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Characteristics of $PM_{2.5}$ speciation in representative megacities and across China

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Abstract. Based on $PM_{2.5}$ chemical data sets from literature and from our surface observations, chemical species and reconstructed speciation of $PM_{2.5}$ in representative Chinese megacities and across China were compared to draw insights into the characteristics of $PM_{2.5}$ speciation. $PM_{2.5}$ mass concentrations and speciation compositions varied substantially over geographical regions in China. Near six-fold variations in average $PM_{2.5}$ concentrations (34.0–193.4 $\mu g\,m^{-3}$) across China were found with high $PM_{2.5}$ levels ($>100\ \mu g\,m^{-3}$) appearing in the cities in the northern and western regions and low levels ($<40\ \mu g\,m^{-3}$) in the remote forest area (Changbai Mountain) and in Hong Kong. The percentages of the sum of sulfate, nitrate and ammonium, organic matter, crustal material, and elemental carbon in $PM_{2.5}$ mass ranged 7.1–57 %, 17.7–53 %, 7.1–43 %, and 1.3–12.8 %, respectively. At both urban and rural sites in the eastern region, the sum of sulfate, nitrate and ammonia typically constituted much higher fractions (40–57 %) of $PM_{2.5}$ mass, indicative of more local formation/production and regional transport of the secondary aerosols, thus more intensive characteristic of "complex atmospheric pollution" compared to the western region. Organic matter had significant contribution to $PM_{2.5}$ over all the sites. Organic matter plus sulfate, nitrate, and ammonia accounted for 53–90 % of $PM_{2.5}$ mass across China. $PM_{2.5}$ speciation across China was also characterized by high content of crustal material, which was usually at more than $\sim 10\ \mu g\,m^{-3}$ level or shared ~ 10 % of $PM_{2.5}$ mass in urban areas, due to transported desert dust and locally induced dust. In four representative megacities (i.e. Beijing, Chongqing, Shanghai, and Guangzhou), $PM_{2.5}$ mass and major components (except sulfate) were at higher levels than those in US continental east by one order of magnitude. Distinct differences in nitrate and sulfate levels and their mass ratio $[NO_3^-]/[SO_4^{2-}]$ imply that mobile sources are likely more important in Guangzhou, whereas in Chongqing it is stationary (coal combustion) sources. The observed intra-city variations in $PM_{2.5}$ mass and speciation indicate that both local emissions and regional transportation contributed significantly to high fine particle loadings in Beijing, while local contribution likely played a predominant role in Chongqing. During the ten-year period from 1999 through 2008 in urban Beijing, both the sum of sulfate, nitrate, and ammonia and $[NO_3^-]/[SO_4^{2-}]$ ratio exhibited steadily increasing trends, implying that the characteristic of "complex atmospheric pollution" and the contribution from mobile sources were being enhanced.

1 Introduction

Atmospheric particulate matter (PM) is composed of a mixture of complex materials from multiple sources which change in emission rate and composition over time and space. The PM mass concentration and chemical composition and their spatial and temporal distributions are determined by the patterns of source emissions, transport, chemical reactions, and dry and wet depositions. Currently, all the air quality standards for PM worldwide are on the basis of its

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mass concentration, whereas its chemical constituents play important or even key roles on human exposure, visibility impairment, and global climate change. In fact, the direct climate effects of aerosol are expressed on the basis of its chemical species, although with the highest uncertainty (IPCC, 2007). $PM_{2.5}$ speciation is key to estimating its chemical extinction and to characterize haziness (Watson, 2002). Lack of chemical composition also limits the application of remotely-sensed aerosol as a spatial proxy for fine PM ($PM_{2.5}$, i.e. particulate matter with aerodynamic diameters less than 2.5 µm) (Paciorek and Liu, 2009). To date, the measured PM species are usually ions and elements but not their compounds; for organic aerosols, sum of the measured compounds amount for only a few percent of the total organic mass, meaning that the analysis of organic aerosols presents difficult challenges. In addition, no one single analytical method can be used to quantify all the species. The measured species are therefore used to reconstruct their compounds to review the whole picture of PM chemical composition (i.e. speciation) and mass balance. The consistency of the various complementary analytical techniques adopted can also be evaluated by mass closure experiments (Putaud et al., 2004).

In China, PM_{10} remains a management issue as the principal air pollutant because exceedances of Chinese annual-average PM_{10} standard of 100 µg m^{-3} still occur in about one-third of all the cities covered in the national ambient air quality surveillance. $PM_{2.5}$ is not yet regulated in China but there have been a number of field studies in the last decade to quantify and characterize $PM_{2.5}$ (Chan and Yao, 2008). It is a complicated pollutant – especially in China – because of the large variations in sources, energy structures, climatic conditions, and living habits across the nation (Feng et al., 2007). Owing to the fact that its secondary aerosols are converted from major gaseous pollutants, $PM_{2.5}$ is also regarded as a representative pollutant in "complex atmospheric pollution", of which the term emerged in the last decade in China as the consequence of mixing pollutants from coal combustion, vehicular emissions, and perhaps biomass burning, in conjunction with fugitive dust (Fang et al., 2009). To understand $PM_{2.5}$ concentration and composition in the ambient air across China, $PM_{2.5}$ data from literature and from our studies conducted in several typical megacities were used to perform their speciation reconstruction. Furthermore, based on more than one-year simultaneous speciation sampling of $PM_{2.5}$ at paired rural/urban sites in Beijing and Chongqing, this study will focus on characterization and comparison of temporal and spatial variations in $PM_{2.5}$ speciation in the two representative megacities with high $PM_{2.5}$ loadings but with distinctly different emissions and meteorological conditions in China.

2 Methodology

2.1 Study locations in Beijing, Chongqing and Guangzhou, and sampling and analyses

The study was conducted in Beijing, Chongqing, and Guangzhou, which are the representative megacities of three regions lying in different climatic regions, i.e. Beijing-Tianjin region, Sichuan basin, and Pearl River Delta Region (PRDR), respectively (Fig. 1). It is noted that the three regions and Yangtze Delta Region (YDR) have frequent hazy days and high aerosol optical depths retrieved with satellite data in China (Guan, 2009). Beijing is located on the northern border of the Great North China Plain, with a population of 15.8 million (http://www.bjstats.gov.cn). The main terrain of Beijing is plain, with surrounding mountains – the Yanshan Mountain – in three directions, and towards the southeast the plain turns into a "dustpan" spreading forward to the Bohai Sea 160 km away. The special geographical environment favors stagnant conditions over the area, where polluted air cannot be easily expelled. Beijing is in the warm temperate zone and has typical continental monsoon climate with four distinct seasons. Two sites with a distance of 70 km were selected to represent the urban influence and rural background (Fig. 1): the urban site was inside the campus of Tsinghua University (TH, 40°19′ N, 116°19′ E), a semi-residential area; the rural site was near the Miyun Reservoir (MY, 40°29′ N, 116°47′ E), about 90 km apart from the northeast of the urban center.

About 1500 km away from Beijing and near the eastern border of Sichuan Basin, Chongqing lies on the Yangtze River in the mountainous area of southwestern China, with a population of 28.2 million (http://www.cqtj.gov.cn/tjnj/2008/). Influenced by the specific topographic condition, Chongqing is within the region of lowest wind speed over China. For example, the annual average wind speed is 0.9–1.6 m s^{-1} (http://www.cqtj.gov.cn/tjnj/2008/). The specific geographical and meteorological conditions favor the accumulation of regional and local pollutants. Two urban sites with 12 km distance apart and one rural background site were chosen in this largest municipality (Fig. 1): a residential urban site was set on a building roof of Chongqing Monitoring Center in Jiangbei District (JB, 29°34′ N, 106°32′ E); an industrial urban site was set on the roof of a governmental office building of Dadukou District (DDK, 29°29′ N, 106°29′ E); and the rural site was set near the Jinyun Mountain in Beibei District (BB, 29°50′ N, 106°25′ E), ∼40 km to the northwest of the urban center.

Guangzhou – with a population of approximately 11 million and an area of 7434 km^2 – is located in PRDR, mainly consisted of floodplains and a transitional zone of the East Asian monsoon system, i.e. a southwest wind in summer from the South China Sea, and a northeast wind in winter from the mainland of China. A $PM_{2.5}$ sampler (TH100-$PM_{2.5}$, Wuhan Tianhong Instruments, Wuhan, China) was

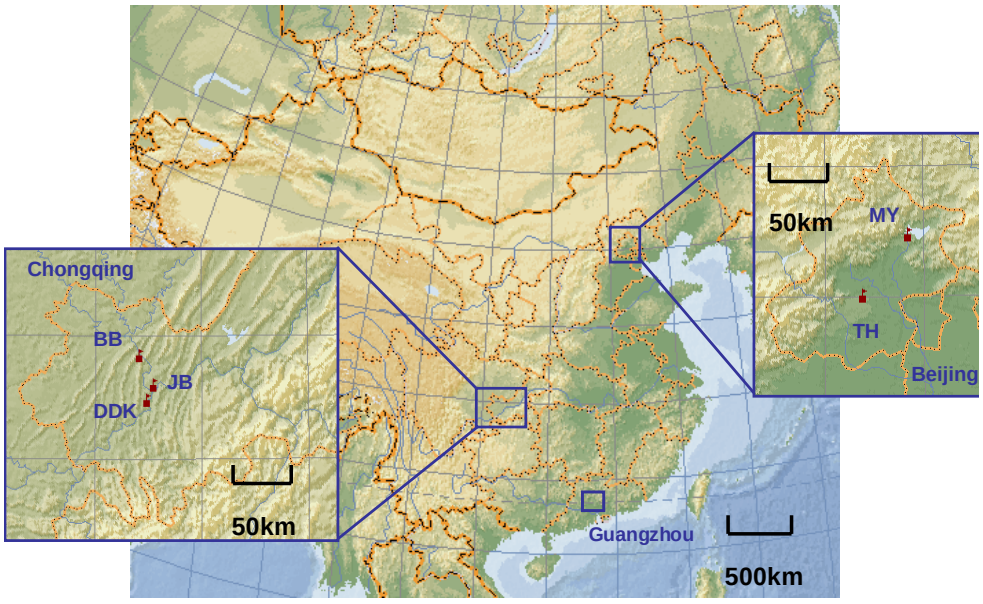

Fig. 1. Sampling sites in Beijing (TH and MY), Chongqing (JB, DDK, and BB), and Guangzhou (Wushan). The topography map was derived from the Microsoft Encarta 2009© 1993–2008.

deployed on the rooftop of a 15 m-tall building of the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences at Wushan (23°15′ N, 113°36′ E) to collect 24-h $PM_{2.5}$ samples from December 2008 through February 2009. The sampling flow rate was 100 l min^{-1}. The site is located in a residential and commercial mixed area.

A three-channel speciation sampler (TCSS, Aerosol Dynamics Inc., Berkeley, CA, USA) was deployed at each site in Beijing and Chongqing to simultaneously collect 7-day integrated $PM_{2.5}$ samples from February 2005 through April 2006. Besides this parallel sampling in the two megacities, we continued collecting $PM_{2.5}$ samples with the same sampler and same sampling duration at TH from 1999 through 2008. Details of sampling procedure and quality control have been provided in our previous work (He et al., 2001; Zhao et al., 2010). Briefly, operating at a flow rate of 0.4 l min^{-1}, the first channel was used to collect $PM_{2.5}$ with a Teflon filter for elemental analysis. The second channel collected the particles for the measurement of water-soluble ions, with a Teflon filter and a following nylon filter after acidic gases were removed by a glass denuder. The third channel was used to collect $PM_{2.5}$ on tandem quartz filters for organic and elemental carbon (OC and EC) analyses.

As described in He et al. (2001) and Zhao et al. (2010), $PM_{2.5}$ mass was weighed and three kinds of chemical species were measured. $PM_{2.5}$ mass concentration was obtained by the gravimetry method with an analytical balance (Mettler Toledo AG285), after stabilizing under constant temperature ($20 \pm 5°$) and humidity ($40\% \pm 5\%$). Using EPA standard method, 23 elements including Al, Na, Cl, Mg, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Cd, Ba, Pb were determined by X-ray fluorescence (XRF, model RIX3000), and nine main ions including K^+, Ca^{2+}, Na^+, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^- and Cl^- were measured by ion chromatography (model Dionex 600). OC and EC were analyzed by the thermal/optical methods (Chow et al., 1993; Huang et al., 2006).

2.2 Collection of chemical data for $PM_{2.5}$ across China

Zhang and Friedlander (2000) have compared the chemical databases for fine particles (including $PM_{2.0}$, $PM_{2.3}$, and $PM_{2.5}$) measured during 1980–1993 in China, of which there were 13–22 inorganic elements but few ionic species and carbonaceous species. Based on more recent publications, Chan and Yao (2008) have summarized chemical compositions in $PM_{2.5}$ in a critical review about air pollution in China, with a focus on Beijing, Shanghai, PRDR (including Guangzhou, Shenzhen and Hong Kong) and immediate vicinities. While this paper mainly focuses on characterization and comparison of temporal and spatial variations in $PM_{2.5}$ speciation composition at paired rural/urban sites in representative megacities, it also aims to present a whole picture of reconstructed $PM_{2.5}$ speciation composition across China. It builds upon previous studies conducted over different regions in China and includes new chemical data sets acquired in the areas rarely explored for fine particles before. In the locations with different studies on $PM_{2.5}$, we prefer those based on long-term observations with bulk chemical composition and focus on internationally peer-reviewed publications. Based on 15 earlier studies conducted in 16 locations across China during 1999–2007, chemical species were assembled to perform their $PM_{2.5}$ speciation reconstruction.

A brief introduction of the locations, sampling and analyses for all these studies is listed in Table 1. Of the 16 locations, 13 locations are large cities, reflecting their great concerns on particulate pollution and data availability, while the rest locations include 1 mountain forest (Changbai Mountain), 1 rural island (Changdao Island) and 1 rural sand land (Tongliao). The study in Shanghai was a $PM_{2.5}$ characterization study (Ye et al., 2003), parallel with that we conducted in Beijing during 1999–2000 (He et al., 2001).

2.3 Reconstruction of $PM_{2.5}$ speciation

As described below, organic and elemental carbon, secondary inorganic ions (i.e. sulfate, nitrate, and ammonium), and crustal species such as Al, Si, Ca, and Fe are often the major constituents of $PM_{2.5}$ in Chinese megacities. The principal types of secondary inorganic aerosols are ammonium sulfate and nitrate formed from gaseous emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) which react with ammonia (NH_3). In this study, we take the sums of sulfate, nitrate, and ammonium (SNA) as secondary inorganic speciation. The material balance of $PM_{2.5}$ was determined by the following types of speciation: SO_4^{2-}, NO_3^-, and NH_4^+, organic mass (OM), EC, crustal material, trace species, and others.

OM is derived from multiplying OC concentrations by the often-adopted factor of 1.4 to account for unmeasured atoms, such as hydrogen, oxygen, and nitrogen in organic materials according to the suggestion by Turpin and Lim (2001). It is noted that the coefficient to convert OC to OM for ambient aerosols is subject to many factors, including the methodology in estimation (Turpin and Lim, 2001; Aiken et al., 2008; Chan et al., 2010). Also of note is that the coefficient may change with season and air mass, i.e. with different emission sources and/or atmospheric processes (e.g. Bae et al., 2006; El-Zanan et al., 2009; Malm et al., 2010), and higher factors are suggested for more aged aerosols.

The reconstruction of crustal material follows the method adopted in our previous study (Zhao et al., 2010). For Al, Si, Ca, and Mg – which were proven to be of predominate crustal origin by computing their enrichment factors – their mineral oxides (Al_2O_3, SiO_2, CaO, and MgO) are derived directly from their elemental concentrations. For other crustal elements of remarkable pollution origin, their mineral oxides (K_2O, Fe_2O_3, MnO, Na_2O, Ti_2O) are estimated from Earth average crustal composition (Taylor and McLennan, 1995), based on their ratios to Al, while their individual excess is taken as a non-mineral part of these elements. Trace species is evaluated by adding the concentrations of all species analyzed by XRF (except for S, Al, Si, Ca, Mg, Fe, Ti, Mn, Na, K, and Cl) and the non-mineral part of Fe, Ti, Mn, Na, and K.

3 Results and discussion

3.1 Chemical species in $PM_{2.5}$

Table 2 compares average concentrations and standard deviations of $PM_{2.5}$ mass and chemical species at urban locations in Beijing, Chongqing, and Guangzhou from this study with those in Shanghai – the largest city in YDR (Ye et al., 2003). All the observations had lasted for at least one year except that conducted in Guangzhou city which lasted for three months and represented a winter case. Beijing and Chongqing exhibited comparable high $PM_{2.5}$ levels (difference <10 %), which both exceeded the national air quality standard of PM_{10} for residential areas (100 $\mu g\,m^{-3}$) and were at least 10 times those (5–10 $\mu g\,m^{-3}$) measured in US continental east (Hidy et al., 2009). The wintertime average $PM_{2.5}$ concentration in Guangzhou represents a seasonal peak. It is reasonable to anticipate that Guangzhou and Shanghai might exhibit comparable $PM_{2.5}$ levels.

The most abundant (>1 $\mu g\,m^{-3}$) species in $PM_{2.5}$ in the four Chinese megacities were OC, sulfate, nitrate, ammonium, EC, K, Cl, Si, and Fe, although their relative abundances varied from location to location. Among these species, all were found to be at the highest concentrations in Chongqing, except NO_3^-, which was at the highest level in Guangzhou. Most of the measured species in Beijing and Chongqing were also at similar levels, whereas some major species differed substantially. The average concentrations of OC and SO_4^{2-} in Chongqing were greater than those in Beijing by 23 % and 62 %, respectively, while the average concentrations of EC and NO_3^- in Beijing were higher than those in Chongqing by 28 % and 84 %. The average concentration of SO_4^{2-} in Guangzhou was comparable with that in US continental east (Hidy et al., 2009), whereas those of OC, EC, NO_3^-, and NH_4^+ in the four Chinese megacities were larger by one order of magnitude than those in the latter. These comparisons indicate that $PM_{2.5}$ and its major species in Chinese megacities were at very high pollution levels, and were mainly attributed to anthropogenic emissions.

The abundances of five major species (OC, EC, SO_4^{2-}, NO_3^-, and NH_4^+) in $PM_{2.5}$ and the mass ratio of OC to EC and that of nitrate to sulfate (i.e. $[NO_3^-]/[SO_4^{2-}]$) in these cities are compared in Fig. 2. Total carbon (TC, i.e. OC plus EC) and SNA amounted to 54–59 % of $PM_{2.5}$ mass in Beijing, Chongqing, and Guangzhou, and 71 % in Shanghai, much less than that (90 %) measured during January 1995 through February 1996 in Los Angeles (Kim et al., 2000). In the four Chinese megacities, the percentages of TC and SNA in $PM_{2.5}$ were very close (differences <2 %). In Los Angeles, SNA shared much more contribution (26 %) to $PM_{2.5}$ mass than TC. This implies that both primary and secondary particles had significant contribution to $PM_{2.5}$ mass in the Chinese megacities, since EC and part of OC are of primary sources. OC was the most abundant single specie and accounted for similar percentages (21–25 %) in $PM_{2.5}$ in the

Table 1. Brief introduction of $PM_{2.5}$ sampling and analyses in selected locations across China.

Location	Site description	Major source influences	Study period (yy.mm.dd)	Sample number	Sampler	Function/ analyses	OC&EC method	Reference
Wrumuqi	Urban-residential	Coal combustion, industry, traffic, dust	07 winter	131	TSP/PM_{10}/$PM_{2.5}$-II	Elements, ions, BC		Li et al. (2008)
Lanzhou	Urban-core	Coal combustion, industry, traffic, dust	05.04.01–06.01.11	18–25 per season	TH-150	Elements, ions		Tao (2009)
Xi'an	Urban-residential	Coal combustion, industry, traffic, dust	07.12.15–08.11.14	123	Mini-volume (sampling $PM_{1.0}$)	Ions, OC&EC	TOR	Shen et al. (2010)
Chengdu	Urban-residential	Coal & biofuel combustion, industry, traffic, dust	02.01.08–22	15		Speciation		Wang et al. (2004)
Chongqing	Urban-residential	Coal & biofuel combustion, industry, traffic, dust	05.02.01–06.04.30	60 (168h)	TCSS	Speciation	TOR	This study
Taiyuan	Urban-core	Coal combustion, industry, traffic, dust	05.12.18–06.02.03	48	TEOM1400a	Mass, OC&EC	TOR	Meng et al. (2007)
Beijing	Urban-residential	Coal combustion, industry, traffic, dust	99.09.30–00.06.08	48×2	TCSS	Speciation	TOR	He et al. (2001)
Tongliao	Rural sand land	Coal & biofuel combustion, sand dust	05.03.03–05.05.31	51	2 Mini-volume	Speciation	TOR	Shen et al. (2007)
Changbai	Rural forest		07.07.23–28		Anderson sampler	Ions, OC&EC	TOR	Li et al. (2010)
Changdao	Rural island	Marine vessels, dust, sea salt	03.04.25–04.01.15	55	TSP/PM_{10}/$PM_{2.5}$-II	Ions, OC&EC	TOT	Feng et al. (2007)
Jinan	Urban-residential	Coal combustion, industry, traffic, dust	06.02–07.02		RAAS	Speciation	TOR	Yang et al. (2008)
Shanghai	Urban-residential	Coal combustion, industry, traffic, marine vessels, dust	99.03.20–00.03.27	53 (168 h)	TCSS	Speciation	TOR	Ye et al. (2003)
Nanjing	Urban-residential	Coal combustion, industry, traffic, dust	01.02.01–06, 01.09.21–28	15 (12 h)	Andersen sampler	Ions, OC&EC	TOT	Yang et al. (2005)
Guangzhou	Urban-residential	Coal combustion, industry, traffic, marine vessels, dust	02.10, 02.12, 03.03, 03.06	20	RAAS	Speciation	TOT	Hagler et al. (2006)
Shenzhen	Urban-industrial	Coal combustion, industry, traffic, dust	04.11.20–12.04	15	RAAS	Ions, OC&EC	TOT	Niu et al. (2006)
Hong Kong	Background, urban & downwind	Traffic, residual oil combustion, dust, sea salt	02.10, 02.12, 03.03, 03.06	20	RAAS	Speciation	TOT	Hagler et al. (2006)

four Chinese cities. EC percentage was much higher in Shanghai than in other Chinese megacities, but much lower than those in Los Angeles. The two cities both have large seaports, pointing to a common contribution from diesel powered ships cruising at sea near these coastal cities. Accordingly, Shanghai had the lowest average OC/EC ratio among the four Chinese cities. Compared to Beijing, Shanghai had more than double the percentage of diesel vehicle fleet in addition to a large amount of ship emissions from burning of low-quality bunker fuel (Zhou et al., 2009).

The mass ratio of $[NO_3^-]/[SO_4^{2-}]$ has been used as an indicator of the relative importance of stationary versus mobile sources of sulfur and nitrogen in the atmosphere (e.g., Arimoto et al., 1996; Yao et al., 2002). Arimoto et al. (1996) ascribed high $[NO_3^-]/[SO_4^{2-}]$ to the predominance of mobile sources over stationary sources of pollutants. High $[NO_3^-]/[SO_4^{2-}]$ of 2.0 in downtown Los Angeles was attributed in part to the fact that southern California did not use coal (Kim et al., 2000). Among the four Chinese megacities, average $[NO_3^-]/[SO_4^{2-}]$ was highest in Guangzhou, which was greater by factors of 3.4–10 than those in Beijing, Shanghai, and Chongqing, and even greater than that in Los Angeles by 17 %. This comparison implies that mobile sources (including ship emissions in the Pearl River flowing across

Table 2. Comparison of $PM_{2.5}$ mass concentrations and chemical compositions at urban locations in four typical Chinese megacities.

	Beijing 2005.3 ~ 2006.2	Chongqing 2005.3 ~ 2006.2	Shanghai 1999.3 ~ 2000.5	Guangzhou 2008.12 ~ 2009.2
		$\mu g\,m^{-3}$		
$PM_{2.5}$	118.5 ± 40.6	129.0 ± 42.6	67.6	81.7 ± 25.6
OC	24.5 ± 12.0	30.13 ± 11.0	16.80	17.5 ± 7.6
EC	8.19 ± 5.96	6.39 ± 2.56	6.49	4.1 ± 2.0
SO_4^{2-}	15.8 ± 10.34	25.6 ± 9.03	13.00	5.6 ± 2.6
NO_3^-	10.1 ± 6.09	5.46 ± 3.65	5.78	12.0 ± 5.1
NH_4^+	7.30 ± 4.17	7.90 ± 3.78	5.66	4.7 ± 1.7
K	3.52 ± 1.77	4.29 ± 1.65	2.03	3.1 ± 1.15
Cl	2.30 ± 2.41	1.69 ± 1.86	6.13	–
Si	1.79 ± 0.80	2.20 ± 1.38	1.22	–
Fe	1.13 ± 0.41	1.58 ± 0.82	0.90	1.85 ± 1.13
Ca	0.90 ± 0.39	1.12 ± 0.71	0.55	–
Al	0.79 ± 0.32	0.80 ± 0.56	0.46	–
Na	0.61 ± 0.28	0.67 ± 0.27	0.49	3.2 ± 1.62
Zn	0.53 ± 0.22	0.60 ± 0.28	0.54	1.36 ± 0.5
Mg	0.29 ± 0.12	0.28 ± 0.19	0.18	–
Pb	0.24 ± 0.12	0.32 ± 0.12	0.29	0.45 ± 0.21
Ba	0.21 ± 0.16	0.26 ± 0.15	–	0.07 ± 0.02
Mn	0.09 ± 0.03	0.14 ± 0.07	0.09	0.15 ± 0.07
Ti	0.08 ± 0.03	0.16 ± 0.18	–	0.11 ± 0.09
Cu	0.07 ± 0.03	0.06 ± 0.02	0.05	0.19 ± 0.08
		$ng\,m^{-3}$		
Cr	50 ± 30	190 ± 100	–	70 ± 20
Cd	50 ± 30	70 ± 40	–	20 ± 10
Br	30 ± 20	60 ± 30	30	–
V	30 ± 20	50 ± 30	–	20 ± 20
Ni	20 ± 20	30 ± 30	10	–
As	20 ± 10	30 ± 20	–	40 ± 30
Se	20 ± 10	30 ± 20	20	–

–: not determined. In Chongqing, the data were for JB site. In Shanghai, Ye et al. (2003) collected $PM_{2.5}$ samples at urban Shanghai (Hailanlu site) with the same speciation sampler as that adopted in Beijing and Chongqing in this study.

the city) were likely more important in Guangzhou than in the three other megacities. For comparison, annual mean of ambient NO_2 concentration in 2009 was a litter bit higher ($56\,\mu g\,m^{-3}$) in Guangzhou among the four megacities. In Beijing, Shanghai, and Chongqing, the $[NO_3^-]/[SO_4^{2-}]$ ratios were even lower than the value of 0.9 observed during January and February 1999 in Philadelphia in southeast USA (Tolocka et al., 2001), around which coal-fired power plants were concentrated, indicative of the predominance of stationary sources over mobile sources.

Both concentration and percentage of sulfate in $PM_{2.5}$ were found to be highest while the $[NO_3^-]/[SO_4^{2-}]$ ratio was lowest in Chongqing, suggesting that stationary sources were likely more important than mobile sources. In Chongqing, the coal consumption (2.57 million tons) in 2005 was comparable to that in Beijing, whereas the vehicle population (0.47 million) in that year was less than one-quarter that in Beijing (http://www.cqtj.gov.cn/tjnj/2008/). However, the annual average ambient concentration of SO_2 in Chongqing ($73\,\mu g\,m^{-3}$) in 2005 was higher than that in Beijing ($50\,\mu g\,m^{-3}$) by 46 %, which reflected the emission difference of SO_2 as the precursor of sulfate in fine particles. Beijing has been leading the country in implementing strict coal-fired boiler and vehicular emission standards compared to state criteria. Only low-sulfur (coal content <0.5 %) coal has being permitted for use in Beijing since 1998. In contrast, high-sulfur (>3.5 %) coal is produced and consumed in Chongqing (Zhang et al., 2010).

3.2 $PM_{2.5}$ speciation across China

As diagrammed in Fig. 3, $PM_{2.5}$ mass and speciation varied substantially over geographical regions in China. Near six-fold variations of average $PM_{2.5}$ concentrations

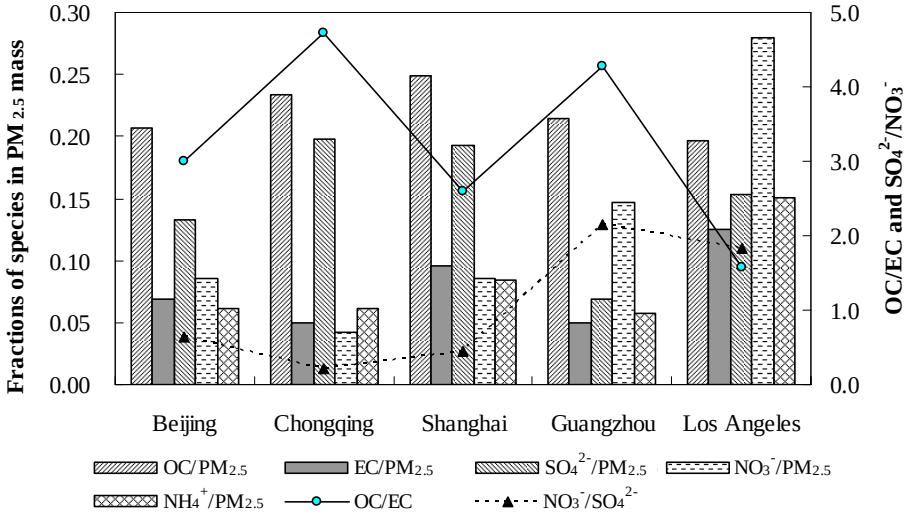

Fig. 2. Relative abundances of five major species in $PM_{2.5}$ and mass ratios of OC-EC and nitrate-sulfate in four Chinese mage cities. Those in Los Angeles are plotted for comparison.

(34.0–193.4 $\mu g\,m^{-3}$) were evident across the nation. High $PM_{2.5}$ levels occurred in the cities in the northern and western regions, where most sites had average mass concentrations in excess of 100 $\mu g\,m^{-3}$. In each region, high $PM_{2.5}$ concentrations usually predominated in winter season. The highest $PM_{2.5}$ concentration was recorded in the winter of 2005 in Taiyuan – the capital city of Shanxi province which had the highest coal and coke production in China. Low $PM_{2.5}$ levels (<40 $\mu g\,m^{-3}$) appeared in remote forest areas (Changbai Mountain) and in Hong Kong.

At both urban (e.g. Jinan, Nanjing, and Shanghai) and rural (e.g. Changbai Mountain and Changdao Island) sites in the eastern region, SNA typically constituted 40–57 % of the average $PM_{2.5}$ mass, indicative of the characteristic of regional fine particulate pollution in this region. The maximum SNA level (68.9 $\mu g\,m^{-3}$) and fraction (57 %) in $PM_{2.5}$ occurred in Jinan and Changdao - the capital city of and a resort island in Shandong province, respectively. SNA formation is significantly influenced by source emissions of their precursors and atmospheric oxidation capacity, while the partition of ammonium nitrate is strongly affected by ambient temperature. Benefiting from "(Economic) Reform and Open (Door) Policy", the eastern region has been experiencing rapid industrialization and urbanization over the past thirty years. At the same time, huge energy consumption for such a development has inevitably enhanced both primary emission and secondary aerosol formation of fine particles in the region (Fang et al., 2009). In fact, this region is largely coincident with that of maximum anthropogenic sulfur dioxide emissions, and Shandong is the greatest single contributor on a provincial basis. Statistically, the eastern region consumes 43 % of gross coal while its land only covers 11.1 % of the total land area of China. As a result, its sulfur dioxide and nitride oxide emissions per land area are 3.3 and 4.4 times their corresponding national averages. For Changdao Island, which is located in the demarcation line between Bohai Sea and Yellow Sea in Northern China, it is reasonable to have abundantly aged and secondary aerosols including SNA when northwesterly winds prevail and carry the continental aerosols heading toward the Pacific Ocean during winter and spring (Feng et al., 2007). In Linan, an inland rural area in YDR, average $PM_{2.5}$ concentration in November 1999 reached as high as 90 $\mu g\,m^{-3}$, and 43 % of the mass was SNA (Xu et al., 2002), putting in evidence for the characteristics of regional fine particulate pollution in YDR.

OM had a constant and significant contribution to $PM_{2.5}$ mass at all the sites with carbonaceous species data available. Along with the associated hetero atoms, roughly one-fifth to over one-half the average fine mass was OM across China, with the highest percentage at the westernmost site (i.e. Wulumuqi) and the lowest one at the easternmost site (i.e. Changbai Mountain). OM plus SNA accounted for 62–90 % of $PM_{2.5}$ mass at all the sites except those devoid of relevant data (i.e., Shenzhen, Taiyua, Lanzhou, and Tongliao), and in Beijing, Wulumuqi, and Xi'an, where SNA and OM explained a similar lower percentage (53–54 %) of $PM_{2.5}$ mass. In Changbai Mountain, a boreal-temperate climatic zone, SNA and OM together accounted for about 70 % of $PM_{2.5}$ mass and more than 45 % were SNA in the summer of 2007 (Li et al., 2010). It is interesting to note that similar results (not shown in Fig. 3) were found for two other forest sites located in temperate (i.e., Dongping National Forest Park in Chongming Island in Shanghai) and subtropical climatic zones (i.e., Dinghu Mountain Nature Reserve in Guangdong province) at that time (Li et al., 2010). Also noted is that all of the three forest areas are located along the north latitude in eastern China.

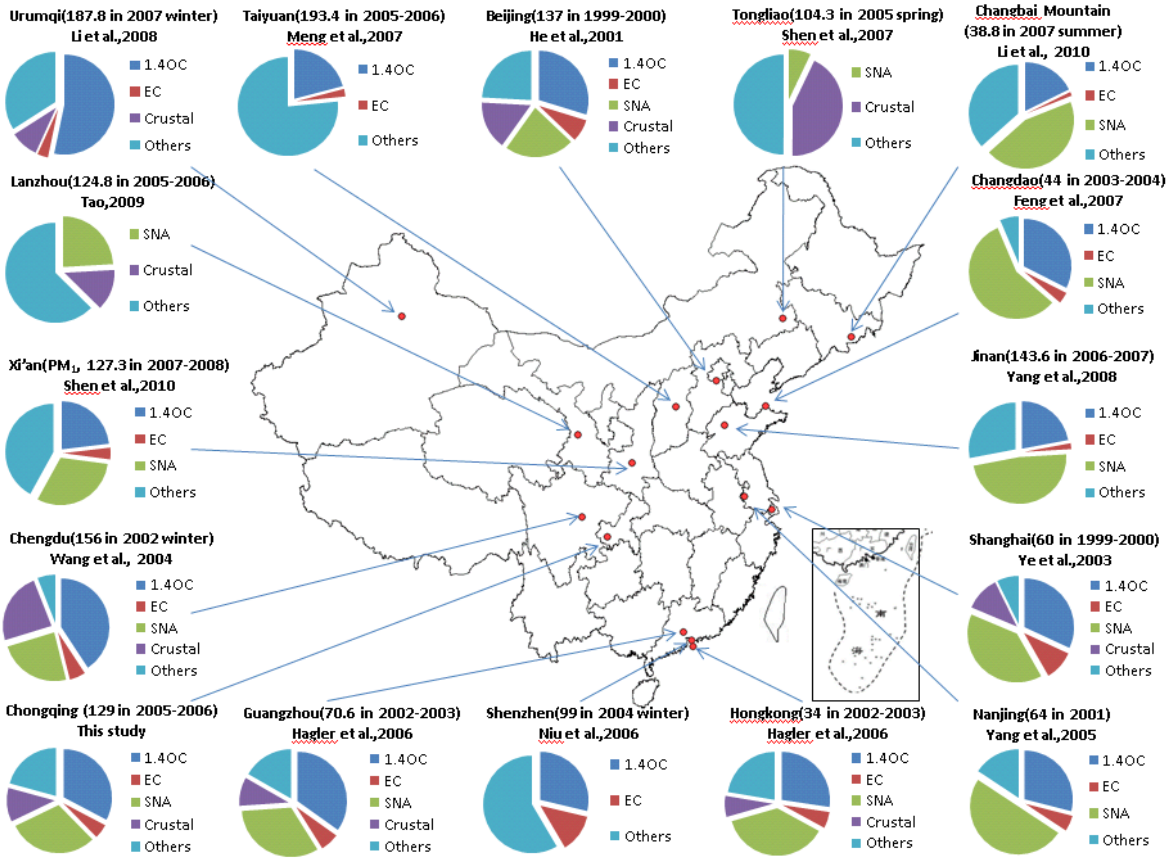

Fig. 3. $PM_{2.5}$ (except $PM_{1.0}$ in Xi'an) speciation at urban and rural locations in China. The rural sites are Changbai Mountain, Tongliao, and Changdao. Averaging periods, average $PM_{2.5}$ mass ($\mu g\,m^{-3}$), and references are indicated. A coefficient of 1.4 to convert OC to OM was adopted for all the sites for fair comparison. For some sites without elements data, crustal material was not reconstructed. In Taiyuan and Shenzhen, only OC and EC were analyzed, while in Lanzhou carbonaceous species were not determined.

Crustal material also contributed significantly to $PM_{2.5}$ mass. In urban areas in mainland China, mineral dust in $PM_{2.5}$ is usually at about 10 $\mu g\,m^{-3}$ level or accounted for about 10 % of total mass. In certain areas and during certain periods susceptible to be influenced by dust events, crustal material loading rose dramatically, even in fine particles. Its fraction in $PM_{2.5}$ mass was high at 43 % in the spring of 2005 at Tongliao site, which is located in the centre of the Horqin sand land in Inner Mongolia (Shen et al., 2007). During the periods of five dust storms, $PM_{2.5}$ mass at Tongliao elevated to more than 200 $\mu g\,m^{-3}$ (ranging 203–299 $\mu g\,m^{-3}$), of which an average of 69 % was mineral dust (Shen et al., 2007). In the spring of 2000 when frequent sand dust invaded Beijing, average concentration of mineral dust was 21.1 $\mu g\,m^{-3}$, comprising 18.6 % of $PM_{2.5}$ mass (Yang et al., 2004). In the week with the severest dust storm sweeping Beijing in that season, its percentage soared to 41.6 %, more than three times as much as its annual average percentage. It is noted that while northern China is apt to be impacted by regional and/or local soil dust since it possesses many deserts and arid loess-land, dust storms come to central and southwestern China, too (Zhao et al., 2010). In addition to the transported desert dust is the high contribution from the local soil dust mainly due to low plant coverage rate (18 % for forest coverage rate in China) and rapid urbanization, as revealed by our previous finding that calcium – one of typical crustal elements and the tracer of construction dust – in $PM_{2.5}$ in Beijing and Shanghai was modestly enriched in relation to aluminum (F. Yang et al., 2005). In Hong Kong and Macao – the two special administrative regions located in PRDR – about 7–12 % of $PM_{2.5}$ mass was crustal material in different locations covering background, urban, kerbside, and downwind urban sites (Wu et al., 2003; Hagler et al., 2006). Even in the three forest locations previously mentioned, crustal material amounted to 2.1–6.3 $\mu g\,m^{-3}$ and explained 7–11 % of $PM_{2.5}$ mass (Li et al., 2010).

In contrast, in the Canadian National Air Pollution Surveillance (NAPS) network, soil-derived oxides contributed only a few percent (3–9 %) of total $PM_{2.5}$ mass, and monthly median concentrations of mineral dust were generally less than 1 $\mu g\,m^{-3}$ (Dabek-Zlotorzynska et al., 2011). It was a similar case in USA (Blancard, 2003). In Pittsburgh,

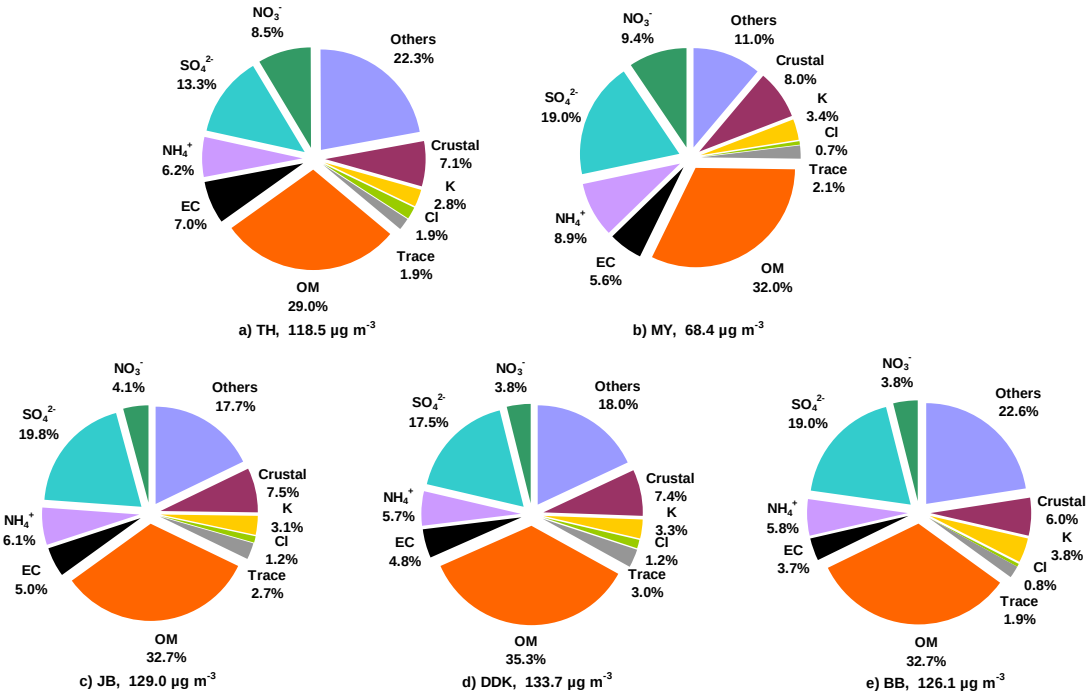

Fig. 4. Average $PM_{2.5}$ speciation at TH and MY in Beijing and at JB, DDK, and BB in Chongqing during March 2005 through February 2006.

Pennsylvania, the average concentration of crustal material was 1 μg m^{-3} and contributed approximately 3–6 % of total $PM_{2.5}$ mass (Rees et al., 2004). Cheung et al. (2011) found that in the Los Angeles area crustal material was the most abundant category in coarse particulate matter with percentage contributions ranging 38.3–44.1 % on a seasonal basis. In Europe, the annual average concentrations of mineral dust were generally no more than 2 μg m^{-3} and accounted for less than 10 % of $PM_{2.5}$ mass, except those measured in the kerbside and urban sites in Spain (Putaud et al., 2010) and Sweden (Querol et al., 2004). High content of mineral dust in $PM_{2.5}$, therefore, is one of the distinct characteristics of fine PM speciation across China.

3.3 $PM_{2.5}$ speciation in two megacites: Beijing and Chongqing

Figure 4 compares the material balance for the average OM, EC, ammonium, nitrate, sulfate, crustal material, potassium, chlorine, and others (unexplained mass) in $PM_{2.5}$ for one whole year from March 2005 through February 2006 at the two sites in Beijing and the three sites in Chongqing. Potassium and chlorine are included separately due to their high abundance). As observed in our previous study in Beijing, assuming that potassium is present as an oxide in mineral dust may not be correct since it was found to be largely soluble and hence is assumed to be associated with biological material (He et al., 2001). In Beijing, annual average urban excess of $PM_{2.5}$ concentration between the paired rural/urban sites was 50 μg m^{-3} – near three quarters the average $PM_{2.5}$ mass at the rural site. In contrast, annual average $PM_{2.5}$ levels in Chongqing showed much less spatial variations with no more than 6 % of urban/rural difference over distances of 30–40 km.

The five sites exhibited similar $PM_{2.5}$ mass balances at first glance although with varying $PM_{2.5}$ levels. OM is the most abundant single species at all the sites except MY, with higher levels in Chongqing than in Beijing. The sums of sulfate, nitrate, and ammonium accounted for comparable percentages (26.0–30.0 %) in $PM_{2.5}$ mass at all of the sites in Chongqing and the urban site in Beijing, whereas the single fractions of sulfate and nitrate were much different. As the second abundant identified species in $PM_{2.5}$, sulfate was much more abundant in Chongqing than in urban Beijing, whereas the percentages of nitrate in Beijing were more than twice those in Chongqing. In Chongqing, high precursor emissions (SO_2) and specific meteorology, such as mild wind (wind speed 0.9–2.1 m s^{-1}), high ambient temperature (5.3–31.3°) and relative humidity (52.3–84.9 %), also favored the accumulation of local emissions and formation of sulfate (Zhao et al., 2010). On the contrary, the high temperature is disadvantageous for ammonium nitrate in particulate status. As the rural site in Beijing, MY site presented a much higher percentage (37.3 %) of SNA than at all the other sites. At this site, both the percentages of nitrate and ammonium were highest and that of sulfate was second highest, making it the only site at which SNA contributed more to $PM_{2.5}$ mass than OM. This probably indicates that there was a significantly

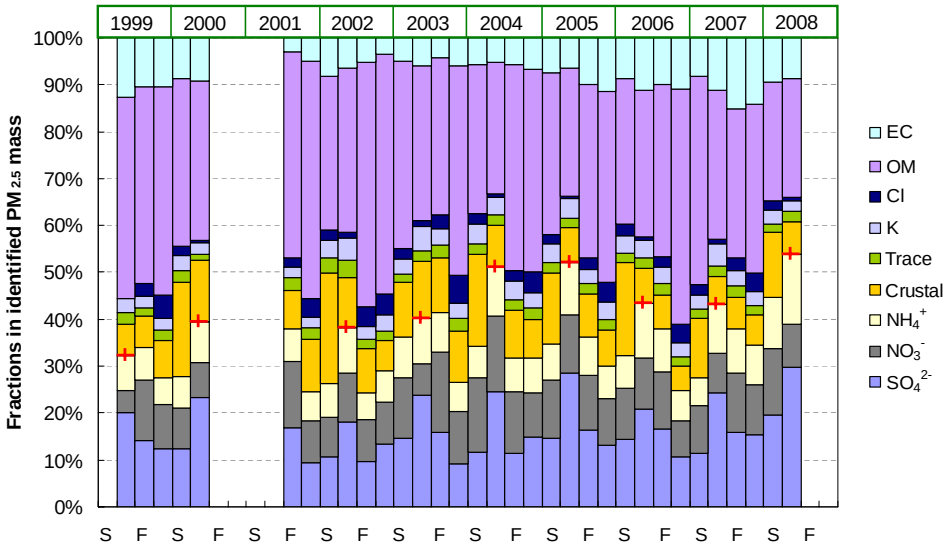

Fig. 5. Seasonal $PM_{2.5}$ speciation abundances at TH in Beijing from the summer of 1999 through the summer of 2008. Sampling years and seasons ("S" means spring and "F" means fall) are indicated. Average percentages of SNA in each summer are marked with cross symbols.

larger fraction of transported secondary aerosols and/or aged aerosols in rural Beijing.

Crustal material, trace elements, potassium, and chlorine individually accounted for comparably small fractions in $PM_{2.5}$ mass at all of the sites, of which the sum ranged 12.5–14.9 %. Crustal material alone shared 6–8 % of $PM_{2.5}$ mass with the higher percentage occurring at MY, probably resulting from a higher contribution of surrounding agricultural activities. In both Beijing and Chongqing, the fraction of potassium was larger at the rural sites whereas the situation is the opposite for EC. Our previous study conducted in Beijing indicates that the majority of potassium is water soluble, which is a tracer of biomass burning (He et al., 2001). This is the case for the current study and implies that biomass burning exerted greater impact on fine particles in the rural areas than in the urban areas. In contrast, the urban-rural variation in EC abundance indicates the much weaken contribution of vehicular emission in the rural areas compared to the urban areas. High abundance of chlorine is believed to be associated with coal combustion and the contribution from sea-salt particles is not important (Yao et al., 2002), since the sampling sites are at least 200 km from the sea.

Figure 5 shows seasonal variations of $PM_{2.5}$ speciation abundances at TH in Beijing from the summer of 1999 through to the summer of 2008. Weekly $PM_{2.5}$ concentrations ranged 12.0–350 $\mu g\,m^{-3}$ and averaged at $116 \pm 50.7\,\mu g\,m^{-3}$ during this period. Annual mean of $PM_{2.5}$ concentrations increased from 113 $\mu g\,m^{-3}$ in the year of 2000 to 126 $\mu g\,m^{-3}$ in 2004 and 2006, then decreased and reached the lowest one (110 $\mu g\,m^{-3}$) in 2008. SNA dominated the temporal variations in inorganic species and exhibited a general increase trend in abundance, especially in the summertime as marked in Fig. 5. On a yearly basis, SNA fraction in identified $PM_{2.5}$ mass rose from 29 % in 2002 to 36 % in 2007. This implies that the contribution from long-range transport was likely on the growth track, thus the characteristic of "complex air pollution" had being enhanced in Beijing. The tendency of annual sulfate and ammonium concentrations were higher in the early years and lower in the latter years (down 5 % and 8 % during 2000–2008, respectively), similar to that of $PM_{2.5}$ mass. On the other hand, nitrate experienced a solid growth by 20 %. The mass ratio of sulfate to nitrate thus showed a slow decrease trend during the period, indicating that the importance of vehicular emissions had also been enhanced. This trend reflects the fact that vehicular fuel consumption kept soaring compared to coal consumption in Beijing over the period. For example, the vehicle fleet and coal consumption amounts in Beijing were 2.1 million and 3.07 million tons in 2005, increased by 120 % and 16 % compared to those in 1999, respectively (http://www.bjstats.gov.cn/tjnj/2008-tjnj).

In summer, high temperatures and humidity and strong atmospheric oxidation (high O_3 concentration) are in favor of sulfate formation from its precursors. In the meantime, particles and their precursors are frequently transported to Beijing from the south with high emissions under the control of the West Pacific subtropical high (Streets et al., 2007; Xu et al., 2006). Sulfate ammonium was a major component in the transported particles (Jia et al., 2008), in which SO_4^{2-} plus NH_4^+ could contribute 90 % of their total amounts (Guo et al., 2010). In contrast, low NO_3^- percentages were usually found in summer. As nitrate tends to be in a gaseous status in transported higher temperature air parcels from the south, its majority is likely formed locally.

Crustal material in $PM_{2.5}$ had the maximum abundance (all >10 %) in spring at both TH and MY, especially when there appeared to be frequent dust incursions. While spring usually saw frequent dust events, their frequency and intensity, thus their impacts on fine particles in Beijing, varied from year to year. In the springs of 2000, 2002, 2004, and 2006 when frequent dust storms occurred (http://www.zhb.gov.cn/plan/zkgb), crustal material showed significantly elevated abundance (up to about 20 %). In the spring of 2006, the crustal contributions were 18.7 % and 23.9 % at TH and MY, respectively. Consistent with increasing dust intrusions in Beijing from 2005 through 2006 (18 versus 4 times) (Wu et al., 2009; http://www.zhb.gov.cn/plan/zkgb), their percentages of total mass at TH and MY were higher in 2006 than those in the spring of 2005 by factors of 1.3 and 1.9, respectively.

Trace elements plus K and Cl accounted for 6.3–10.3 % of $PM_{2.5}$ mass. The abundances of both trace elements and K had no notable seasonal trend or urban-rural difference. In contrast, Cl percentage in $PM_{2.5}$ mass exhibited an order of magnitude variations (in the range of 0.4–4.2 % at TH and 0.2–2.1 % at MY) with the highest percentage in winter and the lowest in summer. This probably implies that it was mainly attributed to local sources, such as coal combustion, and presented as particles in cold weather. This hypothesis remains to be verified in further research.

4 Conclusions

Near six-fold variations in average $PM_{2.5}$ concentrations (34.0–193.4 $\mu g\,m^{-3}$) across China were found with high loadings (>100 $\mu g\,m^{-3}$) occurring in urban areas in the northern and western regions and low levels (<40 $\mu g\,m^{-3}$) in remote forest areas (Changbai Mountain) and in Hong Kong. The highest $PM_{2.5}$ concentration was recorded in the winter of 2005 in Taiyuan – the capital city of Shanxi province with the highest coal production in China. The percentages of the sum of sulfate, nitrate, and ammonium, organic matter, crustal material, and elemental carbon in $PM_{2.5}$ mass ranged 7.1–57 %, 17.7–53 %, 7.1–43 %, and 1.3–12.8 %, respectively. At both urban and rural sites in the eastern region, SNA aerosol typically accounted for 40–57 % of average $PM_{2.5}$ mass, indicative of the characteristics of regional fine particulate pollution and more intensive "complex atmospheric pollution" compared to the western region. OM had constant and significant contribution to $PM_{2.5}$ mass. OM and SNA together constituted 53–90 % of $PM_{2.5}$ mass at all the sites except those sites devoid of relevant data. Due to transported desert dust and local soil and construction dust, high content of crustal material, usually being at $\sim 10\,\mu g\,m^{-3}$ level or accounting for ~ 10 % of total mass in urban areas, is one of the characteristics of $PM_{2.5}$ speciation in China. In the spring of frequent dust storms in the sand land region, it could contribute more than 40 % to $PM_{2.5}$ mass on a seasonal basis.

In the four representative megacities – Beijing, Chongqing, Shanghai, and Guangzhou, $PM_{2.5}$ mass and major components (except sulfate) were at higher levels than those in US continental east by one order of magnitude, indicating that their high $PM_{2.5}$ loading were mainly attributed to anthropogenic sources. The mass ratio of nitrate to sulfate ($[NO_3^-]/[SO_4^{2-}]$) in $PM_{2.5}$ in Guangzhou was greater than those in Beijing, Shanghai, and Chongqing by factors of 3.4–10, implying that mobile sources likely contributed more to $PM_{2.5}$ mass in this megacity in PRDR than in all three others. In contrast, the highest concentrations of sulfate in both amount and percentage of total mass, and the lowest $[NO_3^-]/[SO_4^{2-}]$ all occurred in Chongqing, indicative of that stationary sources being more important in this megacity in the southwestern region with huge consumption of high-sulphur coal. In Beijing, annual average urban excess of $PM_{2.5}$ concentration was as much as 50 $\mu g\,m^{-3}$ (near three quarters of mean concentration at the rural site) between the paired rural/urban sites over a distance of 70 km. The observed intra-city variations in $PM_{2.5}$ mass and constituents imply that both local emissions and regional transport contributed significantly to the high fine particle levels in Beijing. In contrast, annual average $PM_{2.5}$ levels in Chongqing showed much less spatial variations with no more than 6 % of urban/rural excesses over distances of 30 to 40 km, indicative of the predominant contributions from the local sources. During the ten-year period from 1999 through 2008 in urban Beijing, both SNA and $[NO_3^-]/[SO_4^{2-}]$ exhibited steadily increasing trends, implying that the characteristic of "complex atmospheric pollution" and the contribution from mobile sources were both being enhanced.

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