

Characteristics and sources of air-borne particulate in Urumqi, China, the upstream area of Asia dust

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Abstract

A sampling campaign of aerosols over Urumqi from 2004 to 2007 with detailed and systematic analysis was carried out to investigate the severe air pollution in Urumqi, China, which is located nearby the upstream area of Asia dust. It was found that Urumqi city was the severest polluted city over the world. The average $PM_{2.5}$ and TSP concentrations in the winter of 2007 were 187 and $385 \mu\text{g m}^{-3}$ with maximum of 487 and $1313 \mu\text{g m}^{-3}$, respectively, 12 times higher than USA standard for $PM_{2.5}$ and 3 times the National Ambient Air Quality Standard of China for TSP. The city's industrial emissions of sulfur dioxide were converted to sulfate in the air, and sulfate-rich soil dust was transported to Urumqi's air from agricultural fields south of Jungger Basin and surrounding salt lake areas. The mixing of the local anthropogenic aerosol with the transported soil dust from outside the city was the main sources of the high concentration of sulfate, one of the main factors causing the heavy air pollution over Urumqi. The high concentration of ammonium and sulfate salts in the aerosol from both inside and outside city and the low wind speed might be the main factors to form the heavy haze over the Urumqi.

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1. Introduction

It has been well known that the northwestern China, including Xinjiang, is one of the main source areas of the Asian dust, which would be transported to the Pacific, even to the western coast of America (Duce et al., 1991; Arimoto et al., 1997). The

mineral aerosols would mix with those anthropogenic aerosols on the pathway while they are transported from Central Asia to hundred and thousand away over Pacific (Sun et al., 2005; Yuan et al., 2006). The composition and morphology of the dust particles are subject to transform by adsorbing gaseous species, surface reactions, and coagulation with other particles during the transport, especially, while the dust travels through eastern China areas, where the economy and industry are developing rapidly in recent years.

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These processes would impact greatly on the global biogeochemical cycle of the elements or compounds in the aerosols associated with trace gases such as SO_2 , NO_x , and HCl (Zhang et al., 1994; Dentener et al., 1996; Song and Carmichael, 2001; Zhang and Iwasaka, 2001). The long-range transported Asia dust would function in the two aspects: (1) transferring high peak of the dust aerosols with high concentration of those anthropogenic elements or compounds especially in spring dust season; (2) providing high concentration of those nutrients, N, P, Fe, especially the micronutrient, Fe(II), to the marine phytoplankton in the open ocean, which might be the limiting factor for the primary biological productivity in certain regions (Martin, 1992; Martin and Fitzwater, 1988; Martin et al., 1990; Zhuang et al., 1990, 2001). The transport and deposition of the dust aerosols to a certain region of the ocean may control the rate of organism production through controlling the wind-generated trace elements as iron, aluminum, etc., then affect the oceanic ecosystem and have influence on the absorption of CO_2 and the cycle of the variety of the trace elements (especially C, S, and N, etc.), and indirectly impact on the global climate change (Zhuang et al., 1992). Thus, study on the characteristics and the transformation of those dust aerosols collected from the upstream source areas would have the significance of not only the local urban air pollution but also the global change.

Urumqi (E86°37'33"–88°58'24", N42°45'32"–44°08'00"), the capital of Xinjiang Uygur Autonomous Region of China, is in the middle zone of Xinjiang, which is on the north foot of Tian Mountain and the south edge of Jungger Basin (Fig. 1). It is almost in the center of Asia, and located in the north of Taklamagan desert and in the south of Guerbantonggute desert. The urban area of Urumqi is surrounded by Tianshan Mountain from three directions with peaks up to 5000 m, and there is only a mouth facing north, where the wind could carry the soil dust to the urban area of the city. For the past two decades, Urumqi has been heavily air-polluted and it was evaluated as 1 of the 10 heaviest air-polluted cities over World in 1998 (Mamtimin and Meixner, 2007). For the past several years, Urumqi has been suffering from very heavy haze, which has spread throughout central and eastern China (Kaiser and Qian, 2002) and occurred very often over many city groups, such as the Beijing–Tianjin city group and the Yangtzi Delta city group (Shanghai, Hanzhou, Nanjing, etc.) due to increasing vehicle exhausts,



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

coal-fired power plants, domestic heating, and cooking. The severe haze not only damages health and agriculture, but also changes the earth's radiation balance. Haze mainly results from anthropogenic emissions of particles and invisible gases transformed to particles after emission, of which the organic aerosols are the most important components. It was reported that annually average TSP and PM_{10} in Urumqi were as high as 467 and $284 \mu\text{g m}^{-3}$, respectively, in 2002 (Feng et al., 2005). Guo et al. (2006) reported a case of severe air pollution with PM_{10} concentration of 130.3–164.2 $\mu\text{g m}^{-3}$ occurred from 16 December 2003 till 11 January 2004. Li et al. (2005) illustrated the seasonal variation of the particulate over Urumqi with SEM-EDX analysis. Peng et al. (2006) analyzed the sources of PAHs in Urumqi with the composition of carbon isotope. However, to date, there are little study on the detailed chemical composition and the transformation of the components of the aerosols over Urumqi, though the air pollution over Urumqi has been very severe for the past 10 years. This study monitors the TSP, PM_{10} , and $\text{PM}_{2.5}$ aerosols continually for the past 3 years, and investigates systematically the concentration, composition, seasonal variation, transformation, sources as well as the possible formation mechanism of the heavy haze over Urumqi.

2. Experimental

2.1. Sampling

A sampling campaign of aerosols monitoring was carried out continually for the past 3 years from

2004 to 2007 in the downtown of Urumqi. A TEOM series 1400a PM₁₀ monitor on the roof of the building of Institute of Desert and Meteorology, Urumqi, Xinjiang, with a flow of 16.71 min⁻¹ (Rupprecht & Patashnick Co. Inc., Albany, NY, USA) was used for sampling PM₁₀ on-line. 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/PM₁₀/PM_{2.5})-2, flow rate: 77.59 l min⁻¹). The height of the sampling site was 30 m above the ground. On the spring dust season or heavy haze days the sample was collected based on hours 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 related humidity (40 ± 2%). All the procedures were strictly quality-controlled to avoid any possible contamination of the samples.

For study on the sources of the aerosol, surface soil samples were also collected at those typical sites in downtown streets (U1–U5), and basically these sites could be the representatives of different areas and covered the whole urban area of the city. The surface soil samples were also collected at different sites of the south of Jungger Basin (K1, K2, K3; KT: Kuitun (a city located on the south of Jungger Basin)) and at the two sites nearby salt lake. The soil samples from both areas could be wind-transported to the city through the whole year.

2.2. Chemical analysis

2.2.1. Element analysis

The sample filters were digested at 170 °C for 4 h in high-pressure Teflon digestion vessel with 3 ml concentrated HNO₃, 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. Total 19 elements (Al, Fe, Mn, Mg, Ti, Sc, Na, Sr, Ca, Co, Cr, Ni, Cu, Pb, Zn, Cd, V, S, and As) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Model: ULTIMA, JOBIN-YVON Company, France). The detailed analytical procedures were given elsewhere (Zhuang et al., 2001, 2003; Sun et al., 2004). The soil samples were sieved (500 screen meshes, particles of < 30 µm pass through), and then analyzed with the same procedures as mentioned above.

2.2.2. Ion analysis

Eleven inorganic ions (SO₄²⁻, NO₃⁻, F⁻, Cl⁻, NO₂⁻, PO₄³⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺) and four organic acids (formic, oxalic, melonic, and methylsulfonic 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). Detailed was given elsewhere (Yuan et al., 2003).

2.2.3. Black carbon analysis

Black carbon (BC) was analyzed with Smoker-stain Reflectometer (UK, Model, M43D) with Whatman[®] 41 filters.

2.2.4. The meteorological data

The meteorological data, including temperature (Temp.), relative humidity (RH), wind speed, wind direction, etc., was downloaded from <http://www.wunderground.com>.

3. Results and discussion

3.1. The severe air pollution over Urumqi for the past 3 years

In early 1998, Urumqi was evaluated by World Health Organization (WHO) to be one of the ten most polluted cities over the world. Almost 10 years passed since then, the air pollution over Urumqi has not been improved yet, although the government has done many measures. Fig. 2 visualized the heavy air pollution over the city, which lasted for > 4–6 months from fall, winter till spring each year. PM₁₀ concentrations of the aerosols collected daily from the urban area of Urumqi from 2004 to 2007 are shown in Fig. 3 and Table 1. It could be seen clearly that the air pollution over Urumqi was in such a severe situation that most of the days throughout the whole year exceeded the limit of 100 µg m⁻³ regulated by the National Ambient Air Quality Standard of China. The annual average concentrations were 229, 233, and 213 µg m⁻³ in 2004, 2005, and 2006, respectively, more than twice of the limit of the standard in China. The PM_{2.5} and TSP daily concentrations in February–March 2007 are also shown in Fig. 4 and Table 1. The average PM_{2.5} and TSP concentrations in this period were 187 and 327 µg m⁻³, respectively, > 12 and 3 times higher

than the limit of the standard. As there is no limit of the standard yet for PM_{2.5} in China, the annual average of 15 µg m⁻³ as the limit from the US EPA, 1997 was used to compare with the data in this



Fig. 2. Pollution situation in winter in Urumqi (photo taken on 23 February 2007).

study. Table 2 lists the concentrations of PM_{2.5} and TSP in those cities over China, including the mega-cities, Beijing and Shanghai (Sun et al., 2004; Wang et al., 2006, 2007), the coastal city, Qingdao, and the inland cities nearby the desert area, Yulin and Duolun. The comparison illustrated that the average concentrations of either TSP or PM_{2.5} in Urumqi were much higher than any cities in China. Urumqi was the severest polluted city among all cities in China and even over the world.

3.2. Seasonal variation of aerosols over Urumqi

Fig. 3 and Table 1 show the season variation of PM₁₀ concentration over Urumqi from 2004 to 2006. The average concentrations of PM₁₀ in winter, spring, summer, and fall were 412.8, 196.2, 128.2, and 251.5 µg m⁻³ in 2004; 400.6, 181.5, 117.1, and 179.2 µg m⁻³ in 2005; 305.6, 143.0, 97.3, and 326 µg m⁻³ in 2006; respectively. Generally, the air pollution intensity was in the order of winter > spring > fall > summer. It was shown clearly that

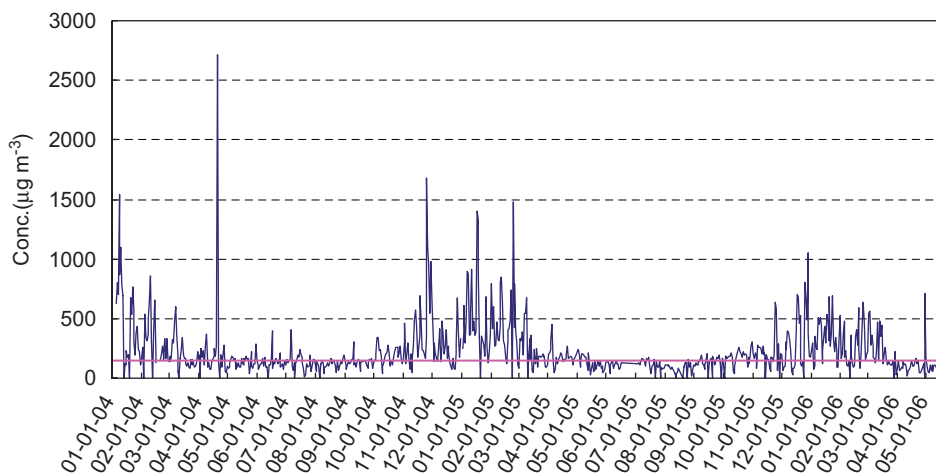


Fig. 3. PM₁₀ concentrations from 2004 to 2006 over Urumqi.

Table 1
PM₁₀ concentrations (µg m⁻³) in the four seasons from 2004 to 2007 over Urumqi

	2004			2005			2006			2007		
	Average	Maximum	Range	Average	Maximum	Range	Average	Maximum	Range	Average	Maximum	Range
Spring	196.2	2634.8	31.2–2634.8	181.5	589.4	42.5–589.4	143.0	780.2	11.2–780.2	385.4	1312.9	19.7–1312.9
Summer	128.2	356.5	7.5–356.5	117.1	562.9	18.8–562.9	97.3	186.6	28.6–186.6			
Fall	251.5	1600.7	59.9–1600.7	179.2	701.8	23.5–701.8	326	978.7	69.3–978.7			
Winter	412.8	1674.7	37.8–1674.7	400.6	1623.4	57.6–1623.4	305.6	1048.5	35.7–1048.5			
Annual	229			233			213					

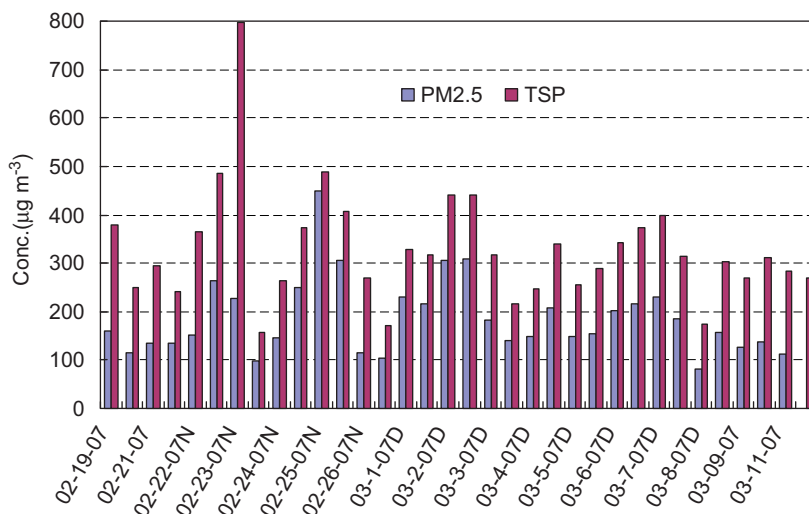


Fig. 4. $PM_{2.5}$ and TSP concentrations in February–March 2007 over Urumqi. D, daytime; N, nighttime.

Table 2

Concentration range of $PM_{2.5}$ and TSP ($\mu g m^{-3}$) in Urumqi and other cities over China

	Urumqi In this work	Duolun (Sun et al., 2004; Wang et al., 2007)	Yulin (Sun et al., 2004; Wang et al., 2007)	Beijing (Sun et al., 2004; Wang et al., 2007)	Qingdao (Sun et al., 2004; Wang et al., 2007)	Shanghai (Sun et al., 2004; Wang et al., 2007)
$PM_{2.5}$	83–487 (187)	10–149 (60)	19–296 (117)	10–255 (103)	70–480 (140)	73–218 (133)
TSP	157–798 (327)	26–463 (153)	21–968 (269)	40–512 (240)	80–564 (209)	133–444 (278)

Number in parentheses () is the average concentration.

Table 3a

Concentrations ($\mu g m^{-3}$) of chemical components in $PM_{2.5}$ and TSP in winter over Urumqi

	Mass	TWSI		OC		BC		Mineral	
		Concentration	%	Concentration	%	Concentration	%	Concentration	%
$PM_{2.5}$	187.8	92.48	49.3	71.51	38.1	6.60	3.5	17.17	9.1
TSP	327.3	132.58	40.5	87.55	26.7	8.69	2.7	98.48	30.1
$PM_{2.5}/TSP$ (%)	57.4	69.8	81.7	75.9	17.4				

TWSI: total water soluble ions; OC: organic carbon; BC: black carbon.

winter was the most polluted season, which was due to the heavy heating with coal combustion in this season. In Urumqi there is a half-year for house heating domestically and industrially from 15 October to 15 April of next year. As Urumqi is located nearby those deserts and those arid and semi-arid areas in northwest China, in spring it is often invaded by soil dust from outside the city, mostly transported from north, Jungger Basin, and Guerbantonggute desert. Thus, it has high concen-

tration of aerosol in this season. Summer was the least polluted season, which was because there was more precipitation plus no heating.

3.3. Size distribution of aerosol and its components over Urumqi

The ratio of $PM_{2.5}/TSP$ of aerosol and its component is shown in Tables 3a–c. The average ratio $PM_{2.5}/TSP$ of aerosols was 57.4%. The ratios

Table 3b
Concentrations ($\mu\text{g m}^{-3}$) of ions in $\text{PM}_{2.5}$ and TSP in winter over Urumqi

	TWSI	%	NH_4^+	%	Na^+	%	K^+	%	Ca^{2+}	%	Mg^{2+}	%
$\text{PM}_{2.5}$	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
$\text{PM}_{2.5}/\text{TSP}$ (%)	70.4	81.1	60.9	85.4	19.8	38.7						
	SO_4^{2-}	%	NO_3^-	%	Cl^-	%	F^-	%	NO_2^-	%	CO_3^{2-}	%
$\text{PM}_{2.5}$	48.51	25.83	9.45	5.03	7.46	3.97	0.38	0.20	0.36	0.19	26.36	14.04
TSP	63.08	19.27	12.28	3.75	9.66	2.95	1.22	0.37	0.49	0.15	35.43	10.82
$\text{PM}_{2.5}/\text{TSP}$ (%)	76.9		76.9		77.2		31.4		73.2		74.4	
	PO_4^{3-}	%	$\text{CH}_2(\text{COO})_2^{2-}$	%	$\text{C}_2\text{O}_4^{2-}$	%	HCOO^-	%	MSA		pH	Mass
$\text{PM}_{2.5}$	0.11	0.05	0.88	0.47	0.12	0.06	0.095	0.05	0.2	0.11	4.33	187.8
TSP	0.26	0.08	1.93	0.59	0.17	0.05	0.095	0.02	1.03	0.31	5.80	327.3
$\text{PM}_{2.5}/\text{TSP}$ (%)	42.3	45.6	70.6	99.6	19.4							

Table 3c
Concentrations ($\mu\text{g m}^{-3}$) and enrichment factors (EF) of elements in $\text{PM}_{2.5}$ and TSP over Urumqi

	Al	Ti	Fe	Ca	Mg	Na	Sr	Mn	Co	Ni
$\text{PM}_{2.5}$	1.37	0.08	1.19	1.55	0.38	1.68	0.03	0.07	0.00	0.01
EF	1	0.1	1.39	0.28	0.12	4.57	0.58	5.11	6.47	6.90
TSP	8.05	0.52	4.69	11.95	1.73	3.25	0.03	0.15	0.01	0.02
EF	1	0.11	0.85	0.36	0.09	1.43	0.50	1.68	3.27	2.38
$\text{PM}_{2.5}/\text{TSP}$ (%)	17.06	14.46	25.45	12.98	22.00	51.68	99.59	47.99	31.85	47.12
	V	P	Cr	Cu	Zn	As	Pb	Cd	S	Sw/St
$\text{PM}_{2.5}$	0.08	0.25	0.03	0.08	0.47	0.04	0.36	0.00	15.88	1.00
EF	3.4	1.97	18.63	95.59	524	1582	1658	1317	2553	
TSP	0.52	0.58	0.03	0.13	0.59	0.07	0.45	0.01	21.67	0.97
EF	2.10	0.73	2.55	23.92	94	382	333	270	541	
$\text{PM}_{2.5}/\text{TSP}$ (%)	14.46	43.28	99.51	62.76	80.61	64.23	79.21	74.50	73.28	

Sw: S in the water soluble form, SO_4^{2-} ; St: total S in the aerosol.

of $\text{PM}_{2.5}/\text{TSP}$ in the total water soluble ions (TWSI), organic carbon (OC), and black carbon were 70.4%, 81.7%, and 75.9%, indicating these species were most in the fine particles, while the ratio in mineral aerosol was 17.4%, which indicated that the mineral aerosol was mostly in the coarse particles. The ratios of $\text{PM}_{2.5}/\text{TSP}$ of the three major ions, NH_4^+ , SO_4^{2-} , NO_3^- were 81.1%, 73.7%, and 77.0%. These results indicated evidently that the secondary anthropogenic species existed mostly in fine particle. The ratios of those pollution elements, S, Pb, As, Cd, and Zn, were 73.3%, 79.2%, 64.2%, 74.5%, and 80.6%, respectively, indicating these pollution elements were mostly in the fine particles, while the crustal elements, Al, Fe,

Ca, Mg, and Ti, were 17.0%, 25.5%, 13.0%, 22.0%, and 14.5%, respectively, showing these crustal elements were mostly in the coarse particles.

3.4. Chemical composition of aerosols over Urumqi and their sources

3.4.1. The mixture of inorganic salts, organic carbon, black carbon, and minerals

Fig. 5 shows the chemical composition of those aerosols collected in winter in Urumqi. The aerosols over Urumqi were the mixture of the four groups: inorganic salts, organic carbon, black carbon, and minerals. The inorganic salts were mainly sulfate, nitrate, chloride, and ammonium salts.

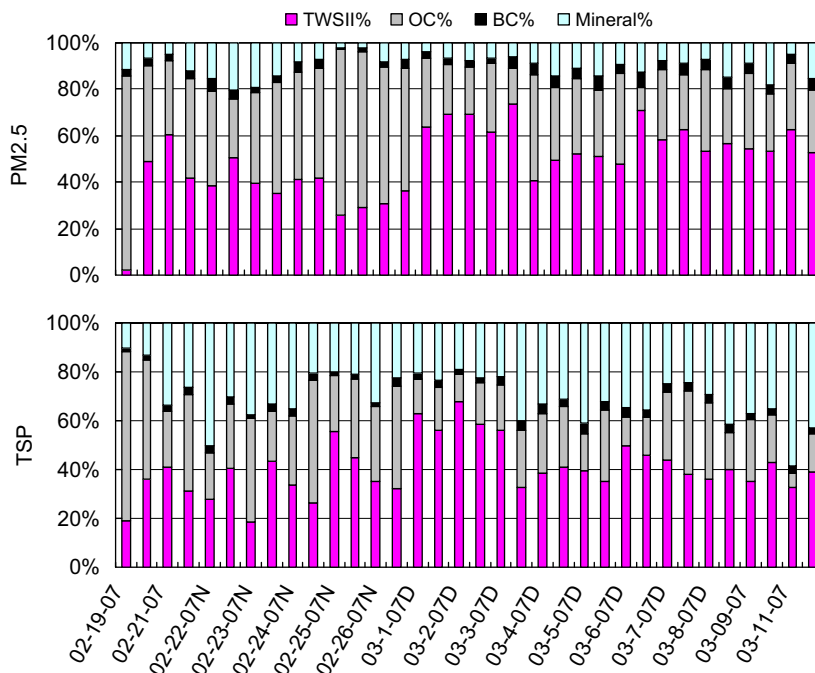


Fig. 5. Composition of $PM_{2.5}$ and TSP over Urumqi. TWSII, total water soluble inorganic ions.

Black carbon was mostly element carbon. In this work, organic carbon was calculated based on the assumption that the total mass of aerosol was the sum of the total inorganic salts, mineral aerosol, organic carbon, and black carbon. Thus, the concentration of organic carbon in the aerosols would equal to the difference of the total mass of the aerosol minus the sum of the total inorganic salts, mineral aerosol, and black carbon. The concentration of mineral aerosol was calculated based on the formula of $Al/0.08$, as the average Al abundance in the crust is $\sim 8\%$ (Lida, 2005/2006). It is shown in Fig. 5 that on average the concentrations of these four groups were in the order of the total inorganic salts > organic carbon > mineral aerosol > black carbon in $PM_{2.5}$, and the total inorganic salts > mineral aerosol > organic carbon > black carbon in TSP. The greatest fraction of the composition of the aerosol over Urumqi was inorganic salts, which was 49.3% and 40.5% in both $PM_{2.5}$ and TSP, respectively. The other major fraction was organic carbon, which was 38.1% and 26.7% in $PM_{2.5}$ and TSP, respectively. The part of mineral aerosol was only 9.1% $PM_{2.5}$ and 30.1% in TSP. The black carbon was the least part, only 3.5% and 2.7%, in $PM_{2.5}$ and TSP, respectively. It must be noted that the mineral aerosol in fine particle, $PM_{2.5}$, was only 9.1%, which clearly

indicated that the secondary aerosol was the major part in the fine particles and it would be strongly related to the formation of the heavy haze, which is discussed further below.

3.4.2. The elemental composition and their sources

The concentrations and their enrichment factors (EF) of 19 elements in the aerosols, which were measured in this study, are shown in Table 3c and Fig. 6. Based on their EF, these elements could be divided to three groups: crustal elements, pollution elements, and crustal/pollution elements. The EF of the crustal elements, including Al, Fe, Ca, Mg, Na, Sr, and Mn, was < 5 , which were mostly from crustal sources, while EF of the pollution elements, including S, Cd, Pb, As, and Zn, was > 50 , which derived from those anthropogenic sources. The rest elements, including P, Cr, Ni, and Cu, could be derived from both crustal and pollution sources.

3.4.2.1. Pollution elements, Pb, As, Cd, and their sources. The EF of elements, Pb, As, Cd, and S, were as high as 1658, 1582, 1317, and 2553 in $PM_{2.5}$, respectively. To find the sources of these highly enriched elements, we collected the surface soil samples on the ground of Urumqi and the surrounding areas over Xinjiang, which could transport aerosols to the city. Table 4 lists the

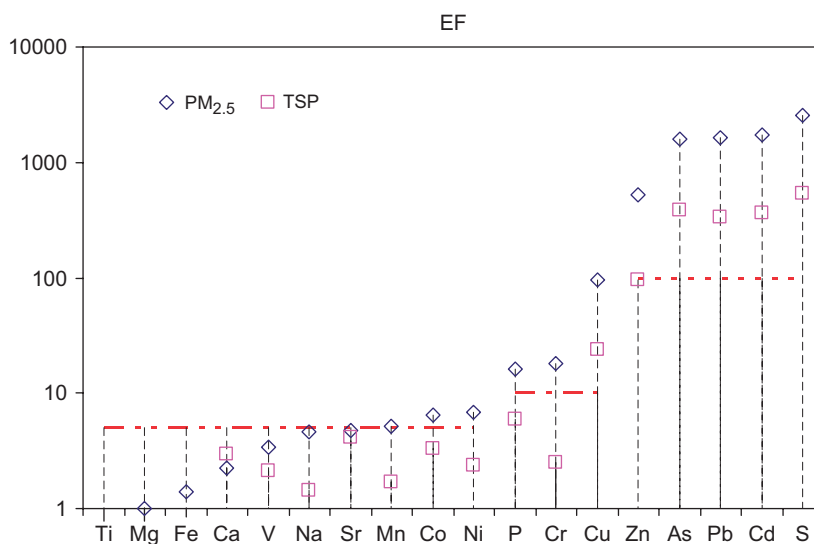


Fig. 6. Enrichment factors of elements in aerosols over Urumqi.

Table 4
Comparison of concentrations of Pb, As, Cd, and S in surface soil and road dust in Xinjiang with their mean abundance in crust

	Abun. ($\mu\text{g g}^{-1}$) (Lida, 2005)	Jungger Basin				Urban Urumqi					Rural Urumqi	
		KT	K1	K2	K3	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	3525	10656	10397	1343	4118	2721	11579	8110	14113	9060	19792
S (in SO_4^{2-})		1943	10781	7291	1328	2270	1347	7793	5611	12697	8146	18849
S (total)/S (in SO_4^{2-})		0.55	1.01	0.70	0.99	0.55	0.49	0.67	0.69	0.90	0.90	0.95
Fold		10.1	30.4	29.7	3.3	11.8	7.8	33.1	23.2	40.3	25.9	56.5

Abun.: Abundance; KT refer to Kuitun city; K1, K2 and K3 refer to the locations in the agriculture fields in the Jungger Basin. U1–U5: five different locations on the ground of Urumqi streets. S1 refers to the sites at the salt lake; S2 refers to the location near by the salt lake Chaiwopu. Fold: the times higher than the mean abundance in the crust.

concentrations of the four elements in these soil samples. It is divided into two groups based on the geographical areas of sampling sites: Urumqi city, the south of Jungger Basin, which could transport the surface soil to Urumqi city in the most of time of the whole year, as these sites are located in the only pathway of the soil dust from the great agriculture field to Urumqi (see Fig. 1). From Table 4, it is shown that the surface soil samples, including the road dust, in Urumqi city (the sites U1, U2, U3, U4, U5) contain as high as 6.6–12.8, 7.6–33.2, 303.8–877.4, 7.8–40.3 times of concentration of Pb,

As, Cd, and S compared to their crustal abundance, which could be from the deposition of these elements in the early years. Although in Urumqi the leaded gasoline was banned firstly on 1 January 1999, such high concentration of Pb in the aerosols indicated that the re-suspended road dust might be one of the sources of Pb in the aerosol. The concentrations of As and Cd in those sites located on the south of Jungger Basin (K1, K2, K3), where is the pathway of the soil dust from the great agriculture field to Urumqi and the surface soil could be transported to Urumqi city, were also

5.6–16.0 and 186.5–239.3 times higher than its crustal abundance. This would mean that the highly enriched As and Cd in the aerosols over Urumqi might come from not only the re-suspended road dust but also the outside transported soil from the south of the Junggur Basin.

3.4.2.2. Pollution element, S, and its sources. It was noticeable that the highest EF of S could reach ~2500 in PM_{2.5}. The concentration of SO₄²⁻ in PM_{2.5} and TSP were 48.51 and 63.08 μg m⁻³, respectively, which approximately equal to 15.88 and 21.67 μg m⁻³, the total sulfur in PM_{2.5} and TSP, respectively, as shown in Table 3c. If calculating S content in SO₄²⁻ only (S/SO₄²⁻ = 1/3), the ratio of the S in the water soluble sulfur, i.e. S in SO₄²⁻, to the total sulfur in the aerosol (Sw/St) were 1.00 and 0.97 in PM_{2.5} and TSP, respectively, as shown in Table 3c. These results clearly demonstrated that the sulfur in PM_{2.5} and TSP aerosol over Urumqi was mostly (97–100%) in the form of sulfate. Such high sulfate concentration would evidently relate to the formation of the heavy haze. Table 4 shows that S abundance in the different sites in south Junggur Basin (K1, K2, K3) and in the salt lake areas (salt lake 1, 2) was in the range of 3.3–56.5 times higher than the average crust, and the sulfur was also mostly in the form of sulfate, as the ratios of the S in SO₄²⁻ to the total sulfur in the soil samples collected from the different places were in the range of 0.7–1.01. South Junggur Basin areas are those modern agriculture farms, where chemical fertilizer was used widely and the surface soil from these field contained high concentration of SO₄²⁻. The surface soil from the areas of salt lakes, where are those early dried lakes, contained also high concentration of sulfate. As mentioned above, the surface soil from these two areas would be suspended and transported to the city area of Urumqi, as the locations was on the pathway of the dust transport. These results indicated obviously that the outside transported soil dust with high concentration of SO₄²⁻ from the Junggur Basin and salt lake areas would contribute to the high sulfate concentration in the aerosol over Urumqi. In addition, the high concentration of SO₄²⁻ in the road dust of Urumqi street would also contribute too, as these surface soil also contained as high as 7.8–40.3 times of sulfate of the crustal abundance (see Table 4). However, the EF of S in PM_{2.5} and TSP was as high as 2553 and 541, respectively, which were much higher than the contribution from both outside

transported soil and inside re-suspended road dust. Therefore, the gas-to-particle conversion of SO₂ to the sulfate was the other major contribution to the sulfate in the aerosol over Urumqi. Thus, the mixing of outside transported soil dust with the anthropogenic aerosol was the mechanism of the formation and the sources of the high concentration of sulfate in the aerosol over Urumqi, which would likely result in the heavy haze over Urumqi.

3.4.3. Ion composition of the aerosol over Urumqi

3.4.3.1. Ion concentration in the aerosols. The water soluble ions, including 10 anions, SO₄²⁻, NO₃⁻, Cl⁻, CH₂(COO)₂²⁻, F⁻, NO₂⁻, PO₄³⁻, MSA, C₂O₄²⁻, and five cations, NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺ were detected for all of those samples collected over Urumqi (see Table 3b). The average concentrations of the total water soluble ions were 93.79 and 135.77 μg m⁻³, which contributed 50.9% and 41.5% to the total PM_{2.5} and TSP mass, respectively. The concentrations of anions were in the order of SO₄²⁻ > NO₃⁻ > Cl⁻ > CH₂(COO)₂²⁻ > F⁻ > NO₂⁻ > PO₄³⁻ > MSA > C₂O₄²⁻ > HCOO⁻ in PM_{2.5}; SO₄²⁻ > NO₃⁻ > Cl⁻ > CH₂(COO)₂²⁻ > F⁻ > MSA > NO₂⁻ > PO₄³⁻ > C₂O₄²⁻ > HCOO⁻ in TSP; the concentration of cations were in the order of NH₄⁺ > Na⁺ > K⁺ > Ca²⁺ > Mg²⁺ in PM_{2.5}; NH₄⁺ > Ca²⁺ > Na⁺ > K⁺ > Mg²⁺ in TSP. The total ion concentrations contributed to 51% and 41% to the total mass of PM_{2.5} and TSP, respectively. The major ions, SO₄²⁻, NO₃⁻, Cl⁻, CH₂(COO)₂²⁻, contributed 25.83%, 5.03%, 3.97%, 0.47%, and 19.27%, 3.75%, 2.95%, 0.59% to the total mass of PM_{2.5} and TSP. The major cations were NH₄⁺, Na⁺, Ca²⁺ ions contributed 12.71%, 1.21%, 1.06%, and 8.99%, 1.14%, 3.08% to the total PM_{2.5} and TSP, respectively. It must be noted that the organic acid, CH₂(COO)₂²⁻, was detected with quite high concentrations of 0.88 and 1.93 μg m⁻³ in PM_{2.5} and TSP, respectively, which suggested that the organic acid would be the important part of the aerosols over Urumqi.

3.4.3.2. The ion balance and carbonate ion. The average concentrations of the total water soluble ions were 93.79 and 135.77 μg m⁻³, which contributed 50.9% and 41.5% to the total PM_{2.5} and TSP mass, respectively. The ion balance expressed by the sum of the equivalent concentrations ratio of the total cations to the total anions (C/A). If all of those cations and anions in the aerosol were measured completely, the ratio of C/A should be equal to 1.

However, in this study carbonate and bicarbonate were not measured due to the limitation of the ion chromatography that was unable to measure them. For the whole data set of the samples collected in Urumqi, the total equivalents of anions was plotted against the total equivalents of cations, and the slope of the regression line was found to be 1.40, which might be attributed to the presence of HCO_3^- or CO_3^{2-} in those samples. A very 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 (Fig. 7). This result revealed that the excess ammonium could be neutralized by carbonate/bicarbonate after it was neutralized by SO_4^{2-} , Cl^- , NO_3^- , $\text{CH}_2(\text{COO})_2^{2-}$. The slope of the regression line was 1.06, and it 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 . The ammonium salts would include $(\text{NH}_4)_2\text{CO}_3$, besides $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , NH_4NO_3 , and $\text{CH}_2(\text{COO})_2(\text{NH}_4)_2$. The equivalent of CO_3^{2-} could be assumed to be equal to the difference of the total equivalents of cations minus the total equivalents of anions, which is listed in Table 3b. 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 be accordingly to be $26.36 \mu\text{g m}^{-3}$. As carbonate are included in the mineral aerosol, the existence of the high concentration of CO_3^{2-} in the aerosol over Urumqi also revealed that the re-suspended road dust or/and the transported mineral aerosol from outside the city could be the major sources besides the local anthropogenic source of the aerosols over Urumqi.

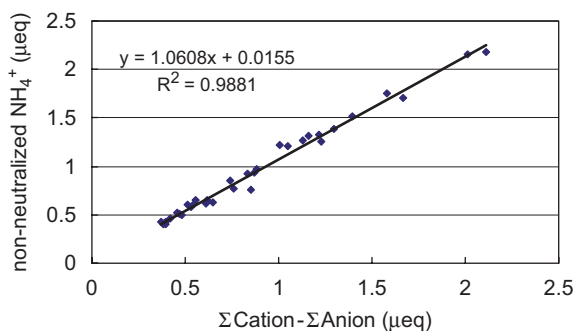


Fig. 7. Plot of the difference of total cations and anions (μeq) vs. non-neutralized NH_4^+ . Non-neutralized NH_4^+ (μeq) = $[\text{NH}_4^+]$ (μeq) - $[\text{neutralized NH}_4^+]$ (μeq).

3.4.3.3. *The speciation of the major ions.* The chemical speciation of those major ions, i.e., SO_4^{2-} , CO_3^{2-} , NO_3^- , Cl^- , NH_4^+ , $\text{CH}_2(\text{COO})_2^{2-}$, in aerosol were identified by bivariate correlation. The correlation coefficient of NH_4^+ and SO_4^{2-} in $\text{PM}_{2.5}$ and TSP was 0.92 and 0.96, respectively, indicating that NH_4^+ closely correlated with SO_4^{2-} . The slope of the regression between NH_4^+ and SO_4^{2-} (μeq vs. μeq) for the whole data set was 2.08 and 2.02 in $\text{PM}_{2.5}$ and TSP, respectively, indicating that SO_4^{2-} was completely neutralized by NH_4^+ and the species formed by SO_4^{2-} and NH_4^+ was $(\text{NH}_4)_2\text{SO}_4$, 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 the major species in both $\text{PM}_{2.5}$ and TSP. It must be noted that in aerosol of Urumqi ammonium salts in equivalents were higher than the sum of SO_4^{2-} , NO_3^- , and Cl^- . Also, in the aerosols of Urumqi, ammonium salts were also much higher than that in any other cities in China. For example, in Beijing and Shanghai the average concentrations of NH_4^+ were only 8.72 and $5.68 \mu\text{g m}^{-3}$ in $\text{PM}_{2.5}$ (Wang et al., 2005, 2006), while in Urumqi it was $23.86 \mu\text{g m}^{-3}$, $\sim 3\text{--}4$ times of Beijing and Shanghai. The NH_4^+ in the aerosols of Urumqi was neutralized by sulfate, nitrate, carbonate, and chloride. Thus, the ammonium salts was most abundant among all of the salts, which might be the main factor to contribute to the formation of the heavy haze over Urumqi.

3.4.3.4. *The acidity of aerosol.* The pH of the aerosol filtrate by the deionized water was used as a parameter to denote the acidity of the aerosol directly. In $\text{PM}_{2.5}$ and TSP over Urumqi the pH were 4.33 and 5.80 in average, which was much lower than that in the coastal city, Shanghai (5.68 and 6.38 for $\text{PM}_{2.5}$ and TSP) (Wang et al., 2006). The low pH value of aerosol were from the acidic ions, such as SO_4^{2-} , NO_3^- , Cl^- , and those organic acids, whereas the basic ions, such as NH_4^+ , Ca^{2+} , and Mg^{2+} , resulted in the increase of the pH values. Urumqi is the city close to the desert area, and it would get much more dust from those desert areas, which contained more basic matter, such as Ca^{2+} , and Mg^{2+} . However, the pH of the aerosol in Urumqi was lower than the coastal city Shanghai. This result should attribute to that there were much high secondary aerosols, mainly sulfate and nitrate, in the aerosols in Urumqi. The high concentrations of sulfate of 48.51 and $63.08 \mu\text{g m}^{-3}$ contributed to 25.8%, 19.3% in $\text{PM}_{2.5}$ and TSP, respectively, which resulted the low pH in the aerosol of Urumqi.

3.5. The effect of meteorological factors

The relationships of TSP/PM_{2.5} concentrations and visibility with wind speed and relative humidity in February–March 2007 are shown in Fig. 8. The TSP/PM_{2.5} concentrations and visibility were positively related to wind speed and negatively related to relative humidity. Among the four seasons, the wind speeds in the winter were the lowest. These results indicate that low wind speed was one of the main factors causing Urumqi’s heavy haze, especially in the winter. The frequency of different wind direction over the year in Urumqi (see Fig. 9) illustrates that during most of the year, especially in the winter, the wind comes from the north. Since Jungger Basin is located just north of Urumqi, these results further confirm that the wind from the north would bring surface soil to urban Urumqi from south of Jungger Basin, where the great modern agriculture farms are located.

4. Conclusion

1. Urumqi city was the severest polluted city over the world. The average PM_{2.5} and PM₁₀ concentrations in the winter of 2007 were 187 and 385 μg m⁻³ with maximum of 487 and 1313 μg m⁻³, respectively, 12 times higher than USA standard for PM_{2.5} and 3 times the National Ambient Air Quality Standard of China for TSP.
2. The city’s industrial emissions of sulfur dioxide were converted to sulfate in the air, and the sulfate-rich soil dust was transported to Urumqi’s air from agricultural fields south of Jungger Basin and surrounding salt lake areas.
3. The mixing of the local anthropogenic aerosol with the transported soil dust from outside the city was the main sources of the high concentration of sulfate, one of the main factors causing the heavy air pollution in the aerosols over Urumqi.

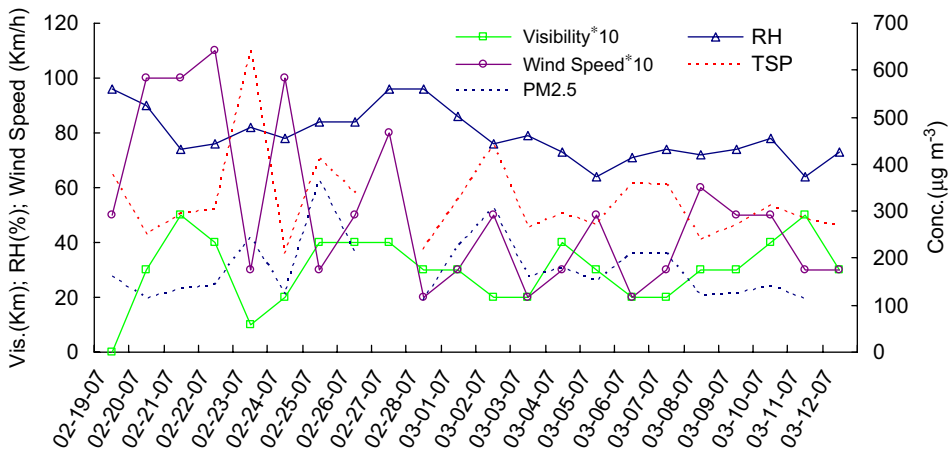


Fig. 8. Relationships of TSP/PM_{2.5} concentrations and visibility with wind speed and relative humidity.

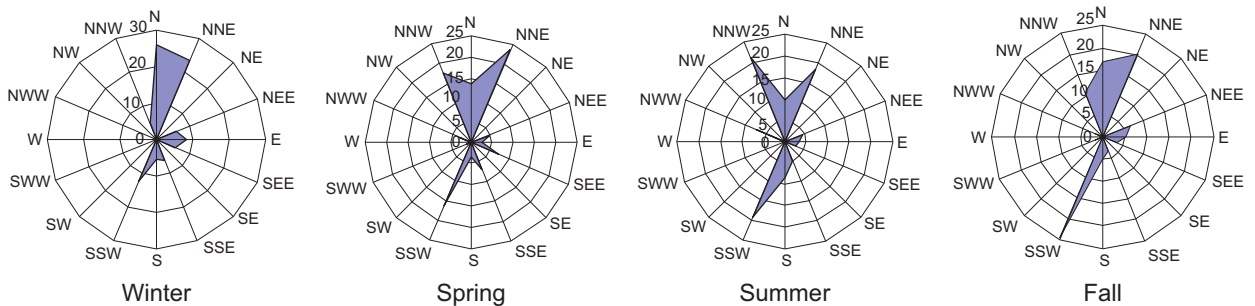


Fig. 9. Frequency of different wind direction over the year in Urumqi.

4. The high concentration of ammonium and sulfate salts in the aerosol from both inside and outside city and the low wind speed might be the main factors to form the heavy haze over the Urumqi.

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