. The control of the quality and quantity of coal burning is the key to improve the air quality and the atmospheric visibility in Urumqi.

Keywords: Haze; Sources; Formation mechanism; Coal burning.

INTRODUCTION

The rapid economic development in the past 30 years has brought serious atmospheric pollution over China, for more than two third of the cities have exceeded the national ambient air quality standards (Yao *et al.*, 2002; Sun *et al.*, 2004; Sun *et al.*, 2006; He *et al.*, 2012). Haze-fog has become the common problems faced by China. Haze becomes one of the weather patterns in China with the severely reduced visibility caused by the interactions of water vapor with aerosols, dust, and soot in the atmosphere (Sun *et al.*, 2006). Generally, the weather with visibility less than 10 km was defined as haze. Haze is a large amount of fine particles with water or vapor adsorbed/condensed on the surface of

aerosols, while fog is a weather type with much tiny droplets containing high concentrations of fine particles. There is no essential difference of fog with haze. In fact, nowadays both haze and fog that occurred in China are the products of air-pollution, and they have a close relationship with the fine particle, i.e., $PM_{2.5}$, which act as "condensation nuclei" to promote the condensation of water vapor and a promoter to speed the growth of the tiny particles. Because $PM_{2.5}$ contains large proportion of anthropogenic sulfate, nitrate, ammonium, and organic acid salt, which are highly hygroscopic and easily promote the fine particle expansion with the water or vapor adsorbed/condensed on the surface of aerosols to form those so-called haze-fog. In the highly polluted atmospheric environment, the visibility would be significantly reduced, down to a few kilometers, even less than 1 km (Fu *et al.*, 2008; Huang *et al.*, 2012a, b, 2014; Wang *et al.*, 2015).

Sun *et al.* (2006) proposed the concept of haze-fog, while it was reported that the concentrations of $PM_{2.5}$, PM_{10}, ions, and elements in Beijing in the haze-fog days were 10

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times higher than that in non-haze days. They found that the gas-to-particle transformation from gaseous precursors of high concentration to be the secondary aerosols was the major formation mechanism of haze in Beijing. In addition to the local sources, $PM_{2.5}$ was also derived from long/middle-range transport (Sun *et al.*, 2010; Huang *et al.*, 2010). Wang *et al.* (2005, 2006) investigated the composition of aerosols in Beijing from 2001 to 2004 and in Shanghai from 2003–2006, and found that the main source of sulfate was from the heterogeneous reaction, while nitrate was from gas phase transformation. Huang *et al.* (2012a) summarized three typical haze types of the major formation mechanism of haze, i.e., the secondary aerosol formation, the dust transport, and biomass burning. It is pointed out that the total soluble ions and relative humidity are the main two factors affecting the visibility in atmosphere. They further found that organic aerosols, sulfate, nitrate and black carbon are the four major components influencing the visibility reduction (Huang *et al.*, 2012b). In addition to the four haze regions, i.e., the North China Plain, the Yangtze River Delta, the Pearl River Delta, and the Sichuan Basin, even in Northwest China, such as the city of Urumqi, have also suffered the same serious haze problems. Li *et al.* (2008, 2009) analyzed the composition of the fog-haze in the spring/winter of 2007 over Urumqi and pointed out that the haze that occurred in Urumqi has three characteristics: high concentration of fine aerosols, frequent occurrence, and rapid formation. They also pointed out that the formation of high concentration of ammonium salt was the main mechanism of such a heavy fog-haze in Urumqi. Based on the most literature results as mentioned above, coal combustion and vehicle emissions were recognized as the two major emission sources that caused the heavy haze-fog over China in the last decade.

In order to elucidate the similarities and differences of the sources and the formation mechanism of the heavy haze-fog in the different areas over China, our research group adhered a long-term continuous monitoring and investigation of PM_1, $PM_{2.5}$, and TSP in those typical regions, including the highly developed Yangtze River Delta and the megacity Shanghai (Fu *et al.*, 2008; Huang *et al.*, 2012a, b, 2013; Lin *et al.*, 2013), the North China Plain areas and the megacity Beijing (Huang *et al.*, 2014), the remote island (the Huaniao Isle) in the East China Sea (Wang *et al.*, 2015), and the dust-storm source areas in the north-western China. Here we investigate the characteristics of aerosol in Urumqi, an inland city in north-western China, to reveal the typical formation mechanism of the heavy haze-fog there. Coal is the major energy source used in north-western China, especially during the heating period that covers half a year and shows distinctly different characteristics of air-quality from that during the non-heating period. Coal combustion for electricity power generation and residential heating contributed a dominant fraction of 64% and 74% to SO_2 and NO_x emissions in Urumqi (Shi, 2012), much higher shares than the developed regions such as Shanghai and the the Pearl River Delta region (Zheng *et al.*, 2009; Huang *et al.*, 2011). Urumqi has been suffering from very heavy haze that forms on more than one third of the year. Early in 1998, Urumqi was recognized as one of the ten heaviest air-polluted cities over the world.

For Urumqi is located in the center of Eurasia hinterland, surrounded by mountains on three sides, with the typical characteristics of basin geomorphology and it is in the source area of Asian dust, its dust/aerosols are transported to the North Pacific as well as the North America, the characteristics of Northwest China's haze-fog would be significant not only to local urban air quality but also to the regional environment and to the global climate change.

METHODOLOGY

Sampling

A sampling campaign of aerosols monitoring was carried out in the downtown of Urumqi in the entire year of 2008–2009, covering spring (March, April, May), summer (June, July, August), autumn (September, October, November), and winter (December, January, February). The heating period in Urumqi is from October 15 to April 15 each year (Li *et al.*, 2008).

$PM_{2.5}$ and TSP samples were daily (normally from 8:00 A.M. to 8:00 A.M. the next day) collected on Whatman® 41 filters (Whatman Inc., Maidstone, UK) by medium-volume samplers (model: ($TSP/PM_{10}/PM_{2.5}$)-2, flow rate: 77.59 L min^{-1}). The height of the sampling site was 30 m above the ground. In the spring dust season or heavy haze days the samples were collected with finer temporal resolution depending on the intensity of dust/haze. All those filters were weighed before and after sampling with an analytical balance (Sartorius 2004MP, reading precision 10 µg) after stabilizing under constant temperature (20 ± 1°C) and relative humidity (40 ± 2%). All the procedures were strictly quality-controlled to avoid any possible contamination of the samples.

Visibility was measured by using a Vaisala Present Weather Detector (Model: FD12P). Its sensor, which combined the functions of a forward scatter visibility meter and a present weather sensor, could measure visibility (meteorological optical range, MOR), precipitation intensity, and precipitation type. The detector measured visibility by using the principle of forward scatter measurement within a range of 10–50000 m.

Chemical Analysis
Ion Analysis

Eleven inorganic ions (SO_4^{2-}, NO_3^-, F^-, Cl^-, NO_2^-, PO_4^{3-}, NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) and four organic acids (formic, oxalic, melodic, and methanesulfonic acid (MSA)) were analyzed by ion chromatography (IC; Dionex ICS 3000, USA) that consists of a separation column (Dionex Ionpac AS 11), a guard column (Dionex Ionpac AG 11), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50) and a gradient pump (Dionex Ionpac GP50). The detailed analytical procedures were given elsewhere (Zhuang *et al.*, 2001; Zhuang *et al.*, 2003; Sun *et al.*, 2004; Wang *et al.*, 2005, 2006).

Element Analysis

Half of each sample and blank filter was digested at 170°C for 4 h in high-pressure Teflon digestion vessel with 3 mL concentrated HNO_3, 1 mL concentrated HCl, and 1 mL

concentrated HF. After cooling, the solutions were dried, and then diluted to 10 mL with distilled deionized water. A total of 24 elements (Al, Fe, Mn, Mg, Mo, Ti, Sc, Na, Ba, Sr, Sb, Ca, Co, Ni, Cu, Ge, Pb, P, K, Zn, Cd, V, S, and As) were measured by using an inductively coupled plasma atomic emission spectroscopy (ICP-OES; SPECTRO, Germany). The detailed analytical procedures were given elsewhere (Zhuang *et al.*, 2001; Sun *et al.*, 2004).

SO_2, NO_2, and OC/EC (Organic Carbon/Elemental Carbon)

The online data of SO_2, NO_2, and OC/EC from March 2008 to February 2009 were obtained from Xinjiang Environmental Monitoring Station. The concentration of OC/EC was measured with an *in situ* Semi-Continuous OC/EC analyzer (RT-3195, Sunset Laboratory, Beaverton, Oregon, USA). The ambient air was first drawn through a $PM_{2.5}$ cyclone inlet (SCC 2.354, BGI Inc.) with a flow rate of 8 L min^{-1}, and then passed through a carbon-impregnated multi-channel parallel-plate diffusion denuder (Sunset Laboratory) to reduce the adsorption of vapor-phase organics by the quartz filter and hence create a positive artifact in measured OC concentrations (Turpin *et al.*, 2000).

RESULTS AND DISCUSSIONS

The Severe Air Pollution in Urumqi
Heavy Haze-Fog Occurrence

Defined as lower than 10 km of the visibility, there were 180 haze-fog days in the entire year from March 2008 to February 2009, of which 77 days in winter, 52 days in fall, 44 days in spring, and 7 days in summer, following a frequency order of winter > fall > spring > summer. The visibility was 6.6 km in spring, 7.4 km in summer, 4.8 km in fall, and 2.4 km in winter on average. In winter, 86% of those haze-fog days were regarded as "heavy haze", defined as visibility lower than 3 km. It was evident that there was high frequency of severe haze-fog with a seasonal variation of winter > fall > spring > summer. During the heating period there were 148 haze-fog days with average visibility of 2.9 km, whereas 32 days of 6.9 km during the non-heating period. It was evident that the visibility decrease, i.e., haze occurrence should be closely related to residential heating, i.e., coal burning.

High Concentrations of Gaseous Pollutants and Aerosols

The daily mean concentrations of SO_2, NO_2 from March 2008 to February 2009 were shown in the Fig. 1. The average concentrations of SO_2 and NO_2 in spring, summer, fall, and winter were 75.7, 22.7, 65.3, and 204.3 µg m^{-3} and 57.8, 52.3, 70.3, and 85.1 µg m^{-3}, respectively, with the same order of winter > fall > spring > summer. There was an obvious seasonal variation of SO_2 with extreme high concentrations in winter while lowest in summer. The mean concentrations of SO_2 in spring, fall and winter all exceeded the National Ambient Air Quality Standards in China (GB 3095-2012, annual grade II standard of 60 µg m^{-3}) with 3.8 times higher than the daily standard in winter and the highest daily concentration of around 400

µg m^{-3}. The mean concentrations of SO_2 in heating and non-heating periods were 153.9 and 28.7 µg m^{-3}, respectively, showing that it was 5.3 times higher in the heating period than the non-heating period. For SO_2 is mainly emitted from coal combustion that is the major energy source in the heating period, the results above clearly showed that coal combustion was the most dominant source impacting air quality in the heating period. As to NO_2, the ratio of SO_2/NO_2 decreased from 1.95 in the heating period to 0.56 in the non-heating period, indicating the concentrations of NO_2 were higher than SO_2 in the non-heating period as shown in Fig. 1, which meant that SO_2 was the dominant gaseous pollutant in the heating period, while NO_2 was dominant in the non-heating period, as NO_2 was dominated by vehicle source in addition to coal combustion.

The yearly average concentrations of $PM_{2.5}$ and TSP were 139.5 and 239.7 µg m^{-3}. The seasonal mean concentrations of $PM_{2.5}$ and TSP were 69.2, 58.8, 164.8, and 259.7 µg m^{-3} and 174.0, 91.3, 263.6, and 428.5 µg m^{-3} in spring, summer, fall, and winter, respectively, with the order of winter > fall > spring > summer, all much higher than the National Ambient Air Quality Standards (annual grade II standard of 35 µg m^{-3}), especially, more than 7 times higher than it in winter. The mean concentrations of $PM_{2.5}$ and TSP in the non-heating period were 58.8 and 91.3 µg m^{-3}, respectively. While during the heating period, they were 165.6 and 289.0 µg m^{-3}, respectively. Both $PM_{2.5}$ and TSP were around 3 times higher in heating than in non-heating period. $PM_{2.5}$ and TSP presented the same seasonal variations and the same dramatic change caused by heating as those two gaseous pollutants, i.e., SO_2 and NO_2, did. Because SO_2 and NO_2 would be oxidized and converted to SO_4^{2-} and NO_3^- in aerosol, and they are the precursors of SO_4^{2-} and NO_3^-, thus, the results above indicated again that the coal combustion was the key factor impacting the air quality in Urumqi. Besides, the ratios of $PM_{2.5}$/TSP all exceeded 60% in summer, autumn and winter, meaning that fine particles were dominant in these season. In comparison, the ratio of $PM_{2.5}$/TSP was lower than 40% in spring, which could be due to the frequent occurring of blowing dust and the transport of more coarse particles to the city in spring.

The Ions in Aerosols and their Sources

Table 1 shows the average concentrations of the major ions (SO_4^{2-}, NO_3^-, Cl^-, NO_2^-, F^-, NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) in $PM_{2.5}$ and TSP in each season and in the heating period. The most abundant anions and cation were in the order of SO_4^{2-} > Cl^- > NO_3^- > NO_2^- > F^-, in both $PM_{2.5}$ and TSP, NH_4^+ > Na^+ > K^+ > Ca^{2+} > Mg^{2+} in $PM_{2.5}$, and NH_4^+ > Ca^{2+} > Na^+ > K^+ > Mg^{2+} in TSP. The yearly mean concentrations of the total water soluble inorganic ions (TWSII) were 63.0 and 84.6 µg m^{-3} in $PM_{2.5}$ and TSP, accounted for 45% and 35% of the total mass of $PM_{2.5}$ and TSP, respectively. The concentrations of TWSII were 27.1, 10.7, 70.3, and 140.0 µg m^{-3} in $PM_{2.5}$ in spring, summer, fall, and winter, respectively, accounted for 46%, 19%, 46%, 54% of the total mass of $PM_{2.5}$.

Table 2 lists the concentrations of the five major ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+) and the three major anions
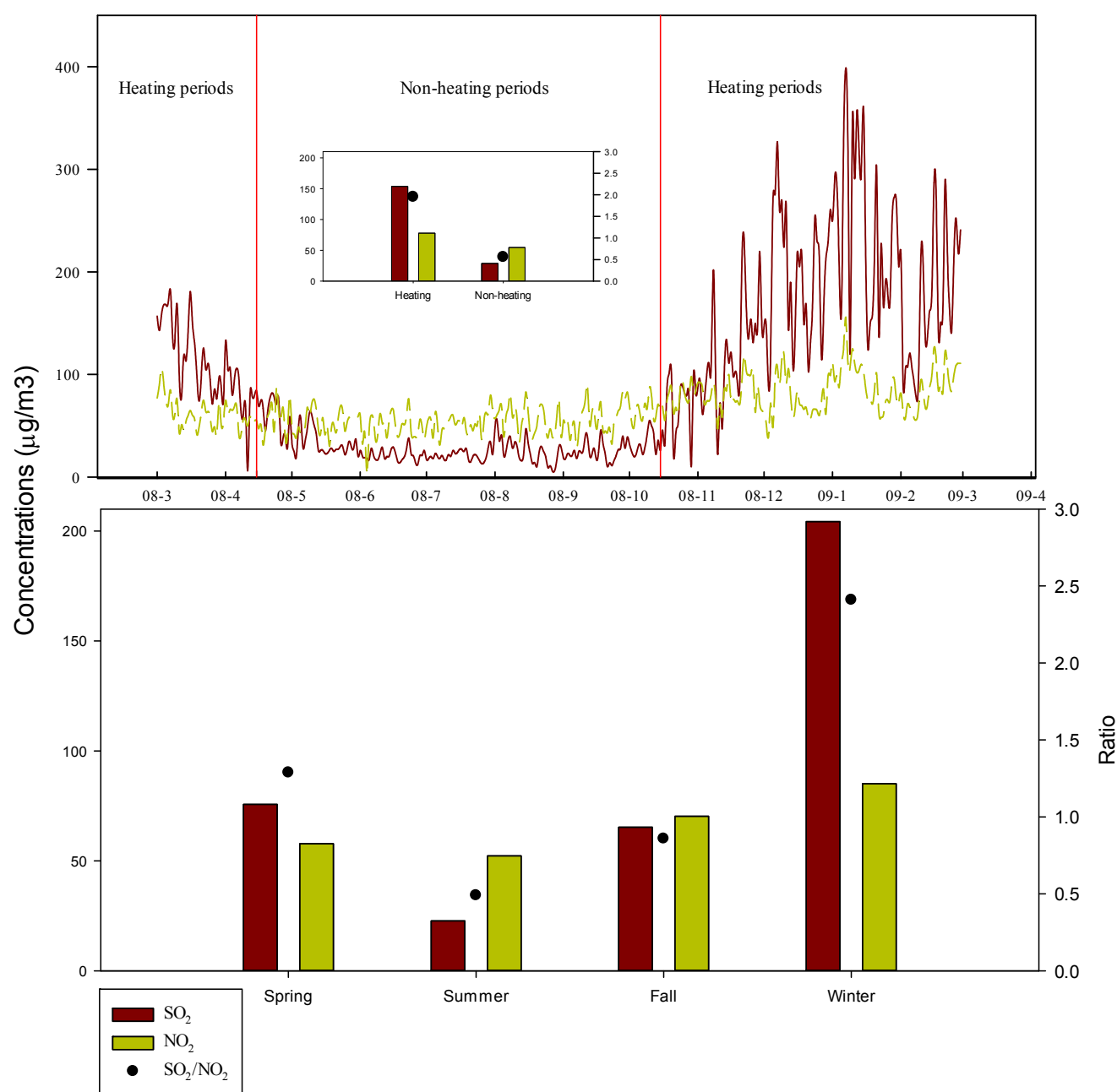
Fig. 1. The daily and seasonal mean concentration of SO_2, NO_2 and the ratio of SO_2/NO_2 in Urumqi from March of 2008 to February of 2009.

(SO_4^{2-}, NO_3^-, Cl^-) in $PM_{2.5}$ and TSP and their ratios of the sum of these ions to the mass concentrations of $PM_{2.5}$ and TSP in four seasons and in heating period. The concentrations of the total five major ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+) accounted for 41% and 31% of $PM_{2.5}$ and TSP, respectively, in the four seasons on average, and accounted for up to 53% and 50% in winter. Furthermore, the mean concentrations of the three major anions (SO_4^{2-}, NO_3^-, Cl^-) accounted for 31% and 24% of $PM_{2.5}$ and TSP in the entire year, and up to 42% and 41% in winter. It could be seen clearly that the five major ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+), especially the three major anions (SO_4^{2-}, NO_3^-, Cl^-), were the most important components in both $PM_{2.5}$ and TSP impacting

the haze formation, for these ions were all highly hygroscopic and easily promote the fine particle growth with the water or vapor adsorbed/condensed on the surface of aerosols to form those so-called haze-fog. Regarding the sources of these major ions in Urumqi, NH_4^+ is mainly from those agriculture sources surrounding the city, while SO_4^{2-} is mainly from oxidation of sulfur dioxide emitted from coal combustion and partially from dust invasion in the spring and summer, in which some primary sulfate existed due to the ancient marine salt (Li *et al.*, 2008; Li *et al.*, 2009; Huang *et al.*, 2010a). NO_3^- is from the oxidation of nitrogen oxides emitted from both coal combustion and vehicle exhausts, while Cl^- is also mainly from coal combustion

Table 1. The concentrations of ions in Urumqi ($\mu g\ m^{-3}$).

	SO_4^{2-}		NO_3^-		Cl^-		NO_2^-		F^-	
	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP
Spring	6.61	9.56	2.98	3.51	4.07	4.95	0.98	1.59	0.32	0.59
Summer	2.37	5.61	1.76	1.85	1.08	2.99	0.29	0.39	0.16	0.18
Fall	23.04	25.72	8.89	5.62	12.06	10.86	0.58	3.22	0.11	0.30
Winter	80.88	135.53	10.23	16.88	17.42	23.83	0.12	0.21	-	-
Mean	28.23	41.22	5.97	6.65	9.13	9.49	0.53	1.54	0.20	0.35
Heating	37.14	52.73	7.34	8.22	11.16	12.58	0.57	0.57	-	-
H/N*	15.65	9.39	4.16	4.44	10.35	4.20	1.97	1.47	0.00	0.00
	NH_4^+		Na^+		Ca^{2+}		K^+		Mg^{2+}	
	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP
Spring	3.57	3.29	1.52	2.47	3.11	7.27	0.56	0.83	0.26	0.47
Summer	1.26	2.88	0.48	0.56	1.72	3.59	0.21	0.37	0.13	0.16
Fall	13.02	12.31	4.09	4.27	2.69	8.31	1.81	2.04	0.24	0.50
Winter	19.64	22.73	8.50	9.43	1.03	6.52	1.40	1.86	0.21	0.62
Mean	9.92	10.61	3.71	4.32	2.14	6.59	1.03	1.31	0.21	0.45
Heating	12.20	13.11	4.75	5.37	2.27	7.36	1.25	1.61	0.24	0.55
H/N	9.68	4.55	9.90	9.59	1.32	2.05	5.94	4.36	1.85	3.44

* H/N: Heating periods/Non-heating periods.

Table 2. The concentrations and the ratios to particles of five major ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+) and three major anions (SO_4^{2-}, NO_3^-, Cl^-) in four seasons and in heating period.

	Concentrations of particles ($\mu g\ m^{-3}$)		The total concentrations of five major ions ($\mu g\ m^{-3}$)		ratio* (%)		The total concentrations of three major anions ($\mu g\ m^{-3}$)		Ratio* (%)	
	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP
Spring	69.2	174.0	19.20	24.34	28	14	13.99	18.45	20	11
Summer	58.8	91.3	6.96	13.90	12	15	5.21	10.46	8.9	11
Fall	164.8	263.6	61.05	58.15	37	22	43.99	42.19	27	16
Winter	259.7	428.5	137.25	213.63	53	50	108.53	176.24	42	41
Mean	139.5	239.7	57.13	73.46	41	31	43.76	58.43	31	24
Heating	165.5	289.0	73.32	92.76	44	32	56.20	73.98	34	26

* Ratio: The sum of these ions to the mass concentrations of $PM_{2.5}$ and TSP.

plus biomass burning and waste incineration. Na^+ is partially from the ancient marine salt plus some from coal combustion. In short, most of these major ions were related to coal combustion in Urumqi.

Both concentrations of total water soluble inorganic ions (TWSII) and concentrations of the sum of the five ions, i.e., SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, and Na^+, in $PM_{2.5}$ and TSP showed clear seasonal variations with the order of winter > fall > spring > summer. More distinct seasonal variation was shown with the comparison of heating with non-heating season. The concentrations of SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, and K^+ in both $PM_{2.5}$ and TSP were more than 4 time higher in the heating period than those in the non-heating period, while the concentrations of SO_4^{2-}, Cl^-, NH_4^+, and Na^+ in $PM_{2.5}$ were more than 9 times higher in the heating period than the non-heating period. The concentrations of TWSII in $PM_{2.5}$ and TSP in the heating period were 80 $\mu g\ m^{-3}$ and 107.3 $\mu g\ m^{-3}$, accounting for 48% and 37% of the total mass of $PM_{2.5}$ and TSP, and 7.5 and 5.5 times higher than those in the non-heating period of only 10.7 and 19.6 $\mu g\ m^{-3}$. It also can be further seen from Table 2 that the five major

ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, and Na^+) in the heating period accounted for up to 44% and 32% of the total mass of $PM_{2.5}$ and TSP, respectively, while the three anions (SO_4^{2-}, NO_3^-, Cl^-) in the heating period could account for as high as 34% and 26%. The ion concentrations in winter were much higher than those in the other seasons, indicating that coal combustion in winter and spring was the key factor impacting the formation of air pollution.

The Elements in Aerosols and their Sources

The enrichment factors (EF) of the typical 17 elements in both $PM_{2.5}$ and TSP and in both heating and non-heating periods were shown in Fig. 2 and Fig. 3. Enrichment factor (EF) is calculated as follows: EF = $(X/Al)_{aerosol}/(X/Al)_{crust}$, where $(X/Al)_{aerosol}$ and $(X/Al)_{crust}$ represent the concentration ratio of element X to Al in aerosol and in the earth's crust. For example, the Ca/Al ratio in TSP and crust was 1.55 and 0.63, respectively. Hence, the EF value of Ca was determined to be 2.45. Based on their enrichment factors, these elements can be categorized into three groups: crustal elements, pollution elements, and crustal/pollution elements. The EFs
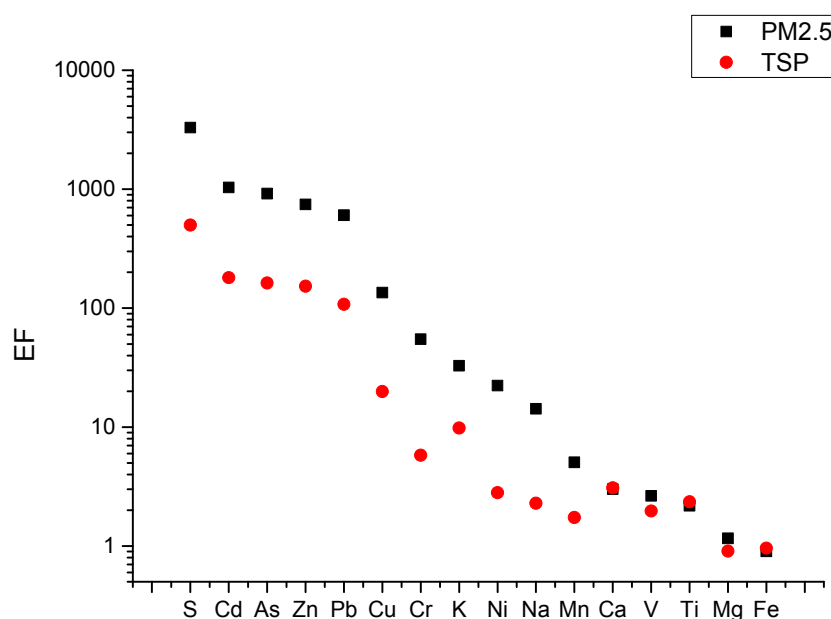
Fig. 2. Enrichment factors (EF) of elements in PM$_{2.5}$ and TSP.
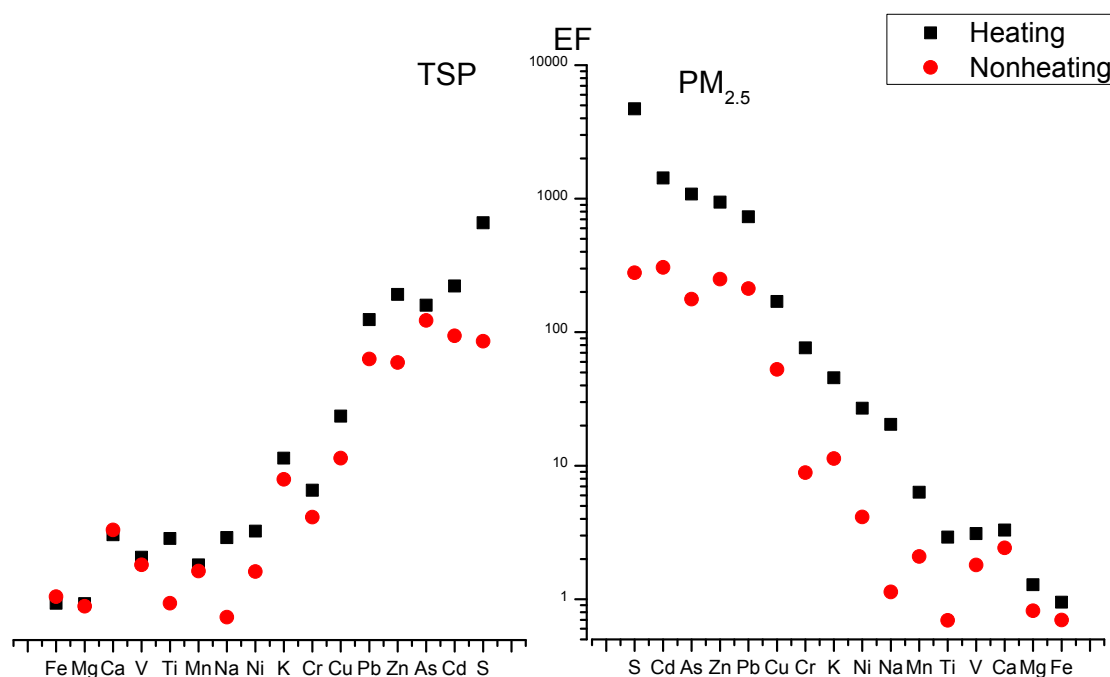

Fig. 3. Enrichment factors (EF) of elements in PM$_{2.5}$ and TSP during both heating and non-heating periods.

of the crustal elements, including Al, Fe, Ca, Mg, Ti, and V, were less than 5, which were mostly from crustal sources. The ratios of EF of these elements in PM$_{2.5}$ to those in TSP and the ratios of EF in the heating period to those in the non-heating period were around 1, indicating that these elements were mainly from the natural mineral sources, i.e., dust. The ratio of elements Ca to Al, i.e., Ca/Al in TSP, was 1.55, very similar to the ratio (1.56 ± 0.14) of soil samples collected from the center area of Taklimakan Desert (Huang *et al.*, 2010a; Wang *et al.*, 2016), indicating that these elements in the aerosol should be mainly from dust

transport. The EFs of those pollution elements, S, Cd, As, Zn, Pb, Cu, and Cr, were more than 100, which could derive from anthropogenic sources. It could be seen in Fig. 3 that EFs of these elements in PM$_{2.5}$ in the heating period were 3–13 times higher than those in the non-heating period, indicating that these elements could be mostly from coal combustion. The ratios of EFs of these elements in PM$_{2.5}$ to those in TSP were in the range of 3–9, indicating that these elements were mostly enriched in PM$_{2.5}$, i.e., in fine particles. The remaining elements, i.e., Na, K, Ni, and Mn, could be derived from both crustal and pollution sources.

The EFs of these elements in both $PM_{2.5}$ and TSP in the heating period were higher than those in the non-heating period, indicating these elements could be partially from coal combustion (Takuwa *et al.*, 2006).

The Major Components in Aerosols and their Sources

According to the physicochemical properties and their effect on the optical properties, the components of the aerosols could be divided to the following four categories: total water-soluble inorganic ions (TWSII), organic matter (OM), mineral, and black carbon (BC). TWSII is the sum of the concentrations of all the ions measured. OM is calculated by the measured organic carbon (OC) multiplied by a factor of 2. Mineral concentration is calculated using the formula: [Mineral] = 2.2 [Al] + 2.49 [Si] + 1.63 [Ca] + 2.42 [Fe] + 1.94 [Ti], where [Si] (concentrations of element Si) was calculated based on the Si/Al ratio of 3.43 in crust. Fig. 4 shows the proportions of the four components in $PM_{2.5}$ and TSP in four seasons as well as in heating and non-heating periods. In winter and fall, these four components in

$PM_{2.5}$ were in the order of TWSII > OM > mineral > BC, wherein the sum of TWSI and OM accounted for 93% and 80% of the total mass of $PM_{2.5}$ in the winter and fall, respectively. For TWSII and OM are mostly from coal burning, these results indicated that the aerosols in winter and in fall were mostly from the coal combustion. In spring, the order of these four components in $PM_{2.5}$ was TWSII > mineral > OM > BC, while in summer it was mineral > OM > TWSII > BC. In TSP the order was mineral > TWSII > OM > BC in fall, while it was mineral > OM ≥ TWSI > BC in summer and spring. The results above were obviously due to the high frequency of dust invasion in spring and summer.

In the heating period, these four components in $PM_{2.5}$ were in the order of TWSII > OM > mineral > BC, wherein the sum of TWSII and OM accounted for 78% of the total mass of $PM_{2.5}$. Compared to a study on aerosol chemistry investigated at 16 urban, rural, and remote sites mainly in the eastern and central regions of China (Zhang *et al.*, 2012), sulfate, nitrate, and ammonium contributed around 16%, 7%,
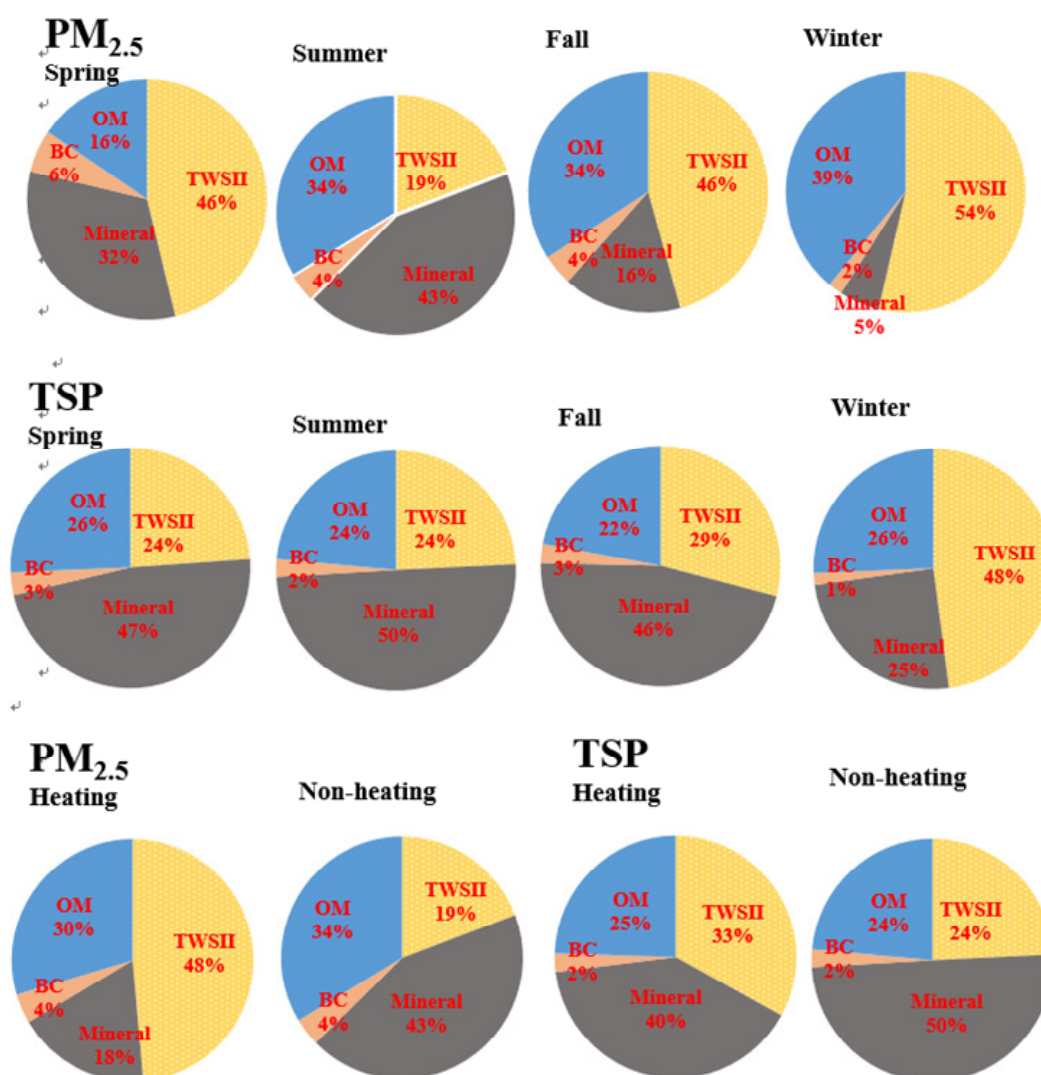

Fig. 4. The proportions of the four components (TWSII, OM, Mineral and BC) in $PM_{2.5}$ and TSP in the four seasons as well as in heating and non-heating periods.

Table 3. Correlation of visibility with the major components of aerosols.

	Visibility		Visibility
$PM_{2.5}$	$-.69^{**}$	NO_2	$-.37^{**}$
TSP	$-.71^{**}$	SO_2	$-.56^{**}$
BC	$-.36^{**}$	Cl^-	$-.84^{**}$
Mineral	$.057$	NO_3^-	$-.82^{**}$
TWSII	$-.79^{**}$	SO_4^{2-}	$-.77^{**}$
OM	$-.55^{**}$	NH_4^+	$-.85^{**}$
Na^+	$-.80^{**}$		

$^{**}P = 0.01$.

and 5% to the aerosol masses, respectively. OC and mineral aerosol contributed around 15% and 35%. Compared to this study (Fig. 4), TWSII showed higher contributions in Urumqi except in summer. OM showed similar contributions considering that it was estimated by multiplying OC with a factor of 2.

The Formation Mechanism of Heavy Haze-Fog
The Relation between Visibility and Major Aerosol Components

Table 3 shows the Pearson correlation of visibility with the major components of aerosols in the entire year. It can be seen clearly that the major components, TWSII (total water soluble inorganic ions, mainly NH_4^+, Cl^-, NO_3^-, Na^+, and SO_4^{2-}) and OM (organic matter) were significantly negatively correlated with visibility. The correlation coefficients of visibility with TWSII, NH_4^+, Cl^-, NO_3^-, Na^+, SO_4^{2-}, and OM were as high as –0.79, –0.85, –0.84, –0.82, –0.80, –0.71, and –0.55, respectively, indicating the high concentrations of these inorganic ions and organic matter were the key cause of the heavy haze. The mean concentrations of SO_4^{2-}, NH_4^+, Cl^-, NO_3^-, and Na^+ in $PM_{2.5}$ in haze days were 8.3, 4.1, 3.6, 3.5, 6.0 times higher than those in non-haze days, indicating these ions were the major components of haze-fog due to their high hygroscopicity. The ratio of SO_4^{2-}/NO_3^- in $PM_{2.5}$ in non-haze days was 2.7, while it was 5.9 in haze days, which indicated that the proportion of SO_4^{2-} in $PM_{2.5}$ in haze days was much higher than that of NO_3^-. Considering that the formation path of SO_4^{2-} was from the oxidation of SO_2 that is mostly from the emission of coal burning, the high portion of SO_4^{2-} in $PM_{2.5}$ in haze days indicated again that coal burning was the major cause of haze in Urumqi.

Contributions of the Major Aerosol Components to Haze Formation

To further reveal the formation mechanism of haze-fog, the contribution of the major species to haze formation, i.e., the contribution of the major species to aerosol extinction should be quantified. Based on the different extinction efficiencies of various components, the chemical species were divided into the following categories: SNA (SO_4^{2-}, NO_3^-, and NH_4^+), OM (organic matter), Cl^- (chloride), BC (black carbon), mineral aerosols, and gaseous NO_2. The extinction coefficient of each component was estimated using the IMPROVE formula (Pitchford *et al.*, 2007) and the corresponding function of humidity. Then, the contribution

proportion to the haze formation of each component, i.e., the contribution to the total aerosol extinction (scattering + absorbing) of major chemical species was estimated based on the extinction efficiencies and the measured concentration in $PM_{2.5}$ of each component mentioned above. As shown in Fig. 5, in the heating period and in winter, the proportion of each chemical category to the light extinction was in the order of SNA > OM > Cl^- > BC > mineral aerosols > gaseous NO_2. The three secondary ions (SO_4^{2-}, NO_3^-, NH_4^+),
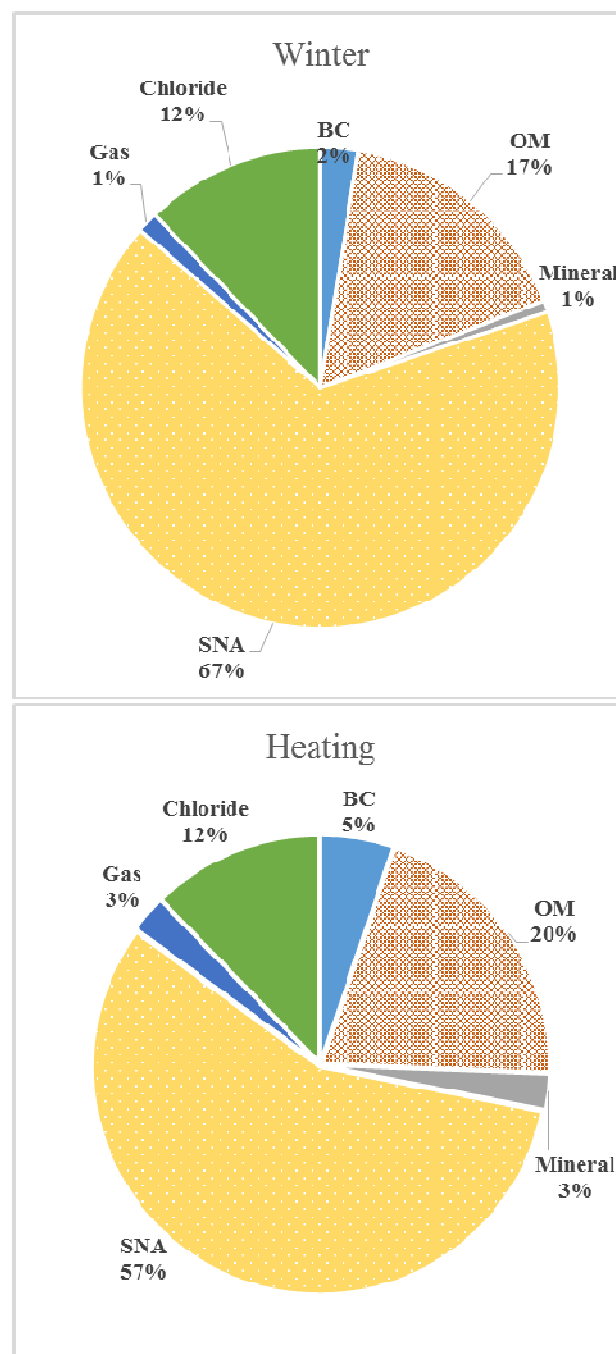

Fig. 5. The contribution proportion of major components (SNA, OM, chloride, BC, mineral aerosols, and gaseous NO_2) in $PM_{2.5}$ to the light extinction in winter and during the heating period.

contributed as high as 67% and 57% in winter and in the heating period, respectively, while organic matter (OM) accounted for 17% and 20%, and chloride of 12% and 12%, respectively. As discussed earlier, in Urumqi, SNA, OM, and Cl⁻ were mostly from coal burning, it could be concluded that the emission from coal burning was the most dominant cause of the occurrence of the severe haze over Urumqi.

CONCLUSION

Severe haze-fog (148 haze-fog days of 182 days) with average visibility of 2.9 km was frequent in the heating period over Urumqi. Sources of the air pollutants that caused severe haze were clarified. The concentrations of SO_4^{2-}, Cl^-, NH_4^+, and Na^+ in $PM_{2.5}$ in the heating period were 9 times higher than those in the non-heating period. The enrichment factors of the pollution elements, i.e., S, Cd, As, Zn, Pb, Cu, Cr, and Na in $PM_{2.5}$ in the heating period were 3–13 times of those in the non-heating period. SNA (the three secondary inorganic ions, SO_4^{2-}, NO_3^-, NH_4^+), organic matter (OM), and chloride (Cl^-) in $PM_{2.5}$ were the three main components to cause extinction in Urumqi. The contributions of SNA, organic aerosol, and chloride to aerosol extinction, i.e., to visibility reduction, were 57%, 20%, and 12% in the heating period, and 67%, 17%, and 12% in winter. The formation mechanism of the severe haze and the micro-mechanism of the visibility reduction in Urumqi in the heating period, especially in winter, were quantitatively revealed. Those ions with high hygroscopicity in aerosols were easy to absorb or adsorb water vapor in the atmosphere, and a large number of tiny water droplets was formed and combined together with the fine particles, leading to the rapid expansion of aerosols and a great reduction of visibility. It was evident that the major source of the air pollutants that caused severe haze in Urumqi was from coal burning, for most of these ions and pollution elements in the aerosols were emitted from coal burning. Therefore, control quality and quantity of coal burning is the key to improve the air quality and the atmospheric visibility in Urumqi.

ACKNOWLEDGMENT

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