**Atmospheric
Chemistry
and Physics**

Chemical characterization of aerosols at the summit of Mountain Tai in Central East China

C. Deng[1], G. Zhuang[1], K. Huang[1], J. Li[1], R. Zhang[1], Q. Wang[1], T. Liu[1], Y. Sun[2], Z. Guo[1], J. S. Fu[3], and Z. Wang[2]

[1]The Center for Atmospheric Chemistry Study, Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China
[2]The Institute of Atmospheric Physics, Chinese Academy of Science, LAPC, Beijing 100029, China
[3]Department of Civil and Environmental Engineering, The University of Tennessee, Knoxville, TN 37996, USA

Abstract. PM$_{2.5}$ and TSP samples were collected at the summit of Mountain Tai (MT) (1534 m a.s.l.) in spring 2006/2007 and summer 2006 to investigate the characteristics of aerosols over central eastern China. For comparison, aerosol samples were also collected at Tazhong, Urumqi, and Tianchi in Xinjiang in northwestern China, Duolun and Yulin in northern China, and two urban sites in the megacities, Beijing and Shanghai, in 2007. Daily mass concentrations of TSP and PM$_{2.5}$ ranged from 39.6–287.6 μg m^{-3} and 17.2–235.7 μg m^{-3} respectively at the summit of MT. Averaged concentrations of PM$_{2.5}$ showed a pronounced seasonal variation with higher concentration in summer than spring. 17 water-soluble ions (SO$_4^{2-}$, NO$_3^-$, Cl$^-$, F$^-$, PO$_4^{3-}$, NO$_2^-$, CH$_3$COO$^-$, CH$_2$C$_2$O$_2^{2-}$, C$_2$H$_4$C$_2$O$_4^{2-}$, HCOO$^-$, MSA, C$_2$O$_4^{2-}$, NH$_4^+$, Ca^{2+}, K$^+$, Mg^{2+}, Na$^+$), and 19 elements of all samples were measured. SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ were the major water-soluble species in PM$_{2.5}$, accounting for 61.50 % and 72.65 % of the total measured ions in spring and summer, respectively. The average ratio of PM$_{2.5}$/TSP was 0.37(2006) and 0.49(2007) in spring, while up to 0.91 in summer, suggesting that aerosol particles were primarily comprised of fine particles in summer and of considerable coarse particles in spring. Crustal elements (e.g., Ca, Mg, Al, Fe, etc.) showed higher concentration in spring than summer, while most of the pollution species (SO$_4^{2-}$, NO$_3^-$, K$^+$, NO$_2^-$, NH$_4^+$, Cl$^-$, organic acids, Pb, Zn, Cd, and Cr) from local/regional anthropogenic emissions or secondary formation presented higher concentration in summer. The ratio of Ca/Al suggested the impact of Asian dust from the western deserts on the air quality in this region.

The high concentration of K$^+$ in PM$_{2.5}$ (4.41 μg m^{-3}) and its good correlation with black carbon ($r = 0.90$) and oxalic acid ($r = 0.87$) suggested the severe pollution from biomass burning, which was proved to be a main source of fine particles over central eastern China in summer. The contribution of biomass burning to the fine particle at MT accounted for 7.56 % in spring and 36.71 % in summer, and even reached to 81.58 % on a day. As and Pb were two of the most enriched elements. The long-range transport of aerosols spread the heavy pollution from coal-mining/coal-ash to everywhere over China. Anthropogenic air-pollution was evidently rather severe at MT, though it has been declared by UNESCO to be a World Heritage site.

1 Introduction

Aerosols have potential impact on the global atmospheric chemistry, cloud properties and precipitation development (Tegen et al., 1996; Arimoto, 2001; Rastogi and Sarin, 2005, 2006). Anthropogenic aerosols, including the primarily emissions and the secondary aerosols, are mainly in fine mode, which has much more adverse impact on climate and hydrologic cycling (Kaufman et al., 2002), visibility (Chan et al., 1999), and human health (Dockery et al., 1993).

Eastern China, including provinces of Hebei, Shandong, Jiangsu, Zhejiang, and the mega-city, Shanghai, is the area with rapidest growth in economy, e.g. Shandong is one of the two provinces in China, whose GDP exceeded 3×10^{11} RMB in 2008 (http://finance.people.com.cn/), which resulted in the increasing emissions of SO$_2$, NO$_2$, and particulate matter, and, in turn, the severe acidic precipitation (Wang et al., 2008). Mountain Tai (200×50 square kilometers), with the highest altitude (1534 m high) in central-eastern China,

Correspondence to: G. Zhuang
(gzhuang@fudan.edu.cn)

is located in Shandong and surrounded by Jiangsu, Anhui, Henan, and Hebei provinces. Aerosols, from the summit of MT could be the representative of the regional pollution. Previous study found that CO and O_3 at the top of MT exhibited high in summer and low in winter, which was attributed to the seasonal changes of meteorological conditions and seasonal variations of sources (Gao et al., 2005; Wang et al., 2001). In addition, VOCs, O_3, and CO were all higher than those observed at other rural mountainous sites (Suthawaree, et al., 2010), which might be due to the strong sources surrounded. Average concentration of peroxides at MT was much lower than that measured at some rural mountain sites, suggesting that significant removal processes took place in this region (Ren et al., 2009). O_3 and CO play key roles in determining the oxidizing capacity of the atmosphere in the presence of sunlight, and they are ideal tracers for anthropogenic pollutions (Novelli et al., 1994, 1998). VOC, O_3, CO, and peroxide are all related to the formations of secondary aerosols in ambient air, which suggested that the characteristics of the aerosols at MT might be different from those at other sites.

Mineral aerosols through long-range transport may directly or/and indirectly affect the properties of air mass by providing surfaces for many chemical and physical processes and serving as carriers of anthropogenic substances, which would affect the global climate/environmental change (Guo et al., 2004; Dentener et al., 1996; Sun et al., 2004; Liu et al., 2002). Northwestern China is one of the main source areas of Asian dust that can be transported to hundred and thousand miles away, passing through central and eastern China and even to the Pacific. The composition of mineral aerosols would subject to transform due to adsorbing gaseous species, surface reactions, and coagulation with anthropogenic aerosol on the pathway during transport.

Little information on aerosols at the summit of MT is available. The studies on aerosols reported in literatures mostly represented those samples collected from ground level, and limited knowledge has been acquired on the aerosols at high elevation over the world. MT is just in the downstream of Asian Dust from northwestern China. Therefore, the summit of MT is an ideal site to examine the long-range transport of Asian dust and to observe the mixing of dust with anthropogenic aerosol. This paper presents the characteristics, sources, formation processes, and the relation with the long-range transport of aerosols collected at MT, which would reveal the air quality in PBL (Planetary Boundary Layer) over central east China.

2 Experimental

2.1 Sampling

TSP and $PM_{2.5}$ aerosol samples were simultaneously collected at the meteorological observation station located at the summit of MT (36.25° N, 117.10° E) in spring (14 March–
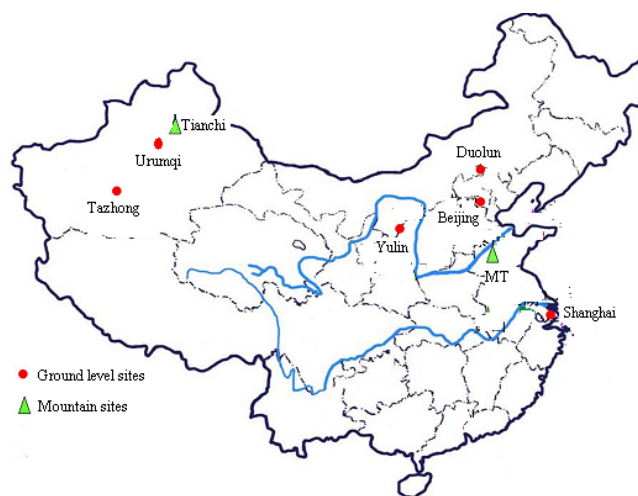

Fig. 1. Map of the sampling sites in this study.

6 May) and summer (2–30 June) in 2006 and in spring (26 March–18 May) in 2007. The sampling duration of each sample was generally 24 h, except a few samples, which was 48 h. All of the samples were 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 samples were put in polyethylene plastic bags right after sampling and reserved in a refrigerator. All of these 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 humidity (40 ± 1.5 %) for over 24 h. All the procedures were strictly quality-controlled to avoid any possible contamination of the samples. For comparison, aerosol samples were also collected at Tazhong, Urumqi, Tianchi in Xinjiang in northwestern China, Duolun and Yulin in northern China, and in two urban sites in the megacities, Beijing and Shanghai (Fig. 1). Information of all samples is list in Table 1. The detailed analytical procedures were given elsewhere (Zhuang et al., 2001).

2.2 Chemical analysis

2.2.1 Ion analysis

One-fourth of each sample and blank filter was extracted ultrasonically by 10 mL deionized water (18 MΩcm^{-1}). After passing through microporous membranes (pore size, 0.45 μm; diameter, 25 mm; made by the affiliated plant of Beijing chemical school), the filtrates were determined for pH with a pH meter (model, Orion 818). Each filtrate was stored at 4 °C in a clean tube for IC analysis. 12 anions (SO_4^{2-}, NO_3^-, Cl^-, F^-, PO_4^{3-}, NO_2^-, CH_3COO^-, $HCOO^-$, MSA, $C_2O_4^{2-}$, $CH_2C_2O_4^{2-}$, $C_2H_4C_2O_4^{2-}$) and 5 cations (NH_4^+, Ca^{2+}, K^+, Mg^{2+}, Na^+) were analyzed by

Table 1. Mass concentrations of aerosols ($\mu g\, m^{-3}$) at the summit of MT and other sampling sites.

Sampling site	Sampling period	Sample number		Average ($\mu g\, m^{-3}$)		Max. ($\mu g\, m^{-3}$)		Min. ($\mu g\, m^{-3}$)	
		$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP
Tazhong	20 Mar 2007–19 Apr 2007	36	35	640.4	1225.2	2295.3	5407.4	45.3	53.3
Tianchi	2 Apr 2007–2 May 2007	31	31	24	57.7	117.7	191	5.3	7.3
Duolun	20 Mar 2007–20 Apr 2007	34	34	64.1	176.2	590.5	1381.7	4.3	16.7
Yulin	20 Mar 2007–21 Apr 2007	31	38	83	354.4	592.1	3187	7.1	25
Beijing	21 Mar 2007–20 Apr 2007	31	31	77.1	160.9	141	351.9	20.8	60.7
	23 Jul 2007–22 Aug 2007	31	31	78.4	114.5	129.8	261.2	10.5	78.4
Urumqi	19 Mar 2007–19 Apr 2007	37	37	81.9	232.5	158.9	523.8	27.7	54.5
	20 Jul 2007–22 Aug 2007	34	34	45.9	172.6	111.1	303.1	18.8	86.1
Shanghai	28 Mar 2006–30 Apr 2007	32	30	32	108	73.3	213.7	7.8	44.5
	1 Aug 2006–26 Aug 2007	26	26	20	61.2	47.5	131.6	12.4	21.8
	20 Mar 2007–21 Apr 2007	32	32	25.3	80.7	115.4	913.9	8.4	17.4
	23 Jul 2007–19 Aug 2007	28	28	30.5	91	105.1	147.7	3.8	7.7
MT	14 Mar 2006–6 May 2006	16	15	46.6	128.1	116.8	287.6	17.2	59.1
	2 Jun 2006–30 Jun 2006	27	21	123.1	135.0	235.7	276.9	48	49.2
	26 Mar 2007–18 May 2007	31	18	70.1	143.8	167.4	230.4	18	39.6

Ion Chromatography (Model: Dionex 3000), which consists of a separation column (Dionex Ionpac AS11 for anion and CS12A for cation), a guard column (Dionex Ionpac AG 11 for anion and AG12A for cation), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50), and a gradient pump (Dionex Ionpac GP50). The gradient mobile phase generated by EG-3000 was used for anion detection, while the weak acid eluent (20 mM MSA) for cation detection. The recovery of each ion was in the range of 80–120 %. The relative standard deviation of each ion was less than 5 % for reproducibility test. The limits of detection (S/N = 3) were less than $0.04\, mg\, L^{-1}$ for anions and $0.006\, mg\, L^{-1}$ for cations. The quality assurance was routinely carried out by using Standard Reference Materials (GBW 08606) produced by National Research Center for Certified Reference Materials, China. Blank values were subtracted from sample determinations. The details were given elsewhere (Yuan et al., 2003).

2.2.2 Element analysis

Half of each sample filter 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 added 0.1 mL concentrated HNO_3, and diluted to 10 mL with deionized water (resistivity of $18\, M\Omega cm^{-1}$). Total 19 elements (Al, Fe, Mn, Mg, Ti, Na, Sr, Ca, Co, Cr, Ni, Cu, Pb, Zn, Cd, V, S, As and P) were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, model: ULTIMA, made by JOBIN-YVON Company, France). All the reagents used were of the highest grade. All the preparation was carried out in a Class-100 clean bench. The recovery rates were measured with standard addition,

and the recoveries of each element were in the range of 95 % to 105 %. The relative standard deviations of each element were less than 2 % for reproducibility test. The geochemistry reference matter (TBW07401) made by the Center for National Standard Matter was also analyzed simultaneously to check the reliability of analysis (Han et al., 2005). The detection limits (3 s) for typical elements of Al, As, Ca, Cd, Co, Fe, Pb, Cu, and Zn were 1.5, 5, 0.03, 0.35, 0.6, 0.5, 5, 0.6, and $0.3\, \mu g\, L^{-1}$, respectively. Black carbon (BC) was analyzed with Smokerstain Reflectometer (UK, Model, M43D). The detailed analytical procedures were given elsewhere (Zhuang et al., 2001).

2.3 Meteorological data, fire spot map and trace gases

The meteorological data, including temperature, relative humidity (RH), dew point, wind speed, wind direction, atmospheric pressure, visibility etc., were collected from http://www.wunderground; Data of SO_2, NO_2 in Shanghai and MT were collected from http://www.envir.gov.cn and http://www.tahb.gov.cn; Fire spot data were got from MODIS Global Fire Mapping Service (http://firefly.geog.umd.edu/firemap/); O_3 and CO were detected with a commercial UV photometric analyzer (Thermo Environment Instruments Inc., Model 49) that had a detection limit of 2 ppbv and a 2-sigma (2-s) precision of 2 ppbv for a 2- min average. CO was measured with a gas filter correlation, a non-dispersive infrared analyzer (Advanced Pollution Instrumentation Inc., Model 300) with a heated catalytic scrubber for baseline determination, which was conducted every 2h. The detection limit was 30 ppbv for a 2-min average, with a 2-s precision of about 1 % for a level of 500 ppbv (2-min average). The overall uncertainty was estimated to be 10 %.

Table 2. Mass concentrations ($\mu g \, m^{-3}$) and size distributions of aerosols at the summit of MT and other sampling sites.

Sites	time	Spring			Summer		
		$PM_{2.5}$	TSP	$PM_{2.5}$/TSP	$PM_{2.5}$	TSP	$PM_{2.5}$/TSP
Shanghai	2003–2005[a]	135.0	293.0	0.46	72.0	167.0	0.43
	2006	32.0	108.0	0.30	20.0	61.2	0.33
	2007	25.3	80.7	0.31	30.5	91.0	0.34
MT	2006	46.6	128.1	0.37	123.1	135.0	0.91
	2007	70.1	143.8	0.49			
Urumqi	2007	81.9	232.5	0.35	45.9	172.6	0.27
Beijing	2002[b]	212.6	1410.1	0.15	79.6	224.6	0.35
	2007	77.1	160.9	0.48	78.4	114.5	0.68
Duolun	2007	64.1	176.2	0.36			
Tianchi	2007	24.0	57.7	0.42			
Yulin	2007	83.0	354.4	0.23			

[a] Wang et al. (2006b); [b] Wang et al. (2006a).

Table 3. Meteorological conditions and concentrations of gases (O_3, CO, Peroxide) in ambient air at MT.

Month	Temp. (°C)	Dew Temp. (°C)	Humidity (%)	Visibility (km)	Windy Speed (mph)	Concentrations (ppbv)		
						O_3	CO	Peroxide
March	2	−10	36	10	20	56	358	0.17
April	7	2	49	10	22	61	425	
June	17	10	60	9.0	16	71	516	0.55

Measurement method of peroxide: A 26-turn coil was used to strip the peroxides out of the air and into a liquid phase by water ($0.42 \, mL \, min^{-1}$), which was sucked through a 10-turn coil ($0.42 \, mL \, min^{-1}$) at which buffer (potassium hydrogen phthalate (KHP, Fisher Scientific) and tetrasodium ethylenediaminetetraacetate (Na4EDTA, Fluka Scientific)) and fluorescence (POPHA (Fluka Scientific), horseradish peroxidase (Sigma Chemical Co.), KHP, and Na4EDTA) solutions were added, then the liquid entered a pH booster cell that contained 30 % ammonium hydroxide (Sigma Chemical Co.) to adjust solution pH from 6 to approximately 10. After going through a debubbler ($0.42 \, mL \, min^{-1}$), where the bubbles were removed, the fluorescence of the dimmer was detected using a fluorimeter (Spectrovision FD-100, Groton Technology Inc., Concord, MA) with excitation and emission wavelength of 326 nm and 400 nm, respectively.

3 Results and discussion

3.1 Overview of particle matters at summit of MT

3.1.1 Mass concentrations of PM and size distribution

Temporal variations of mass concentrations and the corresponding deviations of $PM_{2.5}$ and TSP at MT and other sampling sites are summarized in Fig. 2 and Tables 1–2. TSP were relatively seasonal stable ($128.1 \, \mu g \, m^{-3}$/$143.8 \, \mu g \, m^{-3}$ in spring 2006/2007 and $135.0 \, \mu g \, m^{-3}$ in summer 2006), while $PM_{2.5}$ had highly seasonal variation with much higher concentration in summer 2006 ($123.1 \, \mu g \, m^{-3}$) than in spring 2006/2007 ($46.6 \, \mu g \, m^{-3}$/$70.1 \, \mu g \, m^{-3}$) at MT. $PM_{2.5}$ was relatively higher in spring 2007 (26 March–18 May) compared to that in spring 2006 (14 March–6 May), which was likely attributed to the different sampling periods and it will be interpreted in Sect. 3.2.1. TSP from MT was comparable with those from other sampling sites in ground level, and there

was no obvious decrease at a height of 1534 m compared to those at ground level, as expected. Both TSP and $PM_{2.5}$ at MT were much higher than those at Tianchi that is also located at a high land (1900 m). Aerosol pollutions at MT were as severe as or even worse than those at ground level, e.g. $PM_{2.5}$ at MT were much higher than those at other sites, including the sites in megacities, Beijing and Shanghai, at ground level in summer. The average ratio of $PM_{2.5}$/TSP was 0.37 in spring and 0.91 in summer in 2006, indicating that fine particles dominated in summer while coarse particles in spring. The seasonal variation of fine particles should be firstly attributed to the seasonally different meteorology at MT (Table 3), which showed typical seasonal variations with higher temperature, lower windy speed, lower atmospheric pressure and more solar radiation in summer than those in spring. The meteorology at MT could strengthen the vertical convection of the air, and the regional anthropogenic pollutants on the ground surface could easily transport upward, resulting in the increase of the height of PBL, that
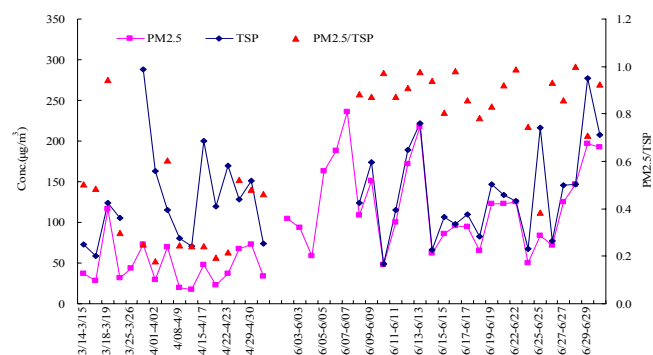
Fig. 2. Daily variations of TSP and PM$_{2.5}$ from 14 March to 30 June in 2006 at MT.

was even higher than the summit of MT. On the contrary, the height of the PBL in spring was so compressed that it used to be below the summit of MT, and the Mountain-valley breezes could not fully develop due to the weak solar radiation and the strong regional winds in ground level. Hence, the transport upward of the regional pollutants to the summit was less frequent in spring than in summer, which resulted in lower concentrations of fine particles in spring. Besides, dust storms mostly occur in spring and MT is located on the very pathway of its long-range transport from central Asia to the northern America (Arimoto et al., 1996; Zhang et al., 1997; Sun et al., 2010). Thus, in those days with high wind speed in spring, higher ratio of those coarse particles to the total aerosol mass was often observed even at elevation of more than 1500 m.

3.1.2 Ionic and elemental composition of the particles at MT

Mass concentrations of ions in PM$_{2.5}$ and TSP at MT are listed in Table 4. Water soluble ions contributed 10.82 % of TSP and 23.99 % of PM$_{2.5}$ in mass in spring, while 40.89 % and 41.08 % in summer. This result revealed evidently that the secondary aerosol possessed much larger part in summer than in spring. The ratios of total ions to the total mass in PM$_{2.5}$ were higher than those in TSP both in summer and spring, suggesting that the pollution components, such as SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, existed more in fine mode. These three major water soluble ions accounted for 61.50 % in spring and 72.65 % in summer of the total ions measured in PM$_{2.5}$, while 69.20 % and 71.47 % in TSP, respectively (Table 5). Also, higher concentration of K$^+$, the tracer of the biomass source, in summer was observed, which could account for 8.26 % of total ions in TSP. Whereas, higher concentration of Ca^{2+}, likely more from the Asian dust source, in spring, accounted for 21.93 % of the total ions in TSP.

Water-soluble ions are proved to play key roles in many atmospheric processes, such as cloud formation, visibility degradation, solar radiation, acidification of cloud, rain, and

Table 4. Water-soluble ions in PM$_{2.5}$ and TSP and the corresponding ratios of summer/spring at MT.

| | Concentration(μg m^{-3}) | | | | Ratio | |
| | Spring | | Summer | | (Summer/Spring) | |
	TSP	PM$_{2.5}$	TSP	PM$_{2.5}$	TSP	PM$_{2.5}$
NH$_4^+$	1.48	0.88	10.40	9.56	7.03	10.86
Na$^+$	0.68	0.56	1.36	1.28	2.00	2.29
K$^+$	0.72	0.48	4.56	4.41	6.33	9.19
Mg^{2+}	0.24	0.16	0.24	0.16	1.00	1.00
Ca^{2+}	3.04	1.72	2.88	1.76	0.95	1.02
F$^-$	0.13	0.11	0.02	0.03	0.15	0.27
Cl$^-$	0.83	0.65	2.18	2.30	2.63	3.54
MSA	0.02	0.01	0.22	0.54	11.00	54.00
HCOO$^-$	0.12	0.06	0.12	0.16	1.00	2.67
CH$_3$COO$^-$	0.27	0.23	1.83	1.32	6.78	5.74
C$_2$O$_4^{2-}$	0.15	0.10	0.37	0.48	2.47	4.80
CH$_2$C$_2$O$_4^{2-}$	0.42	0.22	0.65	0.49	1.55	2.23
C$_2$H$_4$C$_2$O$_4^{2-}$	0.02	0.01	0.04	0.10	2.00	10.00
NO$_3^-$	3.61	3.24	8.82	8.21	2.44	2.53
SO$_4^{2-}$	4.47	2.72	20.73	20.26	4.64	7.45
NO$_2^-$	0.03	0.03	0.12	0.14	4.00	4.67
PO$_4^{3-}$	0.01	n.a	0.01	0.02	1.00	
Total ions (C$_{IC}$)	13.86	11.18	54.47	51.53	3.93	4.61
Total mass (C$_P$)	128.1	46.6	135	123.1	1.05	2.64
C$_{IC}$/C$_P$ (%)	10.82	23.99	40.35	41.86	3.73	1.74
Ca^{2+}/Total ions	21.93	15.38	5.29	3.42		
K$^+$/Total ions	5.19	4.29	8.37	8.56		

C$_{IC}$: Total mass concentrations of water- soluble ions (μg m^{-3}).
C$_P$: Mass concentrations of TSP or PM$_{2.5}$ (μg m^{-3}).

fog, and haze formation because of their affinity with water (Tsai et al., 1999; Novakov et al., 1993; Matsumoto et al., 1997; Facchini et al., 2000). Haze mostly occurred in stable, warm, and moist air, and was characterized by the high level of fine particles with high percentage of certain water soluble ions, such as SO$_4^{2-}$, NH$_4^+$, and NO$_3^-$, in the aerosols. Certain characteristics of the aerosols collected at MT in summer and spring and at Beijing in dust, haze, and clear days are summarized in Table 5. C$_{IC}$/C$_P$, C$_{(S+N+A)}$/C$_{IC}$, SOR and NOR at MT in summer were very similar to those in haze days in Beijing, suggesting that haze could occur frequently in summer at the summit of MT, which could be proved by the lower visibility (9.0 km) on average at MT.

The concentrations of nineteen elements and black carbon (BC) in aerosols at MT are listed in Table 6, which showed clearly that crustal element (Ca, Ma, Al, Mn, Ti, Sr, and Na) were higher in spring, while pollution elements (Pb, Cr, Cd, Zn, Ni, S, BC), except As and Cu, were higher in summer. The elements could be classified into four groups according to their enrichment factors (EFs = (X/Al)$_{aerosol}$/(X/Al)$_{crust}$): high enriched pollution elements (Pb and As), medium enriched (S and Zn), slightly enriched (Ni, Cu and Cr), and non-enriched crustal metals (Ca, Ma, Al, Mn, Ti, Sr and Na). EFs of all crustal elements (see Fig. 3) were higher in TSP

Table 5. SOR, NOR of ambient air and main water-soluble ions in $PM_{2.5}$ and TSP at MT and Beijing.

		MT		Beijing*		
		Spring	Summer	Haze days	Dust days	Clear days
$PM_{2.5}$/TSP	0.37	0.91	0.39	0.21	0.31	
C_{IC}/C_P (%)	$PM_{2.5}$	23.99	41.08	53.20	9.30	15.20
	TSP	10.82	40.89	33.30	3.30	32.2
$C_{(S+N+A)}/C_{IC}$(%)	$PM_{2.5}$	61.50	72.65	87.10	63.70	73.00
	TSP	69.20	71.47	79.90	45.70	66.10
SOR	$PM_{2.5}$	0.08	0.31	0.27	0.29	0.15
	TSP	0.09	0.32	0.24	0.25	0.17
NOR	$PM_{2.5}$	0.09	0.22	0.22	0.09	0.13
	TSP	0.10	0.26	0.29	0.16	0.18

$C_{(S+N+A)}$: The sum of the concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ ($\mu g\,m^{-3}$).
C_{IC}: Total mass concentrations of water- soluble ions ($\mu g\,m^{-3}$).
C_P: Mass concentrations of TSP or $PM_{2.5}$ ($\mu g\,m^{-3}$).
SOR: Sulfur oxidation ratio, $SOR = nSO_4^{2-}/(nSO_4^{2-} + nSO_2)$.
NOR: Nitrogen oxidation ratio, $NOR = nNO_3^-/(nNO_3^- + nNO_2)$ (n refers to the molar concentration).
* Wang et al. (2006a).

Table 6. Concentrations ($\mu g\,m^{-3}$) of elements in $PM_{2.5}$ and TSP and the corresponding ratios of summer/spring at MT.

Elements	Concentration ($\mu g\,m^{-3}$ or $ng\,m^{-3}$)				Ratio	
	Spring		Summer		(Summer/Spring)	
	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	$PM_{2.5}$
Al	3.01	1.20	2.20	1.96	0.73	1.63
Ca	3.95	1.75	2.61	1.72	0.66	0.98
Fe	2.18	0.81	1.69	0.71	0.77	0.88
Mg	1.02	0.35	0.50	0.42	0.50	1.19
Na	0.99	0.59	1.48	1.27	1.49	2.15
Zn	0.49	0.40	0.78	0.45	1.59	1.11
S	1.49	0.90	6.96	6.73	4.52	7.48
BC*	1.49	0.42	2.36	2.06	1.58	4.90
Ti	240.00	81.40	150.00	85.30	0.62	1.05
Sr	22.60	8.71	16.60	15.90	0.60	1.83
Mn	75.30	39.10	72.40	71.90	0.96	1.84
Cu	57.00	24.00	26.20	21.80	0.46	0.91
As	5.71	2.30	4.07	3.58	0.71	1.56
Cd	1.29	1.00	3.60	3.35	2.79	3.35
Co	1.79	1.01	3.48	2.78	1.94	2.75
Cr	23.00	22.90	98.50	85.40	4.28	3.73
Ni	7.49	7.41	22.70	19.80	3.03	2.67
Pb	42.20	15.20	76.50	72.00	1.81	4.74
P	94.60	36.60	130.00	84.60	1.37	2.31
V	5.35	BDL	BDL	BDL		

BDL:Below detection limits; BC: Black carbon; * Unit after BC: $ng\,m^{-3}$.

and lower in $PM_{2.5}$, while pollution elements were higher in $PM_{2.5}$ and lower in TSP. EFs of As and Pb exhibited different seasonal variations with higher EF of Pb in summer and higher EF of As in spring.
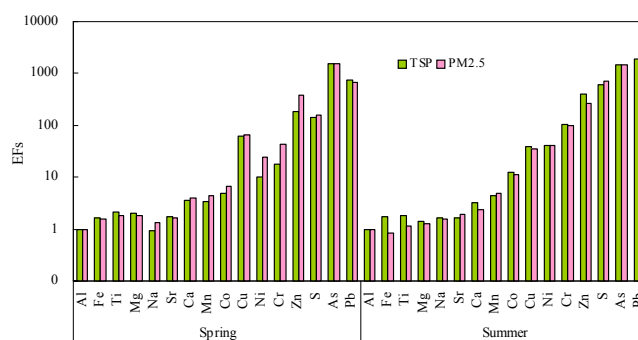

Fig. 3. Enrichment factors (EFs) of elements at MT in spring and summer, 2006.

3.1.3 Acidity of the aerosols at MT

Figure 4 shows the variations of pH of the filtrates of aerosols at MT, and it indicated that pH decreased obviously from spring to summer. The mean pH values of the aqueous filtrates of aerosols collected at MT and other sampling sites are compared in Table 7. The aerosols at MT showed higher acidity for both $PM_{2.5}$ (pH = 4.62) and TSP (pH = 4.92) in summer in comparison with the weak acidity of $PM_{2.5}$ (pH = 5.92) and slight alkalinity (pH = 7.22) of TSP in spring. The pH of aerosols at MT in summer was the lowest, while TSP in spring showed slight alkalinity, which was similar to those from Tazhong (pH = 7.39, original source of dust storm) and from Beijing in supper dust day (pH = 7.25, Wang et al., 2005). The higher acidity of aerosols at MT in summer was further supported by the fact that the pH of rain samples in summer at MT was obviously lower than those in other seasons (Wang et al., 2006c). The measured acidity of

Table 7. pH of aqueous filtrates of $PM_{2.5}$ and TSP aerosols at different sampling sites.

Sites	Spring		Summer		Reference
	$PM_{2.5}$	TSP	$PM_{2.5}$	TSP	
MT	5.92	7.22	4.62	4.92	This study
Shanghai	5.27	6.48	5.29	6.37	This study
Urumqi	5.49	6.21			This study
Tianchi	5.81	6.35			This study
Tazhong	6.61	7.39			This study
Beijing (Normal days)	6.54	6.79	5.92	6.26	Wang et al. (2005)
Beijing (Supper dust days)	7.25	7.54			Wang et al. (2005)
Beijing (Haze days)	5.33	6.27			Wang et al. (2006a)
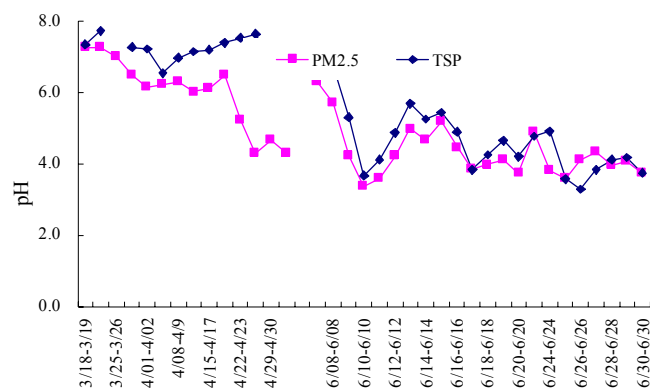
Fig. 4. Daily variations of pH of aqueous filtrates of aerosols at MT, 2006.

aerosols is determined by the presence and the proportions of the cations and anions in the filtrates of aerosols. In addition, the ratio of equivalent concentrations of total cations to total anions (C/A) should be equal to 1, if all the cations and anions in the aerosol were measured. However, CO_3^{2-} and HCO_3^- were not measured in this study due to the limitation of ion chromatography, hence, the difference of the total anions and cations could be used to roughly estimate the amount of CO_3^{2-} and HCO_3^- unmeasured (Wang et al., 2005). C/A of aerosols in spring at MT reached 1.6, while only 1.1 in summer, suggesting that much more carbonate or bicarbonate presented in the aerosols at MT in spring. The remarkable increase of SO_4^{2-}, NO_3^- and organic acids in summer shown in Table 4 indicated that in summer much more aerosols at MT was from secondary pollution, which would lead to the lower pH of the filtrates. Compared to the pH of those aerosols collected from Shanghai in summer (5.29 in $PM_{2.5}$ and 6.37 in TSP), the aerosols at MT showed even higher acidity, suggesting that the secondary air pollution at MT in summer was even severer than that in Shanghai.

3.2 Sources and formation mechanisms of aerosols at summit of MT

3.2.1 Influence of biomass burning

Biomass burning includes those from grassland, forest, and crop residue, among which more than 60 % are from crop residue burning in the world (Streets et al., 2003). With the rapid development of economy in China, crop residue is increasingly being burned openly in the field. In harvest every year $\sim 5.182 \times 10^7$ ton crop residues (accounted for 40.0 % of the total crop residues in China) were directly burnt openly, especially in central eastern China, including Shandong, Jiangsu, Henan, Hebei provinces. Shandong, where MT is located, was in number 1 among those provinces mentioned above with the largest amount of crop residues (1.798×10^7 t) to be burned openly (Cao et al., 2007). Biomass burning emissions are known to contribute a considerable amount of PM and gaseous pollutants to the air, and crop residues contribute more fine particles and gaseous than other biomaterial residues (Cao et al., 2005; Zhu et al., 2005).

Water soluble potassium is a good tracer for aerosols formed from biomass burning (Andreae, 1983). Sources of total potassium ion (K_{Total}^+) in aerosols might be attributed to soot from biomass burning, sea salt, and crustal dust. Elemental Al and Na^+ could be the good markers of crustal dust and sea salt respectively, as the composition of Na, K, and Al in sea water and in crustal dust were found to be: Na: 31 %, K:1.1 %, Al:0 %, and Na: 2.6 %, K:2.9 %, Al:7.7 %, respectively (Wedepohl, 1995), which showed that the percentage of K^+ were much lower than Na^+ in sea salt and also lower than Al in crustal dust. This means that the concentrations of Na^+ and Al in the aerosols would increase more than K^+ if the aerosols were from sea salt and crustal dust. Figure 5 showed that K^+ on certain days in summer was significant higher than Na^+ and Al with remarkable increase from the normal days, which suggested that the high concentrations of $PM_{2.5}$ in summer could likely from biomass burning rather than sea water or crustal dust. It

was reasonably assumed that the total potassium (K_{Total}^+) is the sum of dust-derived potassium (K_{Crust}^+), sea-salt-derived potassium (K_{SS}^+), and biomass burning-derived potassium (K_{BB}^+) i.e. $K_{Total}^+ = K_{Crust}^+ + K_{SS}^+ + K_{BB}^+$ (Virkkula et al., 2006), we can calculate the biomass burning potassium (K_{BB}^+) as $K_{BB}^+= K_{Total}^+ - K_{Crust}^+ - K_{SS}^+$. Assuming Na^+ in aerosol is from crust and sea salt only, i.e. $Na_{Total}^+ = Na_{Crust}^+ + Na_{SS}^+$, where Na_{Total}^+ is the concentration of Na^+ in the aerosol sample, and Al in aerosol is originated from crust only, thus, K_{Crust}^+ and K_{SS}^+ can be estimated through the ratios of K^+/Al and Na^+/Al in the aerosol sample and the ratio of K^+/Na^+ in sea salt, i.e. $K_{Crust}^+ = (K^+/Al)_{crust} \times Al_{crust}$ and $K_{SS}^+ = (Na_{Total}^+ - (Na^+/Al)_{crustl} \times Al_{crustl}) \times (K^+/Na^+)_{sea-salt}$. The ratio of K^+/Na^+ in those particles from sea salt is constant (0.037) (Chester, 1990), whereas the ratios of K^+/Al and Na^+/Al in crustal dust were different between the samples collected from different sites because of the different background and the different influence of the human activities on each site. We now have two methods to estimate the biomass burning derived potassium (K_{BB}^+): (1) Using the minimum ratios of K^+/Al of 0.152 and Na^+/Al of 0.240 in the PM$_{2.5}$ aerosol sample collected at MT on 26 April 006 among all samples collected to calculate the background value of K^+ and Na^+ in crustal dust, then the biomass burning derived potassium (K_{BB}^+) is given from $K_{BB}^+= K_{Total}^+ - K_{Crust}^+ - K_{SS}^+$, where $K_{Crust}^+ = (K^+/Al)_{Aerosol} \times Al_{Aerosol}$, $Al_{Aerosol}$ is the Al concentration measured in PM$_{2.5}$, i.e. $K_{Crust}^+ = 0.152 \times Al_{Aerosol}$, and $K_{SS}^+ = (Na_{Total}^+ - (Na^+/Al)_{Aerosol} \times Al_{Aerosol}) \times (K^+/Na^+)_{sea-salt}$, i.e. $K_{SS}^+ = (Na_{Total}^+ - 0.240 \times Al_{Aerosol}) \times 0.037$, (2) Using the ratios of K^+/Al of 0.107 and Na^+/Al of 0.031 measured in the soil samples collected at MT to calculate the background value of K^+ and Na^+ in crustal dust, then the biomass burning derived potassium (K_{BB}^+) is given from

$$K_{BB}^+= K_{Total}^+ - K_{Crust}^+ - K_{SS}^+, \text{where } K_{Crust}^+$$

$$= (K^+/Al)_{soil} \times Al_{Aerosol}, \text{i.e. } K_{Crust}^+ = 0.107 \times Al_{Aerosol}, \text{and}$$

$$K_{SS}^+ = (Na_{Total}^+ - (Na^+/Al)_{soil} \times Al_{Aerosol}) \times (K^+/Na^+)_{sea-salt},$$

$$\text{i.e. } K_{SS}^+ = (Na_{Total}^+ - 0.031 \times Al_{Aerosol}) \times 0.037,$$

The concentrations of K_{BB}^+ (biomass burning-derived K^+) calculated with two methods mentioned above in PM$_{2.5}$ collected at MT in 2006 are shown in Fig. 6. It can be seen clearly that very similar concentrations of K_{BB}^+ were acquired by the two methods. The averaged K_{BB}^+ were 0.40 and 4.30 µg m^{-3} in spring and summer, respectively, with the method of using the minimum ratios of K^+/Al and Na^+/Al in the aerosol sample to calculate the background value of K^+ and Na^+ in crustal dust, while the K_{BB}^+ were 0.32 and 4.30 µg m^{-3} with the method of using the ratios of K^+/Al and Na^+/Al in the soil samples. The high level of K_{BB}^+
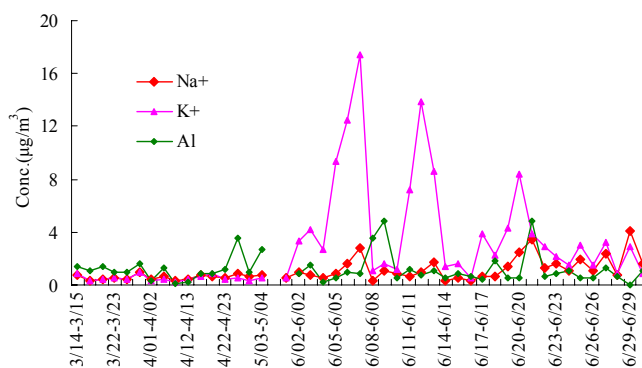
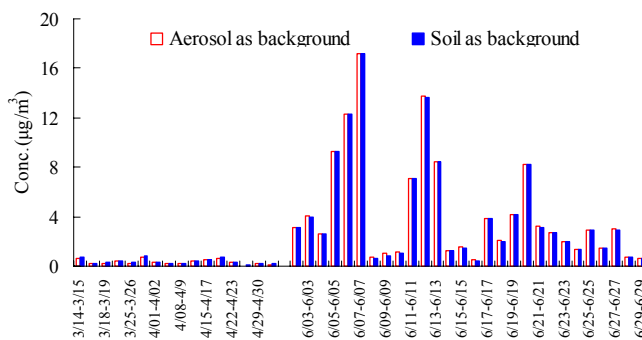**Fig. 5.** Daily variations of K^+, Na^+, and Al in PM$_{2.5}$ from 14 March to 30 June in 2006 at MT.

Fig. 6. Concentrations of biomass burning derived K^+ calculated with two methods in PM$_{2.5}$ in 2006 at MT.

(4.30 µg m^{-3}) in summer indicated that there were the significant part of the aerosols from biomass burning emissions at MT during the summer time. This result could also be confirmed by the fire spot data in this region, as shown in Fig. 7a–f. The amount of those fire spots distributed in the region surrounding MT increases obviously in May (Fig. 7c), and highly active fire disturbance appeared in June (Fig. 7d). The fire spots spread mainly to the south to MT during 1–9 June (Fig. 7e), and then extended to the northern places to MT during 10–19 June (Fig. 7f), which was in accordance to the harvest time of wheat/rice from south to north in this region.

The contributions of biomass burning, crustal dust, and other sources to the fine particles, PM$_{2.5}$, in spring and summer 2006 at MT are shown in Fig. 8. To assess quantitatively the contributions of biomass burning openly from the agriculture residues to the formation of PM$_{2.5}$ at MT, we used the ratio of $K^+/PM_{2.5}$ of 9.56 % (wt %) from the agriculture residues, i.e. biomass burning-derived PM$_{2.5}$ = $K_{BB}^+/0.0956$, to calculate the mass of PM$_{2.5}$ derived from biomass burning, for both Li et al. (2007) and Cao et al. (2008a) reported a very similar content of K^+ in PM$_{2.5}$ emitted from agriculture residues: 9.94 ± 11.8 or 9.56 ± 9.01 (wt %) from wheat straw, and 11.38 ± 8.49 (wt %) from rice straw. The
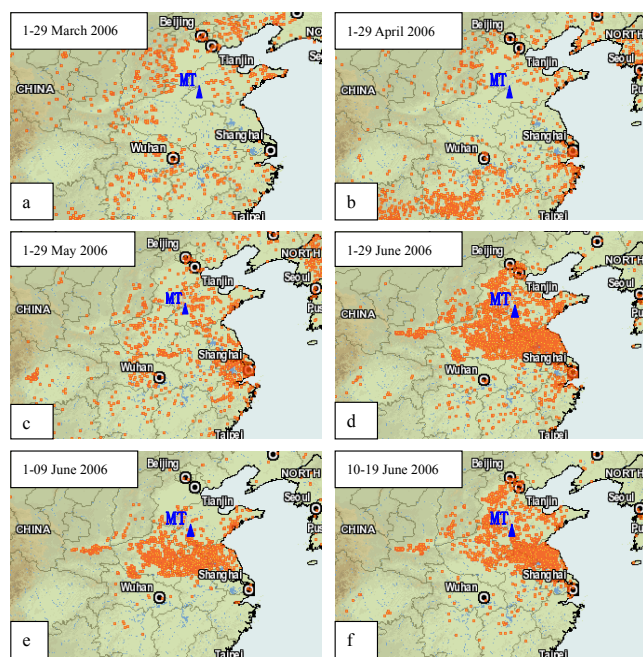
Fig. 7. Fire spot data derived from MODIS Global Fire Mapping during 2006: **(a)** 1–29 March, **(b)** 1–29 April, **(c)** 1–29 May, **(d)** 1–29 June, **(e)** 1–9 June and **(f)** 10–19 June at MT.
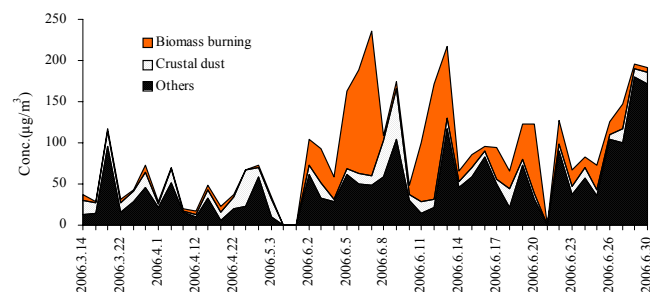

Fig. 8. Daily contributions of biomass burning, crustal dust, and others in PM$_{2.5}$ at MT.

crustal dust-derived PM$_{2.5}$ was calculated with the formula of Al/0.08. The results revealed that the contribution of biomass burning to the fine particle at MT accounted for 7.56 % in spring and 36.71 % in summer, and even reached to 81.58 % on the day of 12 June. In addition, the concentrations of K$^+$ at different sampling sites are summarized in Table 8. The concentration of K$^+$ at MT was much higher than those at other sites, and it showed strong seasonal variation with 4.41 µg m^{-3} in summer and 0.48 µg m^{-3} in spring in PM$_{2.5}$. Also, K$^+$ in PM$_{2.5}$ correlated well to other species that are related to biomass burning, such as BC, C$_2$O$_4^{2-}$, etc. (see Table 9). All of these results demonstrated evidently that biomass burning was one of major contributor to the aerosol pollution in summer over central eastern China, where MT is located.

Table 8. Concentrations of K$^+$ in PM$_{2.5}$ at different sampling sites.

Sites	Year	Spring	Summer	Autumn	Winter
Shanghai	2003–2004[a]	0.73	0.46	0.39	1.79
	2005	0.53	0.29	0.97	0.70
	2006	0.57	0.32	2.39	1.30
	2007	0.30	0.50	1.11	0.94
MT	2006	0.48	4.41		
Urumqi	2007	0.77	0.96	2.68	3.56
Beijing	2002[b]	1.42	1.18		2.80

[a] Wang et al. (2006b); [b] Wang et al. (2006a).
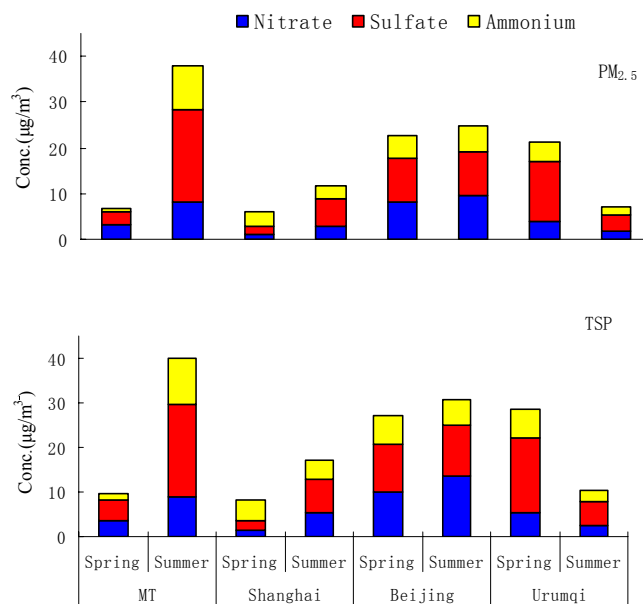

Fig. 9. Seasonal variations of SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ in aerosols at different sampling sites.

3.2.2 Secondary components: SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$

The concentrations of the main secondary species (SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$) in aerosols in spring and summer of 2006/2007 at different sites (MT, Urumqi, Beijing, and Shanghai) are illustrated in Fig. 9. The results showed that these secondary ions in aerosols in summer at MT were ∼5 times higher of those in spring, while there was no big change in Beijing, less change in Shanghai between the two seasons, and they were evidently greater in spring than those in summer at Urumqi. The sum of the three ions at MT in summer was higher than that at any other site, indicating much heavy secondary pollution at this region. Besides, at MT in summer the concentration of SO$_4^{2-}$ was much greater than NO$_3^-$, while in Beijing and Shanghai the concentrations of NO$_3^-$ was close to that of SO$_4^{2-}$. Average concentrations of

Table 9. Correlation coefficients between K^+ and other species in aerosols in summer at MT.

	K^+	$C_2O_4^{2-}$	BC	SO_4^{2-}	Cl^-	NO_3^-	NH_4^+
K^+	1.000						
$C_2O_4^{2-}$	0.869	1.000					
BC	0.904	0.781	1.000				
SO_4^{2-}	0.636	0.749	0.526	1.000			
Cl^-	0.708	0.640	0.742	0.481	1.000		
NO_3^-	0.813	0.903	0.767	0.802	0.753	1.000	
NH_4^+	0.636	0.749	0.526	1.000	0.481	0.802	1.000

SO_4^{2-} and NO_3^- in TSP at MT were 4.47 and 3.61 µg m^{-3} in spring, 20.73 and 8.82 µg m^{-3} in summer respectively, while in Shanghai 2.28 and 1.42 µg m^{-3} in spring, 7.34 and 5.50 µg m^{-3}, in summer 2006, respectively. During the study period, the average concentrations of SO_2 and NO_2 were 46.0 and 24.0 µg m^{-3} in spring, 34.0 and 26.0 µg m^{-3} in summer over MT, while 51.0 and 41.0 µg m^{-3} in spring and 33.0 and 19.0 µg m^{-3} in summer in Shanghai. Mineral aerosols reacted with SO_2 or NO_2 to form a layer of sulfate or nitrate on the mineral surfaces through the heterogeneous reactions (Yaacov et al., 1989), and soil particles would be coated by solutions contained sulfate and nitrate. The reaction of SO_2 on calcium-rich mineral aerosol was likely to play an important role in the downwind regions (Dentener et al., 1996), as many studies confirmed that the composition and morphology of dust particles would be changed during their transport (Underwood et al., 2001; Song et al., 2001). The conversion of SO_2 and NO_2 to be SO_4^{2-} and NO_3^- in ambient air could be their major source in aerosols. Sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) can indicate the efficiency of these transformations. If SOR is smaller than 0.10, the SO_4^{2-} could be from the primary emissions (Pierson et al., 1979; Truex et al., 1980), otherwise, SO_4^{2-} was produced through the photochemical oxidation from SO_2 (Ohta et al., 1990). Though concentrations of the gases were basically in the same levels, the SOR and NOR were significantly different between MT and Shanghai, especially in summer. SOR and NOR in TSP increased from 0.09 and 0.10 in spring to 0.32 and 0.26 in summer at MT, while 0.06 and 0.10 to 0.12 and 0.16 in Shanghai, respectively, in the same sampling time. This result indicated that in summer at MT the transformation efficiency of SO_2 and NO_2 to be SO_4^{2-} and NO_3^- was much higher than that in Shanghai, and it would result in much higher concentrations of sulfate and nitrate at MT than that in Shanghai.

Many factors were likely attributed to the more effective conversion of SO_2 and NO_2 to be SO_4^{2-} and NO_3^- on the summit of the mountain. Firstly, humidity plays a key role in the formation of sulfate from SO_2, for 80–90 % of the global sulfate was produced in the aqueous-phase, (Jill et al.,

2001). At the summit of MT, total cloud days were 5.4 and 7.0 in spring and summer, respectively, and monthly average foggy days could reach 26, sometimes even 30 in summer, while only 10 in spring. The relatively high humidity at the summit in summer is in favor of the formation of sulfate. Secondary, oxidation of SO_2 occurs potentially via three important pathways: oxidation by hydrogen peroxide or ozone, and auto-oxidation catalyzed by Fe (III) and Mn (II), and the former two were proved to be the dominative oxidation processes under certain conditions (Jill et al., 2001). High level of the biomass burning of agriculture residues resulted in increase of those gaseous pollutants, such as O_3, CO and VOCs in summer. Averaged concentration of total peroxide (0.55 ± 0.67 ppbv) was significantly higher in summer than that (0.17 ± 0.26 ppbv) in spring at MT (Ren et al., 2009). The O_3 in 2003 (Gao et al., 2005) and 2006 (Table 3) at MT showed that O_3 was also higher in summer than that in spring. High levels of O_3 and peroxide in ambient air in summer accelerated the conversion of SO_2 and NO_2 to be SO_4^{2-} and NO_3^-. Lastly, at MT there is abundance of hydrocarbon emitted by the abundant foliage that covers more than 90 % of the area of MT (Suthawaree, et al., 2010). O_3 accelerated the formation of SO_4^{2-} by directly reacting with SO_2 and generating OH radical that further to be transformed to peroxide via cooperating with hydrocarbon under light radiation. Hydrocarbon can react with OH radical to produce HO_2 and $RO_2(OH + RH \xrightarrow{[O_2]} RO_2 + H_2O, NO + RO_2 \rightarrow RCHO + HO_2 + NO_2)$ (Ariel et al., 2000), and HO_2 further react with SO_2 and NO_2. Higher CO level produced from biomass burning in summer also contributed to the oxidation of SO_2 by generating peroxide with OH radical $(OH + CO \xrightarrow{[O_2]} HO_2 + CO_2)$. The reactive processes above would benefit the formation of organic acids: $HO_2 + RO_2 \rightarrow ROOH + O_2$. The high concentrations of diacids and the good correlations of diacids with SO_4^{2-}, as shown in Fig. 10, further suggested the formation mechanism of high level of the secondary aerosol in summer at MT. Besides, NH_4^+ increased significantly from 1.48 µg m^{-3} in spring to 10.4 µg m^{-3} in summer, which was likely due to more pesticide sprayed in the large area of farming fields in late May and the stock-raise at MT region, which could produce much more NH_3 in summer than in spring. Also, higher temperature in summer could lead to the higher emission of NH_3 from animal's excrements (Sacoby et al., 2007).

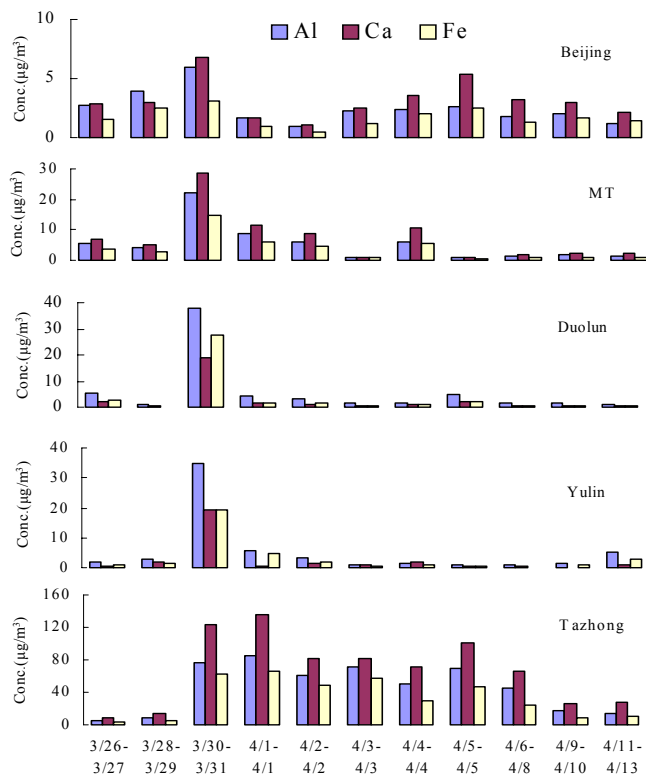### 3.2.3 Mineral dust in spring time

Concentrations of mineral elements (such as Al, Fe, and Ca) are good indicators for crustal aerosols. Daily variation of mineral elements (Al, Fe, and Ca) at different sampling sites in spring, 2007 is shown in Fig. 11. It can be seen clearly that a strong dust storm occurred from 30 March to 2 April and resulted in sharp increase of the three mineral elements at all of these monitoring sites, especially at Tazhong, Yulin,

Table 10. Ratio of Ca/Al in aerosol or surface soil in different sampling sites over China.

Site	Type	Ca/Al	Reference
Tazhong (Taklimakan Desert)	PM$_{2.5}$	1.55 ± 0.22	This study
Yulin, China	PM$_{2.5}$	0.52 ± 0.43	This study
Duolun	PM$_{2.5}$	0.45 ± 0.12	This study
Beijing	PM$_{2.5}$	1.37 ± 0.39	This study
MT	PM$_{2.5}$	1.37 ± 0.22	This study
Taklimakan Desert	Aerosol	1.99	Zhang et al. (1996)
Badain Juran desert	Aerosol	1.2	Zhang et al. (1996)
Hunshandake sandland Soil		0.52	Zhang et al. (1996)
Tongliao, Horqin sand land	PM$_{2.5}$	0.76	Shen et al. (2006)
Loess Plateau	Aerosol	1.14	Zhang et al. (2003)
	TSP	1.22	Cao et al. (2008b)
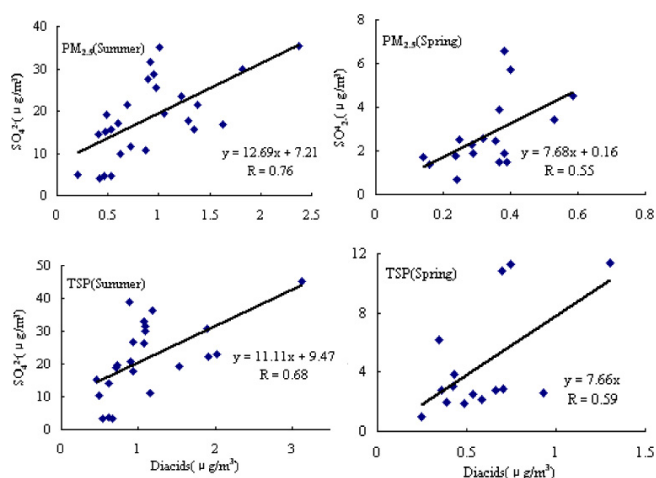
Fig. 10. Scatter plots of SO$_4^{2-}$ vs. decides (sum of CH$_2$C$_2$O$_4^{2-}$, CH$_4$C$_2$O$_4^{2-}$, and C$_2$O$_4^{2-}$).

Fig. 11. Daily variation of mineral elements (Ca, Al and Fe) at different sampling sites in spring, 2007.

Duolun, MT, and Beijing. The ratio of Ca/Al has been proved to be a good tracer for different dust original areas (Wang et al., 2005; Sun et al., 2005), for Ca/Al showed remarkable dependence of the source regions for both dust aerosol and soil samples. Ratios of Ca/Al in aerosol or soil from different sampling sites are shown in Table 10, and it could be seen clearly that Taklimakan desert, the western source of Asian dust, is characterized by high ratio of Ca/Al of greater than 1.5, while the northern source of Asian dust, such as Duolun and Hunshandake Sandland, is characterized by low ratio of Ca/Al of around 0.5. The ratio of Ca/Al (1.37 ± 0.22) in the aerosol at MT indicated that the dust aerosol at MT in spring could be from the long-range transport of the dust from western or northwestern high-dust sources. The facts mentioned above that the coarse particles dominated in spring (PM$_{2.5}$/TSP of 0.37) and the alkalinity (pH = 7.22) of the TSP in spring further confirmed that the long-range transport was the major source of the aerosols in spring at MT.

3.2.4 The pollution elements As and Pb

The pollution elements, As and Pb, were highly enriched in the aerosols with the EF of 1541 and 679, respectively, in spring, while 1470 and 1969 in summer in PM$_{2.5}$ at MT. As and Pb were of different seasonal variations with summer-high/spring-low of Pb, while spring-high/summer-low of As. Correlation analysis (see Table 11) revealed that both Pb and As were highly correlated to those crustal elements in spring with the correlation coefficients of 0.701 for Pb to Al and 0.873 for Pb to Fe, while of 0.837 for As to Al and 0.778 for As to Fe. Furthermore, the correlation coefficient between Pb and As was as high as 0.949. These results indicated that both Pb and As were highly associated with the mineral components, which was long-range transported from northwestern China to MT in spring. Those primary dust aerosols from northwestern China would mix with As and Pb, which were emitted from coal-mining/coal-ash and widely distributed over northwestern China, and act as a carrier for As and Pb. The pollution elements, As and Pb, would gradually be enriched in the dust aerosol during its long-range transport. The results revealed that the long-range transport of aerosols spread the heavy pollution from coal burning everywhere over China. However, in summer the correlation coefficients of Pb to Al and Pb to Fe decreased

Table 11. Correlation coefficients among the certain species in spring and summer at MT.

	SO_4^{2-}	NO_3^-	BC	Al	Fe	Ca	As	Cr	Cu	Cd	Mn	Pb	Zn	Ti	
SO_4^{2-}		.802	.526	.253	.274	.249	.502	.325	.478	.613	.303	.496	.538	−.243	SO_4^{2-}
NO_3^-	.954		.767	.223	.237	.259	.415	.249	.594	.551	.286	.419	.557	−.087	NO_3^-
BC	.748	.792		−.030	−.029	−.002	.358	.090	.323	.378	.023	.476	.081	.004	BC
Al	.225	.185	−.027		.997	.986	.469	.795	.623	.691	.984	−.184	.725	.411	Al
Fe	.353	.239	−.070	.781		.982	.456	.775	.616	.677	.984	−.194	.733	.390	Fe
Ca	.057	.049	−.241	.857	.806		.529	.838	.684	.721	.992	−.139	.755	.482	Ca
As	.326	.234	−.061	.837	.778	.683		.786	.672	.812	.561	.494	.486	.274	As
Cr	.164	.111	−.185	.845	.832	.881	.863		.785	.847	.855	.148	.704	.372	Cr
Cu	.013	−.043	−.026	.284	.332	.313	.407	.484		.802	.700	.337	.825	.308	Cu
Cd	.478	.345	.111	.693	.692	.593	.806	.779	.609		.754	.527	.720	−.204	Cd
Mn	.415	.295	−.004	.815	.963	.805	.764	.851	.320	.782		−.092	.770	.447	Mn
Pb	.438	.359	.086	.701	.873	.554	.949	.774	.591	.704	.735		.134	−.126	Pb
Zn	.358	.250	.057	.403	.511	.455	.850	.600	.752	.572	.661	.717		.105	Zn
Ti	.367	.425	−.051	.763	.749	.793	.687	.809	.354	.994	.960	.679	.599		Ti

(Left margin: Spring; Right margin: Summer)

to −0.184 and −0.194, while of As to Al and As to Fe to 0.469 and 0.456, respectively, and the correlation coefficient between Pb and As decreased to 0.494. These results indicated that in summer the source of Pb and As was not mainly from long-range transport, instead, they could be from those local/regional sources. It could be seen that Pb and As were both correlated well to Cr, Cu, and Zn in summer, suggesting that the source of Pb and As in summer would likely from the same local/reginal anthropogenic discharge as the pollution elements, Cr, Cu, and Zn, did. The strong convections of air mass would result in the elevation to the summit of MT from the ground level of the pollutants. The emission of Pb from the local/regional anthropogenic source in summer could be much more than that from the long-range transport in spring, which led to the higher enrichment of Pb in summer than that in spring.

4 Summary

Aerosols over central eastern China showed significantly season variation, with fine particles dominated in summer while coarse particles in spring. The summit of MT was suffering from the invasion of long-range transported dust from northwestern China, the heavy local/regional anthropogenic emissions from the surrounding areas, and the severe secondary pollutions. The contribution of biomass burning to the fine particle at MT accounted for 7.56 % in spring and 36.71 % in summer, and even reached to 81.58 % on a day. The high levels of peroxides and ozone, as well as the favourable meteorological conditions in the ambient air were in favour of the transformation of SO_2 and NO_x to sulfate and nitrate, which resulted in the even severe secondary pollution in this region. As and Pb were two of the most enriched elements. The long-range transport of aerosols spread the heavy pollution from coal-mining/coal-ash to everywhere over China. Anthropogenic air-pollution was evidently rather severe at MT.

References

Andreae, M. O.: Soot carbon and excess fine potassium: long-range transport of combustion-derived aerosols, Science, 220, 1148–1151, 1983.

Ariel, F. S. and Lamb, D.: The sensitivity of sulfer wet deposition to atmospheric oxidants, Atmos, Environ., 34, 1681–1690, 2000.

Arimoto, R.: Eolian dust and Climate: Relationship to sources, tropospheric chemistry, transport and deposition, Earth Sci. Rev., 54, 29–42, 2001.

Arimoto R., Duce R. A., and Savoie D. L.: Relationships among aerosol constituents from Asia and the North Pacific during PEM-West, J. Geophys. Res. Atmos., 101(D1), 2011–2023, 1996.

Cao, G., Zhang, X., Wang, D., and Zheng, F.: Inventory of atmospheric pollutants discharged from biomass burning in China continent, China Environ. Sci., 25(4), 389–393, 2005 (in Chinese).

Cao, G., Zhang, X., Wang, Y., and Zheng, F.: Estimation of the emission from open burning of crop residues in China continent, Chin. Sci. Bull., 52(18), 1826–1831, 2007 (in Chinese).

Cao, G., Zhang, X., Gong, S., and Zheng, F.: Investigation on emission factors of particulate matter and gaseous pollutants from crop residue burning, Environ. Sci., 20, 50–55, 2008a.

Cao, J. J., Chow, J. C., Watson, J. G., Wu, F., Han, Y. M., Jin, Z. D., Shen, Z. X., and An, Z. S.: Size-differentiated source profiles for fugitive dust in the Chinese Loess Plateau, Atmos. Environ., 42(10), 2261–2275, 2008b.

Chan, Y. C., Simpson, R. W., Mctainsh, G. H., Vowles, P. D., Cohen, D. D., and Bailey, G. M.: Source apportionment of visibility degradation problems in Brisbane (Australia) using the multiple linear regression technique, Atmos. Environ., 33, 3237–3250, 1999.

Chester, R.: Marine Geochemistry, Unwin Hyman, London, 698 pp., 1990.

Dentener, F. J., Carmichael, G. R., and Zhang, Y.: Role of mineral aerosol as a reactive surface in the global troposphere, J. Geophys. Res. Atmos., 101(D17), 22869–22889, 1996.

Dockery, D. W., Pope, A. C., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris Jr., B. G., and Speizer, F. E.: An association between air pollution and mortality in six US cities, New Engl. J. Med., 1753–1759, 1993.

Facchini, M. C. S., Decesari, M., Mircea, S., Fuzzi, and Loglio, G.: Surface tension of atmospheric wet aerosol and cloud/fog droplets in relation to their organic carbon content and chemical composition, Atmos. Environ., 34, 4853–4857, 2000.

Gao, J., Wang, T., Ding, A., and Liu, C.: Observational study of ozone and carbon monoxide at the summit of mount Tai (1534 m a.s.l.) in central-eastern China, Atmos. Environ., 39(20), 4779–4791, 2005.

Guo, J., Kenneth, A., Rahn, and Zhuang, G.: A mechanism for the increase of pollution elements in dust storms in Beijing, Atmos. Environ., 38, 855–862, 2004.

Han, L., Zhuang G., Sun Y., and Wang, Z. F.: Local and non-local sources of airborne particulate pollution at Beijing, Science in China Ser. B Chemistry, 48(4), 1–12, 2005.

Jill, E. R., Oliver, V. R., Katharine, F. M., Christopher J., Eli, D. S., Vincent, A. D., Sonia, M. K., Liaquat, H., and Collett Jr., J.: Drop size-dependent S (IV) oxidation in chemically heterogeneous radiation fogs, Atmos. Environ., 35, 5717–5728, 2001.

Kaufman, Y. J., Tanre, D., and Boucher, O.: A satellite view of aerosols in the climate system, Nature, 419, 215–223, 2002.

Li, X., Wang, S., Duan, L., Hao, J., Li, C., Chen, Y., and Yang, L.: Particulate and Trace Gas Emissions from Open Burning of Wheat Straw and Corn Stover in China, Environ. Sci. Technol., 41(17), 6052–6058, 2007.

Liu, C. L., Zhang, J., and Liu, S. M.: Physical and chemical characters of materials from several mineral aerosol sources in China, Environ. Sci., 23, 28–32, 2002.

Matsumoto, K., Tanaka, H., Nagao, I., and Ishizaka, Y.: Contribution of particulate sulfate and organic carbon to cloud condensation nuclei in the marine atmosphere, Geophys. Res. Lett., 24, 655–658, 1997.

Novakov, T. and Penner, J. E.: Large condensation of organic aerosols to cloud-condensation nuclei concentration, Nature, 365, 823–826, 1993.

Novelli, P. C., Masarie, K. A., Tans, P. P., and Lang, P. M.: Recent changes in atmospheric carbon monoxide, Science, 263, 1587–1590, 1994.

Novelli, P. C., Masarie, K. A., and Lang, P. M.: Distributions and recent changes of carbon monoxide in the lower troposphere, J. Geophys. Res., 103(D51), 19015–19033, 1998.

Ohta, S. and Okita, T.: A chemical characterization of atmospheric aerosol in Sapporo, Atmos. Environ., 24A, 815–822, 1990.

Pierson, W. R., Brachaczek, W. W., and Mckee, D. E.: Sulfate emissions from catalyst equipped automobiles on the highway, J. Air Pollut. Control Assoc., 29, 255–257, 1979.

Rastogi, N. and Sarin M. M.: Long-term characterization of ionic species in aerosols from urban and high altitude sites in western India: Role of mineral dust and anthropogenic sources, Atmos. Environ, 39, 5541–5554, 2005.

Rastogi, N. and Sarin, M. M.: Chemistry of aerosols over a semi-arid region: Evidence for acid neutralization by mineral dust, J. Geophys. Res. Lett., 33, L23815, doi:10.1029/2006GL027708, 2006.

Ren, Y., Ding, A., Wang, T., Shen, X., Guo, J., Zhang, J., Wang, Y., Xu, P., Wang, X., Gao, J., Jeffrey, L., and Collett, J.: Measurement of gas-phase total peroxides at the summit of Mount Tai in China, Atmos. Environ., 43, 1702–1711, 2009.

Sacoby, M. W. and Marc, L.: Examination of atmospheric ammonia levels near hog CAFOs, homes, and schools in Eastern North Carolina, Atmos. Environ., 41, 4977–4987, 2007.

Shen, Z. X., Cao, J. J., Li, X. X., Wang, Y. Q., Jie, D. M., and Zhang, X. Y.: Chemical characteristics of aerosol particles (PM$_{2.5}$) at a site of Horqin Sand-land in northeast China, Environmental Sciences-China, 18(4), 701–707, 2006.

Song, C. H. and Carmichael, G. R.: A three-dimensional modeling investigation of the evolution processes of dust and sea-salt particles in East Asia, J. Geophys. Res.-Atmos., 106(D16), 18131–18154, 2001.

Streets, D. G., Yarber, K. F., Woo, J. H., and Carmichael, G. R.: Biomass burning in Asia: Annual and seasonal estimates and atmospheric emissions, Global Biogeochem. Cy., 17(4), 1099, doi:10.1029/2003GB002040, 2003.

Sun, Y., Zhuang, G., Wang, Y., Han, L., Guo, J., Dan, M., Zhang, W., Wang, Z., and Hao, Z.: The air-borne particulate pollution in Beijing-concentration, composition, distribution and sources, Atmos. Environ., 38, 5991–6004, 2004.

Sun, Y., Zhuang, G., Wang, Y., Zhao, X., Li, J., Wang, Z., and An, Z.: Chemical composition of dust storms in Beijing and implications for the mixing of mineral aerosol with pollution aerosol on the pathway, J. Geophys. Res., 110, D24209, doi:10.1029/2005JD006054, 2005.

Sun, Y., Zhuang, G., Huang K., Li J., Wang, Q., Wang Y., Lin, Y., Fu, J., Zhang, W., Tang, A., and Zhao, X.: Asian dust over northern China and its impact on the downstream aerosol chemistry in 2004, J. Geophys. Res., 115, D00K09, doi:10.1029/2009JD012757, 2010.

Suthawaree, J., Kato, S., Okuzawa, K., Kanaya, Y., Pochanart, P., Akimoto, H., Wang, Z., and Kajii, Y.: Measurements of volatile organic compounds in the middle of Central East China during Mount Tai Experiment 2006 (MTX2006): observation of regional background and impact of biomass burning, Atmos. Chem. Phys., 10, 1269–1285, doi:10.5194/acp-10-1269-2010, 2010.

Tegen, I., Lacis, A. A., and Fung, I.: The influence of climate forcing of mineral aerosols from disturbed soils, Nature, 380(4), 419–422, 1996.

Truex, T. J., Pierson, W. R., and Mckee, D. E.: Sulfate in diesel exhaust. Environ. Sci. Technol., 14, 1118–1121, 1980.

Tsai, Y. I. and Cheng, M. T.: Visibility and aerosol chemical compositions near the coastal area in central Taiwan, Sci. Total Environ., 231, 37–51, 1999.

Underwood, G. M., Li, P., Al-Abadleh, H., and Grassian, V. H.: A Knudsen cell study of the heterogeneous reactivity of nitric acid on oxide and mineral dust particles, J. Phys. Chem. A., 105(27),

6609–6620, 2001.

Virkkula, A., Teinilä, K., Hillamo, R., Kerminen, V.-M., Saarikoski, S., Aurela, M., Viidanoja, J., Paatero, J., Koponen, I. K., and Kulmala, M.: Chemical composition of boundary layer aerosol over the Atlantic Ocean and at an Antarctic site, Atmos. Chem. Phys., 6, 3407–3421, doi:10.5194/acp-6-3407-2006, 2006.

Wang, T., Cheung, A., Vincent, T. F., Anson, M., and Li, Y. S.: Ozone and related gaseous pollutants in the boundary layer of eastern China: overview of the recent measurements at a rural site, Geophys. Res. Lett., 28(12), 2373–2376, 2001.

Wang, Y., Zhuang, G., Sun, Y., and An, Z.: Water-soluble part of the aerosol in the dust storm season – evidence of the mixing between mineral and pollution aerosols, Atmos. Environ., 39, 7020–7029, 2005.

Wang, Y., Zhuang, G., Sun Y., and An, Z.: The variation of characteristics and formation mechanisms of aerosols in dust, haze, and clear days in Beijing, Atmos. Environ., 40, 6579–6591, 2006a.

Wang, Y., Zhuang, G., Zhang, X., Huang, K., Xu, C., Tang, A., Chen, J., and An, Z.: The ion chemistry, seasonal cycle, and sources of PM$_{2.5}$ and TSP aerosol in Shanghai, Atmos. Environ., 40, 2935–2952, 2006b.

Wang, Y., Ge, F., Liu, X., Wang, W., Jia, H., and Wang, D.: Analysis of the ionic characteristics for wet droplets at Mountain Tai, China Environ. Sci., 26(4), 422–426, 2006c (in Chinese).

Wang, Y., Wai, K., Gao, J., Liu, X., Wang, T., and Wang, W.: The impacts of anthropogenic emissions on the precipitation chemistry at an elevated site in North-eastern China, Atmos. Environ., 42, 2959–2970, 2008.

Wedepohl, K. H.: The compositions of the continental crust, Geochim. Cosmochim. Acta, 59, 1217–1232, 1995.

Yaacov, M. and Judith, G.: Heterogeneous reactions of minerals with sulfur and nitrogen oxides, J. Aerosol Sci., 20(3), 303–311, 1989.

Yuan, H., Wang, Y., and Zhuang, G.: The simultaneous determination of organic acid, MSA with inorganic anions in aerosol and rainwater by ion chromatography, J. Inst. Anal., 6, 12–16, 2003 (in Chinese).

Zhang, X. Y., Zhuang, G. Y., Zhu, G. H., Zhang, D., An, Z. S., Chen, T., and Huang, X. P.: Element tracers for Chinese source dust, Science in China (Series D), 39(5), 512–521, 1996.

Zhang, X. Y., Arimoto, R., and An, Z. S.: Dust emission from Chinese desert sources linked to variations in atmospheric circulation, J. Geophys. Res.-Atmos., 102(D23), 28041–28047, 1997.

Zhang, D., Zang, J., Shi, G., Iwasaka, Y., Matsuki, A., and Trochkine, D.: Mixture state of individual Asian dust particles at a coastal site of Qingdao, China, Atmos. Environ., 37(28), 3895–3901, 2003.

Zhu, B., Zhu, X., Zhang, Y., Zeng, L., and Zhang, Y.: Emission factors of PM$_{2.5}$ from crop straw burning, Res. Environ. Sci., 18(2), 29–33, 2005 (in Chinese).

Zhuang, G., Guo, J., Yuan, H., and Zhao, C.: The compositions, sources, and size distribution of the dust storm from China in spring of 2000 and its impact on the global environment, Chin. Sci. Bull., 46(11), 895–900, doi:10.1007/BF02900460, 2001.