

The chemistry of heavy haze over Urumqi, Central Asia

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Abstract A sampling campaign of aerosols over Urumqi from 2001–2007 and soil samples in the surrounding areas were carried out to investigate the severe air pollution in Urumqi, a typical inland city, located in the center of Asia. Urumqi is one of the heavy polluted cities in the world, as the days of haze spanned over one third of the year and accounted for 60–80% of the heating period for the past 6 years. High concentration of fine aerosols, frequent occurrence, and rapid formation of heavy haze were the three main characteristics. With comparison of the pollution elements, As, Cd, and S, and the ratio of Ca/Al in aerosols and soils in those sites located on the south of Jungger Basin as tracers, it was found that As, Cd, and S highly enriched in the aerosols over urban Urumqi were not only from the re-suspended road dust but also from the soil transported from south of the Jungger Basin. Different from the most cities in China, the high concentration of sulfate in Urumqi was partially from the primary soil dust transported from the surrounding areas. The mixing of the local anthropogenic aerosols with the soil transported from outside the city was the main source of the high sulfate concentration. Ammonium salts were higher than the summed equivalents of SO_4^{2-} , NO_3^- , and Cl^- in Urumqi and much higher than that in other Chinese cities. The total water soluble ions and the total ammonium salts were as high as

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57.8% and 51.0% in $PM_{2.5}$. The high concentration of soluble salts with high hygroscopicity, especially ammonium and sulfate salts, were the main factors contributing to the heavy haze over Urumqi.

Keywords Haze · Source · Ammonium · Sulfate · Mixing · Formation mechanism

1 Introduction

In the last decade, most cities in China have been suffering from much more serious air pollution than ever before, caused by the rapid urbanization and motorization. The particulate-matter pollution two third of the cities remains at a much higher level than the National Ambient Air Quality Standard (He et al. 2001; Sun et al. 2004; Yao et al. 2002). Haze, a new weather pattern, has occurred much more often in the past several years over many city groups, such as Beijing-Tianjin and the Yangzi Delta city group. It has also spread throughout central and eastern China (Kaiser and Qian 2002) due to increasing vehicle exhausts, coal-fired power plants, domestic heating, and cooking. Chameides et al. (Chameides et al. 1999) assessed that a 5–30% reduction in the yields of rice and wheat would occur in China because of the effect of anthropogenic aerosols and regional haze in the atmosphere.

Haze, defined as a weather phenomenon that leads to visibility of less than 10 km, is formed from moisture, dust, smoke, and vapor in the atmosphere. The formation of haze is closely related to meteorological factors and atmospheric pollution (Watson 2002). Most haze in the atmosphere results from excessive particulate matter from anthropogenic sources and gas-to-particle transformation (Chameides et al. 1999; Watson 2002). Haze pollution has attracted much interest in recent years for its impact on visibility, cloud formation, public health, agriculture, and even the global climate change (Schichtel et al. 2001; Chen et al. 2003; Yadav et al. 2003; Kang et al. 2004). Kang et al. (2004) investigated the chemical characteristics of acidic gas pollutants and $PM_{2.5}$ species during hazy episodes in Seoul, South Korea. They found that major ionic species, NO_3^- , SO_4^{2-} , and NH_4^+ , and organic materials were the two highest contributors to $PM_{2.5}$. Chen et al. (2003) studied the summer haze in the mid-Atlantic region, and they observed high fractions of SO_4^{2-} (~60%), signifying the role of SO_4^{2-} in haze formation. Schichtel et al (2001) presented the patterns and trends of haze over the United States from 1980 to 1995 and found that the haze decline was consistent with reductions in $PM_{2.5}$ and sulfur emissions.

It must be noted that recently heavy haze occurs not only in eastern China, where the economy is rapidly developing, but also in northwestern China. Urumqi, a city located in the central Asia, is in north of the Taklimakan desert and south of the Guerbantonggute desert. Urumqi has been suffering from very heavy haze that forms on more than one third of the year. In 1998, Urumqi was evaluated as one of the ten heaviest air-polluted cities in the world. Urumqi's urban area is surrounded on three sides by Tianshan Mountains, with peaks of up to 5,000 m. Only one open mouth facing north exists, which allows the wind to carry dust soil from the Jungger Basin to the city's urban area. However, though the air pollution over Urumqi has been very severe for the past 10 years, little research has been conducted on the detailed chemical composition and transformation of the aerosol components.

It is well known that northwestern China, including Urumqi, is a main source area of Asian dust aerosols, which are transported to the Pacific Ocean and even to America's western coast (Arimoto et al. 1997). The mineral dust mixes with anthropogenic aerosol on the pathway while they are transported from central Asia to the Pacific Ocean (Sun et al. 2005; Yuan et al. 2006). The composition and morphology of the dust particles are subject

to transformation through absorption of gaseous species, surface reactions, and coagulation with other particles during transport. These processes have great impact on the global biogeochemical cycle of aerosol elements or compounds associated with trace gases such as SO_2 , NO_x , and HCl (Dentener et al. 1996). The chemical characteristics and formation mechanisms of haze in Urumqi are surely different from those of normal urban aerosols and of typical invading dust aerosols. Since Urumqi is located in the source area of Asian dust, the haze in Urumqi is related to both dust invasion and the anthropogenic sources of aerosols. Thus, studies on Urumqi's aerosols would be significant not only to local urban air quality but also to the regional environment and to global climate change. This study investigates the composition of aerosols in Urumqi and the surface soil in the surrounding areas, with the emphasis on the transformation, sources, and formation mechanism of the heavy haze in Urumqi.

2 Experimental

2.1 Sampling

2.1.1 Aerosol sampling

PM_{10} online sampling was carried out continually from 2001–2006 in downtown Urumqi with TEOM series 1,400a PM_{10} monitor (Rupprecht & Patashnick Co., Inc. Albany, NY, USA) at a flow rate of 16.7 L/min. $\text{PM}_{2.5}$ and TSP samples were collected daily (normally from 8:00 A.M. to 8:00 A.M. the next day) by medium-volume samplers (model: (TSP/ PM_{10} / $\text{PM}_{2.5}$)-2, flow rate: 77.59 L min^{-1}) with Whatman® 41 filters (Whatman Inc., Maidstone, UK) in 4 months (each month to be the representative of each of the four seasons) of the whole year of 2007. These samples were taken on the roof (~30 m above the ground) of the Institute of Desert and Meteorology, Urumqi, Xinjiang. During days with heavy dust or heavy haze, the samples were collected for a few hours each. All filters were weighed before and after sampling with an analytical balance (Sartorius 2004MP, reading precision 10 μg) after stabilizing under constant temperature ($20 \pm 1^\circ\text{C}$) and related humidity ($40 \pm 2\%$). All procedures were strictly quality-controlled to avoid any possible contamination of the samples.

2.1.2 Soil sampling

Surface soil samples were collected from downtown Urumqi streets (U1–U5) and also from surrounding areas. These samples included K1, K2, K3 in the agriculture fields, south of the Jungger Basin; KT in Kuituan, a city located in west of Urumqi and south of the Jungger Basin; S1, S2 in the Salt Lake, east of Urumqi; TZ in Tazhong, in the center of the Taklimakan desert; and XT in Xiaotang, north of Taklimakan desert. These samples represent the different areas surrounding Urumqi (See Fig. 1).

2.2 Chemical analysis

2.2.1 Element analysis

Nineteen total elements in the aerosol samples (Al, Fe, Mn, Mg, Ti, Sc, Na, Sr, Ca, Co, Cr, Ni, Cu, Pb, Zn, Cd, V, S, and As) were measured by inductively coupled plasma atomic

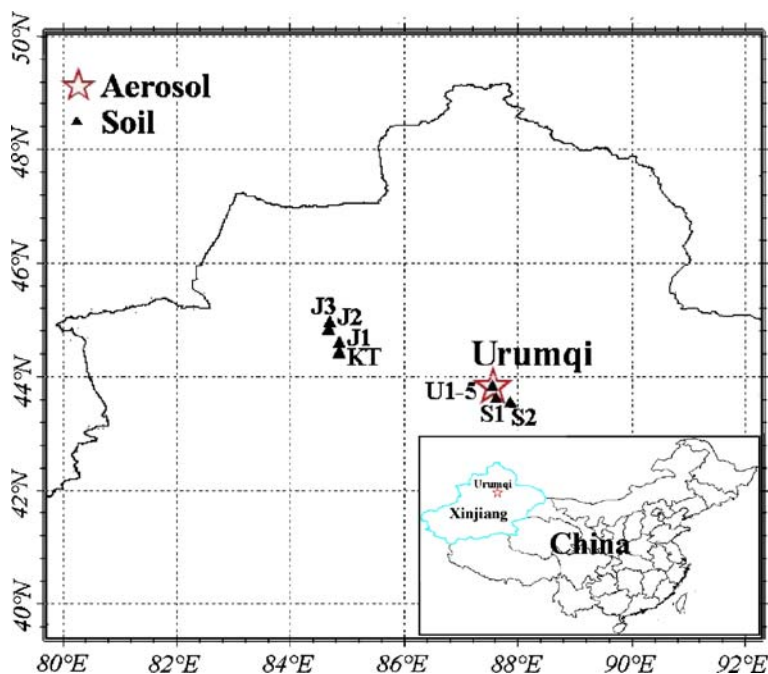


Fig. 1 Sampling sites of aerosol, surface soil and road dust in Urumqi and its surrounding areas

emission spectroscopy (ICP-AES, Model: ULTIMA, JOBIN-YVON Company, France). The detailed analytical procedures are given elsewhere (Zhuang et al. 2001; Sun et al. 2004). The soil samples were dried naturally, sieved (74 μm , 200 meshes; 30 μm , 500 meshes; Shangyu Analytical Instrumental Factory, Zhejiang), and then analyzed using the same procedures as the aerosol samples.

2.2.2 Ion analysis

Six inorganic anions (SO_4^{2-} , NO_3^- , Cl^- , F^- , PO_4^{3-} , NO_2^-), five organic acid anions (formic, acetic, oxalic, melonic, and methylsulfonic acid (MSA)) and five cations (NH_4^+ , Ca^{2+} , K^+ , Mg^{2+} , Na^+) were analyzed by Ion Chromatography (IC, Dionex ICS 3000, USA). The aerosol was leached via deionized water and the pH of the filtrate measured by a pH meter was used as a parameter to directly denote aerosol acidity. Detailed was given elsewhere (Yuan et al. 2003).

2.2.3 Black carbon analysis

Black carbon (BC) in the aerosols was analyzed with a Smokerstain Reflectometer (UK, Model, M43D)

2.2.4 The meteorological data

The meteorological data were downloaded from <http://www.wunderground.com>.

3 Results and discussion

3.1 The three main characteristics of the air-pollution in Urumqi

3.1.1 Aerosol concentrations

The daily TSP and PM_{2.5} of in 4 months (each in one of the four seasons) of the whole year of 2007 and the daily PM₁₀ concentrations from 2001~2006 in urban Urumqi are shown in Fig. 2. The mean concentrations of aerosols in winter, spring, summer, and autumn were 79.6, 64.7, 131.6, 223.7 and 216.0, 162.5, 355.7, 388.0 with the maximum of 142.4, 111.1, 285.2, 488.4 and 523.8, 303.1, 533.0, 596.8 $\mu\text{g m}^{-3}$ in PM_{2.5} and TSP, respectively. The annual mean concentrations of PM₁₀ were 201, 284, 127, 229, 233, and 213 $\mu\text{g m}^{-3}$ with the mean of 307.1, 341.2, 245.2, 385.4, 400.6, and 305.6 $\mu\text{g m}^{-3}$ in winter in 2001, 2002, 2003, 2004, 2005, and 2006, respectively. It was evident the air pollution in Urumqi was in such a severe situation that PM_{2.5} at seasonal average was 4–15 times higher than the limit of 15 $\mu\text{g m}^{-3}$ with the daily maximum of 14 times higher than the limit of 15 $\mu\text{g m}^{-3}$

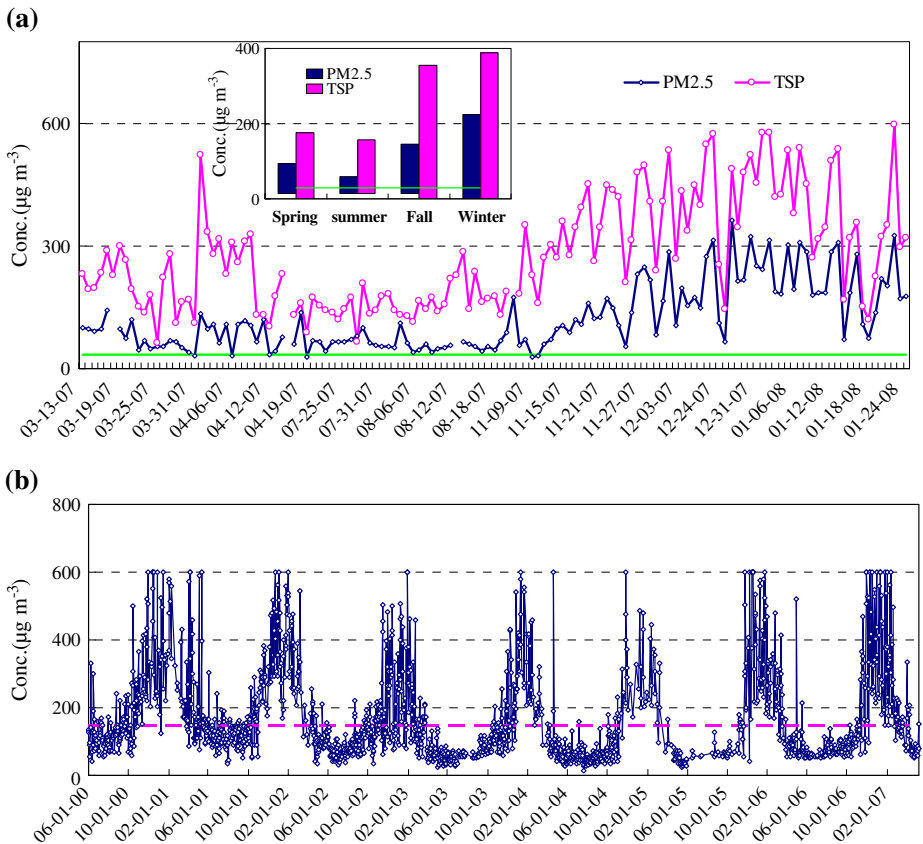


Fig. 2 **a** The daily TSP and PM_{2.5} of in 4 months (each in one of the four seasons) of the whole year of 2007. The line of 35 $\mu\text{g m}^{-3}$ is the daily limit of PM_{2.5} regulated by WHO. **b** The daily PM₁₀ concentrations from 2001~2006 in urban Urumqi The red line of 150 $\mu\text{g m}^{-3}$ is the daily limit of PM₁₀ regulated by the National Ambient Air Quality Standard of China

regulated by WHO. It was also shown clearly that in any days except in summer in the past 7 years PM_{10} exceed the limit of $150 \mu\text{g m}^{-3}$ regulated by the National Ambient Air Quality Standard of China. Winter and autumn were the much heavy polluted season, due to the heavy heating with coal combustion from October 15 to April 15 in Urumqi. In spring, soil and dust transported from the northwest, the Jungger basin, and the Guerbantonggute desert often invades the city and causes the higher aerosol concentrations. As a comparison, $PM_{2.5}$ and TSP in 2007 winter were higher than many cities over China, including the mega-cities Beijing (103 and $240 \mu\text{g m}^{-3}$) and Shanghai (133 and $278 \mu\text{g m}^{-3}$), the coastal city, Qingdao (140 and $209 \mu\text{g m}^{-3}$), and the inland cities near the desert area, Yulin (117 and $269 \mu\text{g m}^{-3}$) and Duolun (60 and $153 \mu\text{g m}^{-3}$) (Wang et al. 2006, 2007). The results indicated that Urumqi was one of the heavy polluted cities in China and in the world.

3.1.2 The visibility in Urumqi

Figure 3 shows the amount of the haze days in Urumqi during the heating period from 2001 to 2006. The haze (defined as the visibility is less than 10 Km and the relative humidity (RH) is less than 100%) days accounted for 60–80% of the heating period for the past 7 years. Haze is neither cloud nor fog, but heavy aerosols, arising mostly from the mixing of variety of fine aerosols and it has been a new weather pattern in recent years.

3.1.3 The formation of the heavy haze

Figure 4 visualizes the heavy haze and PM_{10} concentrations on February 23, 2007. The heavy haze formed so rapidly that PM_{10} increased from ~ 50 to over $500 \mu\text{g m}^{-3}$ in only 1–2 h.

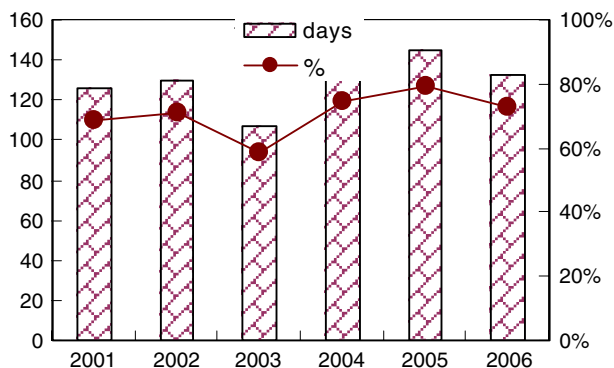
High concentration of fine aerosols, frequent occurrence, and rapid formation of heavy haze were the three main characteristics air pollution in Urumqi.

3.2 Elemental composition of aerosols over Urumqi and their sources

3.2.1 The enrichment factors of elements and their sources

Table 1 shows the concentration and enrichment factors (EF) of 19 elements in the aerosols collected from February through March of 2007 in urban Urumqi. The enrichment factor is defined as $EF = [X/Ref]_{\text{sample}} / [X/Ref]_{\text{source}}$, where $[X/Ref]_{\text{sample}}$ represents the concentration ratio of an element interested to the reference element in a sample, $[X/Ref]_{\text{source}}$ represents

Fig. 3 The amount of the haze days in Urumqi during the heating period from 2001 to 2006



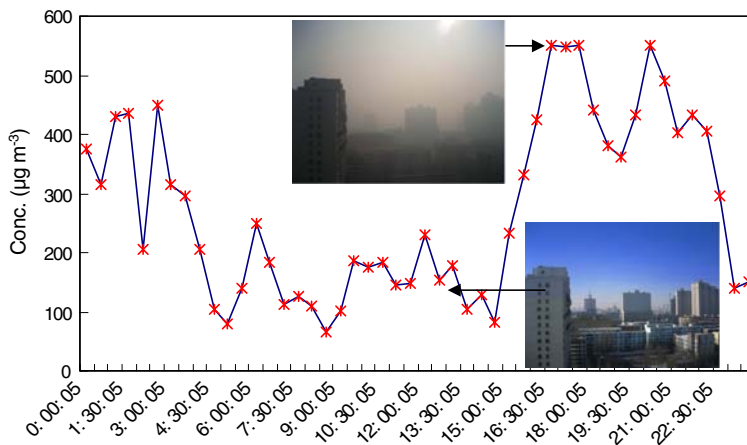


Fig. 4 PM₁₀ concentrations on the day of Feb. 23, 2007

the concentration ratio of an element interested to the reference element in source area. The typical crustal element, Al, was used as a reference of crustal source, thus $EF = [X/Al]_{\text{sample}} / [X/Al]_{\text{crust}}$. The EF of Al, Fe, Ca, Mg, Na, Sr, and Mn was less than 5 and these elements were derived from crustal sources, while the EF of elements S, Cd, Pb, As, and Zn was more than 50 and these elements were derived from anthropogenic sources. The remaining elements, P, Cr, Ni, and Cu, were derived from both crustal and pollution sources.

3.2.2 Pollution elements, Pb, As, Cd, S, and their sources

The EF of elements Pb, As, Cd, and S was as high as 1658, 1582, 1317, and 2553 in PM_{2.5}, respectively. To find the sources of these highly enriched elements, the surface soil samples on the ground of Urumqi and its surrounding areas, which could be emitted and transported to be aerosols over the city, were also collected and measured. Table 2 lists the concentrations of the four elements in these soil samples. Samples are divided into two groups based on the geographical areas of sampling sites: samples from the Urumqi city proper and samples from south of Jungger Basin. The latter can be transported to the urban Urumqi during most of the year, since these sites are located on the pathway of Asian dust to Urumqi. Table 2 shows that the surface soil samples in Urumqi city (the sites U1, U2, U3, U4, U5) contained as high as 6.6–12.8, 7.6–33.2, 303.8–877.4, and 7.8–40.3 times of Pb, As, Cd, and S, respectively, compared to their crustal abundance. Although the leaded gasoline was banned in Urumqi on Jan. 1, 1999, the high concentration of Pb in the aerosols indicated that re-suspended road dust might be one of the sources of Pb in the aerosols. The concentrations of As, Cd, and S in those sites located on the south of Jungger Basin (JB1, JB2, JB3) were 5.6–16.0, 186.5–239.3, and 3.8–30.4 times, respectively, higher than their crustal abundances. This implied that the highly enriched As, Cd, and S in the aerosols over urban Urumqi might come not only from the re-suspended road dust but also from the soil transported from south of the Jungger Basin.

3.2.3 Ratio of Ca/Al in aerosols/soils and the implied sources

Table 3 lists the ratios of Ca/Al in Urumqi aerosols and in soil samples collected from different sites inside and outside Urumqi. The ratios of Ca/Al in PM_{2.5} and TSP aerosols

Table 1 Concentration ($\mu\text{g m}^{-3}$) and enrichment factor (EF) of elements in PM_{2.5} and TSP over Urumqi

	crystal										crystal/pollution						pollution					
	Ti	Mg	Fe	Ca	V	Na	Sr	Mn	Co	Ni	P	Cr	Cu	Zn	As	Pb	Cd	S				
PM _{2.5} Conc.	0.08	0.38	1.19	1.55	0.08	1.68	0.03	0.07	0.002	0.01	0.25	0.03	0.08	0.47	0.04	0.36	0.004	15.88				
EF	0.8	1.0	1.4	2.3	3.4	4.6	4.8	5.1	6.5	6.9	16	18	96	524	1,582	1,659	1,755	2,554				
TSP Conc.	0.52	1.73	4.69	11.95	0.52	3.25	0.03	0.15	0.01	0.02	0.58	0.03	0.13	0.59	0.07	0.45	0.01	21.67				
EF	0.9	0.8	0.9	3.0	2.1	1.4	4.1	1.7	3.3	2.4	6	3	24	95	383	333	369	541				

Table 2 Concentration of pollution elements S, Pb, As, and Cd in soil samples

	Jungger Basin					Urban Urumqi					Rural Urumqi		
	Abun. (Lide 2005)	KT	JB1	JB2	JB3	U1	U2	U3	U4	U5	S1	S2	
Pb	14	77.0	21.5	29.9	21.1	119.0	92.2	166.3	178.9	148.4	26.3	18.2	
fold		5.5	1.5	2.1	1.5	8.5	6.6	11.9	12.8	10.6	1.9	1.3	
As	1.8	25.7	28.7	11.6	10.1	59.7	13.7	52.1	38.4	36.5	13.2	10.3	
fold		14.3	16.0	6.4	5.6	33.2	7.6	28.9	21.3	20.3	7.3	5.7	
Cd	0.15	35.9		33.7	28.0		45.6	113.0	131.6	123.6	49.9	23.2	
fold		239.3		224.5	186.5		303.8	753.6	877.4	823.8	332.7	154.9	
S(total)	350	3,525	1,0656	1,0397	1,343	4,118	2,721	11,579	8,110	14,113	9,060	19,792	
fold		10.1	30.4	29.7	3.3	11.8	7.8	33.1	23.2	40.3	25.9	56.5	
S(in SO ₄ ²⁻)		1,943	10,781	7,291	1,328	2,270	1,347	7,793	5,611	12,697	8,146	18,849	
S _{in SO₄²⁻} / S _{total}		0.55	1.01	0.70	0.99	0.55	0.49	0.67	0.69	0.90	0.90	0.95	

Abun.: Mean abundance in crust

KT: Kuitun city, JB1, JB 2, JB 3 : the different locations in the agriculture fields in the south of Junggur Basin

U1-5: Five different locations on the ground of Urumqi streets

S1-a site nearby Salt Lake, S2 : the site at Chaiwopu, close to Salt lake

TZ: Tazhong located in the center of Takelamgan desert; XT: Xiaotiang located at the north edge of Takelamgan desert

Fold: refer to the multiple of the concentration compared to the mean crustal abundance of the elements

Table 3 Ratio of Ca/Al in aerosol and soil samples

Aerosol		road-dust							surface soil					
		Urumqi area							Jungger Basin			Ta.Desert		
PM _{2.5}	TSP	U1	U2	U3	U4	U5	S1	S2	KT	JB1	JB2	JB3	TZ	XT
1.14	1.48	0.8	0.9	1.1	1.1	1.3	0.8	1.3	0.9	1.2	1.2	1.1	2.2	2.1

Ta. Desert, Taklimakan Desert

over Urumqi were 1.13 and 1.48, respectively, which were similar to the ratios of Ca/Al in soil samples from sites in Jungger Basin (JB1, JB2, JB3 ~ 1.2), in Salt Lake areas (S1, S2—0.8–1.2), and in the urban streets (U1–U5—0.8–1.3). These results further confirm that the aerosols over Urumqi might be partially composed of transported soil from Jungger Basin and from its suburban Salt Lake area. However, the ratios of Ca/Al in the central (Tazhong, TZ) and northern (Xiaotang, XT) areas of Taklimakan desert, which is located south of Urumqi, were ~2.2, much higher than that of Urumqi aerosols. Since Tianshan Mountain, with an altitude of over 4,000 m, stands between Urumqi and the Taklimakan desert, it would obstruct the dust from the Taklimakan desert from entering Urumqi.

3.3 Ion composition of the aerosol over Urumqi

3.3.1 Aerosol acidity

The pH of the aerosol filtrate via deionized water was used as a parameter to directly denote aerosol acidity. In PM_{2.5} and TSP, the respective pH was 4.33 and 5.80 on average, much lower than even that of the coastal city, Shanghai (5.68 and 6.38 for PM_{2.5} and TSP, respectively) (Wang et al. 2006). Acidic ions, such as SO₄²⁻, NO₃⁻, Cl⁻, and organic acids lead to lower aerosol pH values, whereas basic ions, such as NH₄⁺, Ca²⁺, and Mg²⁺, result in higher pH values. Although Urumqi is near deserts and thus should receive much more dust containing basic ions, Ca²⁺ and Mg²⁺, from the desert areas, higher concentrations of sulfate in Urumqi (48.51 and 63.08 μg m⁻³ contributed to 25.8%, 19.3% in PM_{2.5} and TSP, respectively) resulted in the lower pH in Urumqi aerosols.

3.3.2 Ion concentrations

Eleven water-soluble anions (SO₄²⁻, NO₃⁻, Cl⁻, CH₂(COO)₂²⁻, F⁻, NO₂⁻, PO₄³⁻, MSA, C₂O₄²⁻, HCOO⁻, and CH₃COO⁻) and five water-soluble cations (NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺) were detected for all of the aerosol samples. In total, the average concentrations of water-soluble ions were 93.79 and 135.77 μg m⁻³, which contributed 50.9% and 41.5% to the total mass of PM_{2.5} and TSP, respectively. Ordered by greatest concentration, the anion concentrations were SO₄²⁻ > NO₃⁻ > Cl⁻ > CH₂(COO)₂²⁻ > F⁻ > NO₂⁻ > PO₄³⁻ > MSA > C₂O₄²⁻ > HCOO⁻ in PM_{2.5}; and SO₄²⁻ > NO₃⁻ > Cl⁻ > CH₂(COO)₂²⁻ > F⁻ > MSA > NO₂⁻ > PO₄³⁻ > C₂O₄²⁻ > HCOO⁻ in TSP. The cation concentrations were NH₄⁺ > Na⁺ > K⁺ > Ca²⁺ > Mg²⁺ in PM_{2.5}; and NH₄⁺ > Ca²⁺ > Na⁺ > K⁺ > Mg²⁺ in TSP.

The major ion concentrations for samples collected in February through March 2007 in urban Urumqi are listed in Table 4. The total ion concentrations contributed 51% and 41% to the total mass of PM_{2.5} and TSP, respectively. The major anions SO₄²⁻, NO₃⁻, Cl⁻,

Table 4 Concentrations ($\mu\text{g m}^{-3}$) of major ions and black carbon (BC) and their percentage in aerosol samples

	TWSI	%	NH₄⁺	%	Na⁺	%	K⁺	%	Ca²⁺	%	Mg²⁺	%
PM_{2.5}	95.64	50.93	23.86	12.71	2.28	1.21	2.1	1.12	1.99	1.06	0.36	0.19
TSP	135.77	41.48	29.43	8.99	3.74	1.14	2.46	0.75	10.08	3.08	0.93	0.28
	SO₄²⁻	%	NO₃⁻	%	Cl⁻	%	CO₃²⁻	%	PO₄³⁻	%	CH₂(COO)₂²⁻	%
PM_{2.5}	48.51	25.83	9.45	5.03	7.46	3.97	26.36	14.04	0.11	0.05	0.88	0.47
TSP	63.08	19.27	12.28	3.75	9.66	2.95	35.43	10.82	0.26	0.08	1.93	0.59
	Mass	pH	BC	%	C₃O₄²⁻	%	HCOO⁻	%	Σ Cation	%	Σ Anion	%
PM_{2.5}	187.8	4.33	7.65	4.07	0.12	0.06	0.095	0.05	31.01	16.51	65.94	35.11
TSP	327.3	5.80	10.06	3.07	0.17	0.05	0.095	0.02	47.55	14.53	90.08	27.52

$$\Sigma \text{ cation} = \text{NH}_4^+ + \text{Na}^+ + \text{K}^+ + \text{Mg}^{2+} + \text{Ca}^{2+}; \Sigma \text{ Anion} = \text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^- + \text{NO}_2^- + \text{PO}_4^{3-} + \text{CH}_3(\text{COO}_2)^{2-} + \text{C}_2\text{O}_4^{2-} + \text{MSA} + \text{HCOO}^- + \text{F}^-$$

$\text{CH}_2(\text{COO})_2^{2-}$ contributed 25.83%, 5.03%, 3.97%, 0.47% to the total mass of $\text{PM}_{2.5}$ and 19.27%, 3.75%, 2.95%, 0.59% to TSP. The major cations NH_4^+ , Na^+ , and Ca^{2+} contributed 12.71%, 1.21%, and 1.06%, to the total mass of $\text{PM}_{2.5}$ and 8.99%, 1.14%, and 3.08% to TSP. It must be noted that the organic acid $\text{CH}_2(\text{COO})_2^{2-}$ was detected in high concentrations (0.88 and $1.93 \mu\text{g m}^{-3}$ in $\text{PM}_{2.5}$ and TSP, respectively); this suggested that organic acid could be the important part of Urumqi aerosols.

3.3.3 Ion balance and the carbonate ion CO_3^{2-}

The ion balance is expressed as the ratio of the total cation equivalents to the total anion equivalents (C/A). If all of the cations and anions in the aerosol were measured completely, the ratio of C/A should be equal to 1, based on the principle of electro-neutralization. In this study, carbonate and bicarbonate were not measured because of the limitations of the ion chromatography that was used. For the entire data set of Urumqi samples, the total anion equivalents were plotted against the total cation equivalents. The slope of the regression line was found to be 1.40, which can be attributed to the presence of HCO_3^- or CO_3^{2-} in the samples.

A very strong positive correlation ($R=0.98$) was found when the difference of NH_4^+ minus SO_4^{2-} , NO_3^- , Cl^- , and $\text{CH}_2(\text{COO})_2^{2-}$ was plotted against the difference of the total cations minus the total anions. This result revealed that ammonium ions in Urumqi aerosols might be neutralized by carbonate/bicarbonate after they were neutralized by SO_4^{2-} , Cl^- , NO_3^- , and $\text{CH}_2(\text{COO})_2^{2-}$. While the difference of the total cations minus the total anions was assumed to be CO_3^{2-} and the unit of all of those species was μeq , the slope of the regression line was 1.06, and this suggested that the species formed by NH_4^+ with CO_3^{2-} could be $(\text{NH}_4)_2\text{CO}_3$, instead of NH_4HCO_3 . Thus, ammonium salts could include $(\text{NH}_4)_2\text{CO}_3$, in addition to $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , NH_4NO_3 , and $\text{CH}_2(\text{COO})_2(\text{NH}_4)_2$. The equivalent of CO_3^{2-} can be assumed to be equal to the difference of the total cation equivalents minus the total anion equivalents. The average equivalent of the difference of the total cations and anions was $0.87 \mu\text{eq}$, and the average CO_3^{2-} concentration could accordingly be $26.36 \mu\text{g m}^{-3}$. Since dust soil usually contains more carbonate, the high concentration of CO_3^{2-} in Urumqi aerosols also revealed that the re-suspended road dust and/or the transported mineral aerosols from outside the city could be the other major source of Urumqi's aerosols, besides the local anthropogenic source.

3.3.4 The speciation of major ions

The chemical speciation of major ions (i.e. SO_4^{2-} , CO_3^{2-} , NO_3^- , Cl^- , NH_4^+ , and $\text{CH}_2(\text{COO})_2^{2-}$) in aerosols was evaluated by bivariate correlation. The correlation coefficient of NH_4^+ and SO_4^{2-} concentrations in $\text{PM}_{2.5}$ and TSP was 0.92 and 0.96, respectively, indicating that NH_4^+ is closely correlated with SO_4^{2-} . The difference of NH_4^+ minus CO_3^{2-} , NO_3^- , Cl^- , and $\text{CH}_2(\text{COO})_2^{2-}$ was plotted against SO_4^{2-} (μeq vs. μeq) for the whole data set, in which the slope of the regression was 0.95 and 1.09 in $\text{PM}_{2.5}$ and TSP respectively. The slope indicated that the species formed by SO_4^{2-} and NH_4^+ was most likely to be $(\text{NH}_4)_2\text{SO}_4$, instead of NH_4HSO_4 . In addition, $\text{Ca}(\text{NO}_3)_2$, NaCl , $(\text{NH}_4)_2\text{CO}_3$, NH_4Cl , NH_4NO_3 were major species in both $\text{PM}_{2.5}$ and TSP.

It must be noted that in Urumqi aerosols, equivalents of ammonium salts were higher than the summed equivalents of SO_4^{2-} , NO_3^- , and Cl^- . Also, ammonium salt concentration was much higher in Urumqi than that in any other Chinese cities. For

example, in Beijing and Shanghai the average NH_4^+ concentrations were 8.72 and 5.68 $\mu\text{g m}^{-3}$, respectively, in $\text{PM}_{2.5}$ (Wang et al. 2006, 2005). However, in Urumqi, the average NH_4^+ concentration was 23.86 $\mu\text{g m}^{-3}$, ~3–4 times of those in Beijing and Shanghai. South Jungger Basin areas are those modern agriculture farms, where chemical fertilizer was used widely and the surface soil from these field contained higher concentration of ammonium salts, such as $(\text{NH}_4)_2\text{SO}_4$. Thus ammonium salts were most abundant among all the salts and might be the main factor contributing to the formation of Urumqi's heavy haze.

3.3.5 Sulfate in the aerosols and its sources

The enrichment factor of sulfur was noticeably the highest among all the elements measured, and it could reach ~2,500 in $\text{PM}_{2.5}$. The concentrations of SO_4^{2-} in $\text{PM}_{2.5}$ and TSP were 48.51 and 63.08 $\mu\text{g m}^{-3}$, while the total sulfur content in $\text{PM}_{2.5}$ and TSP was 15.88 and 21.67 $\mu\text{g m}^{-3}$, respectively, as shown in Table 4. If calculating S content in SO_4^{2-} only ($\text{S}/\text{SO}_4^{2-} = 1/3$), the ratio of the S in the water-soluble sulfur (i.e. S in SO_4^{2-}) to the total sulfur in the aerosol (Sw/St) was 1.00 and 0.97 in $\text{PM}_{2.5}$ and TSP, respectively. These results clearly demonstrated that the sulfur in $\text{PM}_{2.5}$ and TSP was mostly in the form of sulfate. Such high sulfate concentrations would evidently relate to the formation of the heavy haze.

Sulfur abundance in the sites in south Jungger Basin (JB1, JB2, JB3) and in the salt lake areas (S1, S2) was 3.3~56.5 times higher than the average crust abundance. This sulfur content was also mostly in the form of sulfate; for in these soil samples the ratio of the sulfur content in SO_4^{2-} to the total sulfur content ranged from 0.7 to 1.00 (see Table 2). South Jungger Basin areas are modern agriculture farms, where chemical fertilizers are used widely, and thus the surface soil from these fields contained higher concentrations of SO_4^{2-} . The surface soil from the nearby Salt lakes, early dried salt lakes, also contained higher concentrations of sulfate. As mentioned above, the surface soil from these two areas are suspended and transported by wind to urban Urumqi, since their locations are on the pathway of dust transport. These results obviously indicated that transported soil dust with high concentration of SO_4^{2-} from the Jungger Basin and from Salt lake areas would contribute to the high sulfate concentration in the Urumqi aerosols.

In addition, the high concentration of SO_4^{2-} in the road dust of Urumqi streets would also contribute, since these surface soils contained as high as 7.8–40.3 times the sulfate concentration in the crust (see Table 2). The EFs of sulfur in $\text{PM}_{2.5}$ and TSP was as high as 2553 and 541, respectively, which were much higher than either the contributions from outside transported soil or the contributions from inside re-suspended road dust. Therefore, the gas-to-particle conversion of SO_2 to sulfate is the other major contributor to the sulfate in the Urumqi aerosols. The mixing of outside transported dust soil with the anthropogenic aerosols is the formation mechanism and the source of the high sulfate concentration in Urumqi aerosols, which most likely results in the heavy haze over Urumqi.

3.4 The formation mechanism of the heavy haze over Urumqi

3.4.1 The high concentration of total water-soluble ions and ammonium salts

Figure 5 shows the concentration of the total water-soluble ions (TWSI) and ammonium salts, which were the products of the major anions (SO_4^{2-} , CO_3^{2-} , NO_3^- , Cl^- and $\text{CH}_2(\text{COO})_2^{2-}$) neutralized by NH_4 and included $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , $(\text{NH}_4)_2\text{CO}_3$, NH_4Cl , NH_4NO_3 , and $(\text{NH}_4)_2\text{CH}_2(\text{COO})_2$, as well as their respective percentages in $\text{PM}_{2.5}$

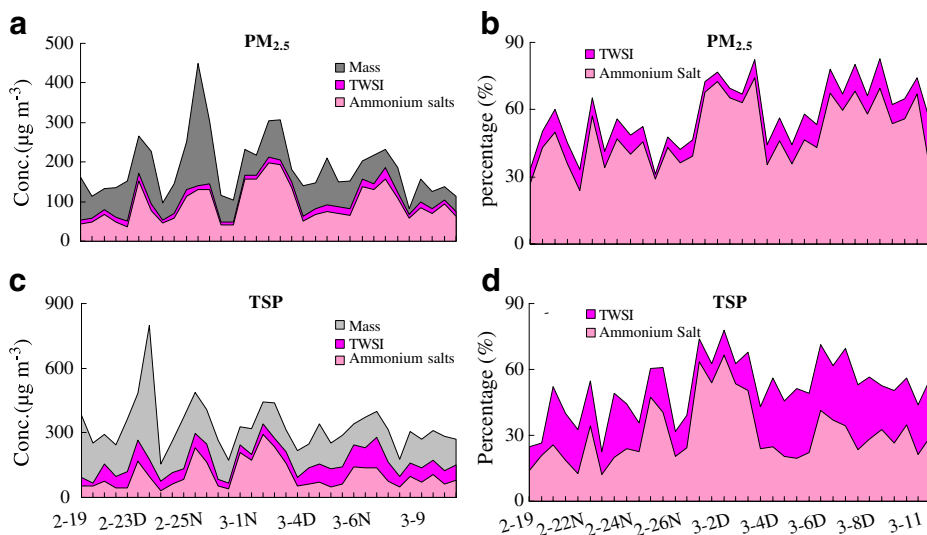


Fig. 5 Concentrations (a, c) and percentage (b, d) of TWSI and ammonium salts in PM_{2.5} and TSP

and TSP aerosols over Urumqi, from February through March 2007. The average concentrations of TWSI and ammonium salts reached 107.8 and $94.0 \mu\text{g m}^{-3}$ in PM_{2.5}; 167.5 and $103.7 \mu\text{g m}^{-3}$ in TSP. The mean percentage of TWSI and ammonium salts in PM_{2.5} and TSP were 57.8%, 49.5% and 51.0%, 31.0%, respectively, and the maximum percentage of TWSI and ammonium salts in PM_{2.5} and TSP even accounted for 83%, 74% and 78%, 66%, respectively. Such high percentages of TWSI and ammonium salts are unprecedented in any Chinese cities. It is well known that the TWSI, especially ammonium salts, adsorb water vapor strongly and quickly since they have very high hygroscopicity. When the RH changes from 80% to 90%, the ratio of the NH_4HSO_4 volume under this RH to the volume under dry conditions (which can be used as a measure of the hygroscopicity) would increase 2.4 times. However, when the RH changes only 1% from 90 to 91%, the ratio of the volume of NH_4HSO_4 particle would increase 8 times (Seinfeld and Pandis 1998). Thus, ammonium salts have the highest hygroscopicity among all of the inorganic salts. In Urumqi, the ammonium salts account for extremely high percentages of the aerosols, implying that they could be a main reason for the formation of heavy haze with such high concentration, high formation rate, and high frequency.

3.4.2 The relationships of visibility with PM_{2.5}, TWSI, SO_4^{2-} and NH_4^+

The visibility was also strongly related to the nature of the aerosols' chemical components. We did the statistical correlation analysis for the entire data set of aerosol samples collected from Beijing and Shanghai during all of spring 2004. The correlation coefficients of relationships of visibility with NH_4 , SO_4^{2-} , TWSI, and PM_{2.5} respectively, were -0.726 , -0.696 , -0.678 , -0.520 in Shanghai and -0.637 , -0.484 , -0.427 , -0.534 in Beijing. It was evident that these four components are all negatively related to the visibility at some degree and that among the four components, ammonium salts are the most strongly related to visibility. As mentioned above, the concentration of ammonium salts was 94.0 and $103.7 \mu\text{g m}^{-3}$, respectively, in PM_{2.5} and TSP aerosols of Urumqi, accounting for

percentages as high as 49.5% and 31.0% of $PM_{2.5}$ and TSP, respectively. Thus, high ammonium salts in Urumqi was one of the major factors forming the heavy haze.

4 Conclusion

- 1) Urumqi is one of the heavy polluted cities in the world, as the days of haze spanned over one third of the year and accounted for 60–80% of the heating period for the past six years. High concentration of fine aerosols, frequent occurrence, and rapid formation of heavy haze were the three main characteristics.
- 2) As, Cd, and S were highly enriched in the aerosols over urban Urumqi, and they were not only from the re-suspended road dust but also from the soil transported from south of the Jungger Basin.
- 3) Different from the most cities in China, the sulfate in Urumqi aerosol was partially from the primary soil dust transported from the agricultural fields, south of Jungger Basin and surrounding salt lake areas. The mixing of the transported soil dust from outside the city with the local anthropogenic aerosols was the main source of the high concentration of sulfate in Urumqi.
- 4) The total water soluble ions and the total ammonium salts were as high as 57.8% and 51.0% in $PM_{2.5}$. The high concentration of soluble salts with high hygroscopicity, especially ammonium salts and sulfate salts, were the main factors contributing to the heavy haze over Urumqi.
- 5) As Urumqi is located in the source area of Asia dust, both dust invasion and the anthropogenic sources caused the heavy air-pollution. Studies on the heavy haze occurred in Urumqi would have the significance of not only the improvement of local urban air quality but also the regional environmental and even the global climate change.

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