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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 database from literature and our observations, chemical species and reconstructed speciation of $PM_{2.5}$ in several representative Chinese megacities and across China were compared to draw insights into the characteristics of $PM_{2.5}$ speciation. $PM_{2.5}$ mass and speciation 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 along northern region and in western urban areas. At both urban and rural sites in eastern region, sum of sulfate, nitrate, and ammonia (SNA) typically constituted 40–57% of $PM_{2.5}$ mass, indicative of the regional characteristics of fine particulate pollution and more intensive "complex atmospheric pollution" compared to western region. Particulate organic matter (POM) had constant and significant contribution to $PM_{2.5}$ mass. POM plus SNA accounted for 62–90% of $PM_{2.5}$ mass at most of the sites. $PM_{2.5}$ speciation in China was also characterized by high content of mineral dust. In four representative megacities (i.e. Beijing, Chongqing, Shanghai, and Guangzhou) with substantially higher levels of all the species except that NO_3^-, NH_4^+, and EC in $PM_{2.5}$ than those in Los Angeles, distinct differences in nitrate and sulfate levels and their mass ratio $[NO_3^-]/[SO_4^{2-}]$ imply that mobile source is likely more important than stationary (coal combustion) source in Guangzhou whereas in Chongqing the situation is contrary. The observed intra-city variations in $PM_{2.5}$ mass and speciation indicate that local emissions and regional transportation both contributed significantly to high fine particles levels 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 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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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. The PM mass concentration and 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 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 estimate its chemical extinction and to characterize hazy (Watson, 2001). Lack of particle 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, as exceedances of Chinese annual-average PM_{10} standard of 100 µg m^{-3} still occur in about one-third of all the cities monitored. $PM_{2.5}$ 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

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across the nation (Feng et al., 2007). $PM_{2.5}$ 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 to perform their speciation reconstruction. Furthermore, based on more than one-year simultaneous speciation sampling of $PM_{2.5}$ at paired rural/urban sites, this paper will focus on characterization and comparison of temporal and spatial variations in $PM_{2.5}$ speciation in two representative megacities with high $PM_{2.5}$ loadings but distinctly different emissions and meteorological conditions in China, Beijing and Chongqing.

2 Experimental and reconstruction of $PM_{2.5}$ speciation

2.1 Study locations and sampling and analysis

The study was conducted in Beijing, Chongqing, and Guangzhou, which are the representative mega cities of three regions lying in different climatic regions, i.e. Beijing-Tianjin region, Sichuan basin, and Pearl Delta Region (PDR), 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 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 can not be easily expelled. 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

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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 100 km apart to the northeast of downtown.

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 was 0.9–1.6 m s^{-1} from 1979 to 2007 (http://www.cqtj.gov.cn/tjnj/2008/). The specific geographic and meteorological conditions favor the accumulation of regional and local pollutants. Two urban sites with 12 km 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 on the roof of governmental office building of Dadukou District (DDK, 29°29′ N, 106°29′ E); and a rural site was near the Jinyun Mountain in Beibei District (BB, 29°50′ N, 106°25′ E), ∼ 40 km to the northwest of downtown.

Guangzhou, with a population of approximately 11 million and an area of 7434 km^2, is located in the Pearl Delta region, a transitional zone of the East Asian monsoon system, i.e. southwest wind in summer from South China Sea and northeast wind in winter from Mainland China. A domestic sampler (TH100-$PM_{2.5}$, Wuhan) was 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 mixture area.

A three-channel speciation sampler (Aerosol Dynamics Inc., Berkeley, CA) 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 kept collecting $PM_{2.5}$ samples with the same sampler at TH from 1999 through 2008. Details of sampling procedure and quality control have been

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provided in our previous work (He et al., 2001). 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 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 from gravimetry method with an analytical balance (Mettler Toledo AG285), after stabilizing under constant temperature ($20 \pm 5^{\circ}$) and humidity ($40\% \pm 5\%$). Using EPA standard method, twenty three 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 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 reflectance method.

2.2 Reconstruction of $PM_{2.5}$ speciation

As described below, organic and elemental carbon, secondary inorganic ions (i.e. sulfate, nitrate, and ammonium, SNA), 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 sum of 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^+ (or simply SNA), particulate organic mass (POM), EC, crustal material, trace species, and others.

POM 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

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organic materials according to the suggestion by Turpin and Lim (2001). The coefficient to convert OC to POM 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 noted 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 proved 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 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 1 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, Los Angels, and Brisbane from literatures. All the observations had lasted for at least one year except that conducted in Guangzhou City lasted for three months and represented a winter case. Shanghai is the largest city in YDR. Los Angels is a mega city of relatively high air pollution level in the United States, while Brisbane is a clean subtropical coastal city in Australia. It is noted that

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average $PM_{2.5}$ concentrations were classified into three orders of magnitudes over these cities. 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 $\mu g\,m^{-3}$). 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, which were more than twice the annual mean of $PM_{2.5}$ concentration in Los Angeles in 1995.

The most abundant (> 1 $\mu g\,m^{-3}$) species in the four Chinese megacities were OC, sulfate, nitrate, ammonium, EC, and K, Cl, Si, and Fe, although their relative abundances varied from site to site. Most of measured species in $PM_{2.5}$ 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%. Compared to those measured in Los Angeles, the concentrations of NO_3^-, NH_4^+, and EC in the four Chinese cities were comparable while those of other species were greater by factors of 1–30. These differences were even greater compared to those measured in Brisbane, since the concentrations of all the species except EC, Na, and Br were larger by at least one order of magnitude. 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 $PM_{2.5}$ mass 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%) in Los Angels. In the four Chinese megacities, the mass fractions of TC and SNA in $PM_{2.5}$ were very close (differences < 2%). In contrast, SNA occupied much more share (26%) in $PM_{2.5}$ mass than TC in Los Angeles. This implies that both primary and secondary particles had significant contribution to $PM_{2.5}$ mass in

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the Chinese megacities, whereas secondary particles were predominant contributors in Los Angeles. OC was the most abundant single specie and accounted for similar percentages (21–25%) in $PM_{2.5}$ in the four Chinese cities. EC percentage in $PM_{2.5}$ mass was much higher in Shanghai than in other Chinese megacities, but much lower than those in the two foreign cities. These three cities all 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, which was still much higher than that in Los Angels. Compared to Beijing, Shanghai had more than doubled percentage of diesel vehicle fleet besides large amount of ship emissions from burning of low-quality of 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 source over stationary source of pollutants. High $[NO_3^-]/[SO_4^{2-}]$ of 2.0 in downtown Los Angeles was attributed in part to 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 were likely more important than stationary sources (including ship emissions in the Pearl River) in Guangzhou. In the three other Chinese megacities, the $[NO_3^-]/[SO_4^{2-}]$ ratios were even lower than the value of 0.9 observed by Tolocka et al. (2001) during January and February 1999 in Philadelphia in Southwest USA, where coal-fired stationary sources were concentrated, indicative of the predominance of stationary sources over mobile sources.

In Chongqing, 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, suggesting that stationary sources were likely more important than mobile sources. In Chongqing, the coal consumption

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(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 of 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 to use in Beijing since 1998, whereas high-sulfur (> 3.5%) coal is produced and consumed in Chongqing (Zhang et al., 2010). In addition, warm and humid weather and mild wind in Chongqing also favor formation and accumulation of sulfate.

3.2 $PM_{2.5}$ speciation in 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 (34.0–193.4 $\mu g\,m^{-3}$) were evident across the nation. High $PM_{2.5}$ levels occurred along northern region and in western urban areas, where most sites exhibited 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 2005 winter in Taiyuan, the capital city of Shanxi province which had the highest coal production in China at that time.

At both urban (e.g. Jinan, Nanjing, and Shanghai) and rural (e.g. Changbai mountain and Changdao) sites in eastern region, SNA aerosol typically constituted 40–57% of the average $PM_{2.5}$ mass. Maximum SNA level (68.9 $\mu g\,m^{-3}$) and percentage (57%) 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 and atmospheric oxidation capacity. Benefiting from "(Economic) Reform and Open (Door) Policy", eastern region has been experiencing rapid industrialization and

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urbanization over the past thirty years. At the same time, huge energy consumption for such development has inevitably enhanced both primary emission and secondary 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 contributor on a provincial basis. Statistically, the eastern region consumes 43% of gross coal while its land area only accounts for 11.1% of total land area. As a result, its SO_2 and nitride oxides emissions per land area are 3.3 and 4.4 times their corresponding national average, respectively. For Changdao county in Shangdong province, which is located in the demarcation line between Bohai Sea and Yellow Sea in Northern China and in the transport path of the continental aerosols heading toward the Pacific Ocean in winter and spring due to the East Asia Monsoon (Feng et al., 2007), it is, therefore reasonable to have abundant aged and secondary aerosols including SNA. 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), indicative of the regional characteristics of fine particulate pollution in this region.

POM had constant and significant contribution to $PM_{2.5}$ mass at all the sites with carbonaceous species data. Along with the associated hetero atoms, roughly one-fifth to over one-half the average fine mass was POM 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). POM plus SNA accounted for 62–90% of $PM_{2.5}$ mass at all the sites except those sites devoid of relevant data (i.e. Shenzhen, Taiyua, Lanzhou, and Tongliao), and those sites in Beijing, Wulumuqi, and Xi'an, where SNA plus POM explained a similar lower percentage (53–54%) of $PM_{2.5}$ mass. In Changbai Mountain, a boreal-temperate climatic zone, SNA and POM together accounted for about 70% of $PM_{2.5}$ mass and more than 45% were SNA in 2007 summer (Li et al., 2010). It is interesting that similar results (not shown in Fig. 3) were found for other two 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

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Guangdong province) at that time (Li et al., 2010). Also noted is that all the three forest areas are located along north latitude in eastern China.

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 $\sim 10\,\mu g\,m^{-3}$ level or accounted for $\sim 10\%$ total mass. Even in Hong Kong and the four forest locations previously mentioned, mineral dust explained 7%$\sim$ 10% of $PM_{2.5}$ (Hagler et al., 2006; Li et al., 2010). In certain areas and during certain periods susceptible to be influenced by dust events, crustal material loadings, even in fine particles rose sharply. It accounted for 43% of $PM_{2.5}$ mass in 2005 spring at Tongliao site, which is located in the centre of the Horqin sand land, and about 5 km from downtown Tongliao in Inner Mongolia (Shen et al., 2007). During the periods of five dust storms, $PM_{2.5}$ mass at Tongliao elevated to more than $200\,\mu g\,m^{-3}$ ($203–299\,\mu g\,m^{-3}$), of which 69% on average was mineral dust (Shen et al., 2007). In 2000 spring in 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, average mineral dust concentration reached $27.8\,\mu g\,m^{-3}$ and its percentage soared to 41.6%, more than three times its annual average percentage (Yang et al., 2004). At 16 representative urban and rural locations in North America, the contents of mineral dust in $PM_{2.5}$ were very low except that it was one of the dominant ($\sim$ 25%) chemicals at Netzahualcoyotl site in Mexico City, which had the highest $PM_{2.5}$ mass ($55.4\,\mu g\,m^{-3}$ in 1997) among all the sites (Blancard, 2003). Different from developed countries, high content of mineral dust in $PM_{2.5}$, therefore, is one of characteristics of fine PM speciation in China.

3.3 Temporal and spatial variations of $PM_{2.5}$ speciation in two representative mega cites: Beijing and Chongqing

Figure 4 gives the material balance for the average POM, EC, ammonium, nitrate, sulfate, crustal material, potassium, chlorine, and other (unexplained mass) in $PM_{2.5}$ for

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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 abundances. As observed in our previous study in Beijing, assuming potassium to be 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 $PM_{2.5}$ concentrations varied by 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 local emissions and regional transportation both contributed much to high fine particles loadings 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 predominant local contribution.

The five sites presented similar $PM_{2.5}$ mass balances at first glance although with varying $PM_{2.5}$ levels. POM is the most abundant single species at all the sites, with higher levels in Chongqing than in Beijing. Secondary inorganic species (i.e. SNA) accounted for comparable percentages (26.0–30.0%) in $PM_{2.5}$ mass at all the sites in the two mega cites except MY, the rural site in Beijing. MY site showed a much higher percentage (37.3%) and was the only site in which SNA contributed more to $PM_{2.5}$ mass than POM. This probably indicates there was significantly larger regional contribution of SNA at this rural site. In Chongqing, high precursor emissions and specific meteorology, such as mild wind (wind speed 0.9–2.1 $m\,s^{-1}$), high temperature (5.3–31.3°) and humidity (52.3–84.9%), also favored accumulation of local emissions and formation of secondary aerosols (Zhao et al., 2010). It is no doubt that the contributions of POM and SNA to $PM_{2.5}$ mass became greater on shorter time scale, i.e. on seasonal or weekly basis. At JB site in Chongqing, for instance, POM and SNA contributed up to 63.4% and 70.5% of weekly $PM_{2.5}$ mass, respectively. Higher concentrations and contributions of sulfate and potassium in $PM_{2.5}$ in Chongqing than in Beijing, and the contrary situation for nitrate imply that the contribution from coal and biomass burning played

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a more important role in Chongqing, whereas vehicular emissions showed stronger regional influence in Beijing.

Figure 5 shows seasonal variations of $PM_{2.5}$ speciation abundances at TH in Beijing from 1999 summer through 2008 summer. SNA dominated temporal variations in inorganic species and presented a general increase trend in abundance, especially in summertime from 1999 through 2008, implying that the characteristic of "complex air pollution" had being enhanced in Beijing. The mass ratio of sulfate to nitrate also showed a slow increase trend during 1999–2008, indicating that the importance of vehicle emissions had also being 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 population and coal consumption amount 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).

Inorganic species exhibited distinct seasonal pattern in decreasing order as: summer, spring, fall, winter. Take the year 2005 for example, the seasonal percentages of inorganic species in $PM_{2.5}$ mass were: summer, 63.5% > spring, 56.0% > fall, 51.8% > winter, 47.7%. Among SNA, sulfate presented strongest seasonal variations with the maximum abundance occurring in the summer of each year during the study period. In the summer of 2005, SNA accounted for 49.7% and 57.8% of $PM_{2.5}$ mass at TH and MY, respectively, and about 60% of SNA was sulfate. SNA had higher seasonal abundances and variations at MY than at TH. In 2005, SO_4^{2-}, NH_4^+ and NO_3^- varied seasonally by factors of 2.2, 1.6, and 1.2 at TH, and by factors of 2.7, 2.0, and 1.4 at MY, respectively. The spatial variations were likely mainly due to the difference in their respective secondary PM formation, implying again that larger regional contribution of SNA at the rural area compared to the urban area in Beijing. The seasonal variations of SNA shares in $PM_{2.5}$ mass could be ascribed to the seasonal variations of local and regional contributions from emissions/production and transport. In summer, high temperature and humidity and strong atmospheric oxidation (high O_3 concentration) are in favor of SNA formation from their precursors. In the meantime, particles and

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their precursors are frequently transported to Beijing from south with high emissions under the control of West Pacific subtropical high (Streets et al., 2007; Xu et al., 2005), and SNA were major components in the transported particles (Jia et al., 2008), in which SO_4^{2-} and 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 gaseous status in transported high-temperature air parcel from south Beijing, its majority is likely contributed locally.

Crustal material in $PM_{2.5}$ had the maximum abundance in spring at both TH and MY, especially when there appeared frequent dust incursions. In the spring of 2000, 2002, 2004, and 2006 when frequent dust storms occurred (http://www.zhb.gov.cn/plan/zkgb), crustal material showed considerable growth in abundance (up to about 20%) in $PM_{2.5}$ mass. Its seasonal average percentages in $PM_{2.5}$ mass were all above 10% in spring but all less than 10% in other seasons. The spring peaks and their mass concentrations of crustal material are largely dependent on the frequency dust events occurred in Beijing in this season. While spring usually saw frequent dust events, their frequency and intensity, thus their impacts on fine particles in Beijing varied from year to year. For example, the crustal percentages in 2006 spring were 18.7% and 23.9% at TH and MY, respectively. Consistent with increasing dust intrusions in Beijing from 2005 (18 versus 4 times) (Wu et al., 2009; http://www.zhb.gov.cn/plan/zkgb), these percentages were higher than those in 2005 spring by factors of 1.3 and 1.9.

Trace elements plus K and Cl accounted for 6.3–10.3% of $PM_{2.5}$ mass seasonally. The abundances of both trace elements and K had no notable seasonal trend and urban-rural difference. In contrast, Cl percentage in $PM_{2.5}$ 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 implied that it was mainly attributed to local sources, such as coal combustion, and presented stably as particles at low temperature condition. This hypothesis remains to be verified in further research.

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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 $PM_{2.5}$ levels (> 100 $\mu g\,m^{-3}$) appearing along northern region and in western urban areas. The highest $PM_{2.5}$ concentration was recorded in 2005 winter in Taiyuan, the capital city of Shanxi province which had the highest coal production in China. At both urban and rural sites in eastern region, SNA aerosol typically accounted for 40–57% of average $PM_{2.5}$ mass, indicative of the regional characteristics of fine particulate pollution and more intensive "complex atmospheric pollution" compared to western region. POM had constant and significant contribution to $PM_{2.5}$ mass. POM and SNA together constituted 62–90% of $PM_{2.5}$ mass at most of the sites. High content of mineral dust, usually being at ~10 $\mu g\,m^{-3}$ level or accounting for ~ 10% of total mass in urban areas, is one of characteristics of $PM_{2.5}$ speciation in China. In the spring of frequent dust storms in northern region, it could explain for more than 40% of $PM_{2.5}$ mass.

In the four representative megacities, Beijing, Chongqing, Shanghai, and Guangzhou, average concentrations of all the species in $PM_{2.5}$ were higher than those in Los Angeles by factors of 1–30, except that NO_3^-, NH_4^+, and EC were at comparable concentration levels. 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 to 10, implying that mobile source likely contributed more to $PM_{2.5}$ mass than stationary source in Guangzhou. In contrast, the highest concentration, the maximum percentage of sulfate, and the lowest $[NO_3^-]/[SO_4^{2-}]$ all occurred in Chongqing, indicative of that stationary source was a more important contributor than mobile source in this area with huge consumption of high-sulphur coal. In Beijing, annual average $PM_{2.5}$ concentrations varied by 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 local emissions and regional transportation both contributed much to the high fine particles levels in

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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 predominant local contribution. 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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Table 1. Comparison of $PM_{2.5}$ mass concentrations and chemical compositions ($\mu g\,m^{-3}$) at urban locations in four typical Chinese megacities and in Los Angeles and Brisbane.

	Beijing 2005.3~ 2006.2	Chongqing 2005.3~ 2006.2	Shanghai 1999.3~ 2000.5	Guangzhou 2008.12~2009.2	Los Angeles 1995.1~ 1996.24	Brisbane 1993.12~ 1995.11
$PM_{2.5}$	118.5 ± 40.6	129.0 ± 42.6	67.6	81.7 ± 25.6	30.32	7.30
OC	24.5 ± 12.0	30.13 ± 11.0	16.80	17.5 ± 7.6	5.96	–
EC	8.19 ± 5.96	6.39 ± 2.56	6.49	4.1 ± 2.0	3.81	1.39
SO_4^{2-}	15.8 ± 10.34	25.6 ± 9.03	13.00	5.6 ± 2.6	4.63	0.788
NO_3^-	10.1 ± 6.09	5.46 ± 3.65	5.78	12.0 ± 5.1	8.47	0.190
NH_4^+	7.30 ± 4.17	7.90 ± 3.78	5.66	4.7 ± 1.7	4.55	–
Si	1.79 ± 0.80	2.20 ± 1.38	1.22	–	0.21	0.080
Al	0.79 ± 0.32	0.80 ± 0.56	0.46	–	0.09	0.029
Fe	1.13 ± 0.41	1.58 ± 0.82	0.90	1.85 ± 1.13	0.21	0.051
K	3.52 ± 1.77	4.29 ± 1.65	2.03	3.1 ± 1.15	0.1	0.055
Na	0.61 ± 0.28	0.67 ± 0.27	0.49	3.2 ± 1.62	0.33*	0.28*
Mg	0.29 ± 0.12	0.28 ± 0.19	0.18	–	0.12	0.038*
Ca	0.90 ± 0.39	1.12 ± 0.71	0.55	–	0.07	0.029
Ti	0.08 ± 0.03	0.16 ± 0.18	–	0.11 ± 0.09	0.01	0.005
V	0.03 ± 0.02	0.05 ± 0.03	–	0.02 ± 0.02	0.01	–
Mn	0.09 ± 0.03	0.14 ± 0.07	0.09	0.15 ± 0.07	0.01	0.004
Cl	2.30 ± 2.41	1.69 ± 1.86	6.13	–	0.23*	0.197
Zn	0.53 ± 0.22	0.60 ± 0.28	0.54	1.36 ± 0.5	0.04	0.026
Pb	0.24 ± 0.12	0.32 ± 0.12	0.29	0.45 ± 0.21	0.01	0.048
Ba	0.21 ± 0.16	0.26 ± 0.15	–	0.07 ± 0.02	–	–
Cu	0.07 ± 0.03	0.06 ± 0.02	0.05	0.19 ± 0.08	0.03	–
Ni	0.02 ± 0.02	0.03 ± 0.03	0.01	–	0.01	–
As	0.02 ± 0.01	0.03 ± 0.02	–	0.04 ± 0.03	–	–
Se	0.02 ± 0.01	0.03 ± 0.02	0.02	–	–	–
Br	0.03 ± 0.02	0.06 ± 0.03	0.03	–	0.01	0.017
Cr	0.05 ± 0.03	0.19 ± 0.10	–	0.07 ± 0.02	0.01	–
Cd	0.05 ± 0.03	0.07 ± 0.04	–	0.02 ± 0.01	–	–

*water-soluble ions; – : not determined.

In Chongqing, the data were for JB site. In Los Angels Kim et al. (2000) collected 24-h $PM_{2.5}$ samples in downtown with a multi-channel fine particle (MCFP) sampler with varying frequencies, i.e. once every sixth day during January–March, and once every third day during April–June, and once everyday during July–December. In Brisbane, Chan et al. (1997) conducted 24-h $PM_{2.5}$ sampling with a dichotomous sampler at an urban conservation forest area. In Shanghai, Ye et al. (2003) collected weekly (i.e. 7-day-integrated) $PM_{2.5}$ samples at urban Shanghai (Hailanlu site) with a same speciation sampler as adopted in Beijing and Chongqing in this study.

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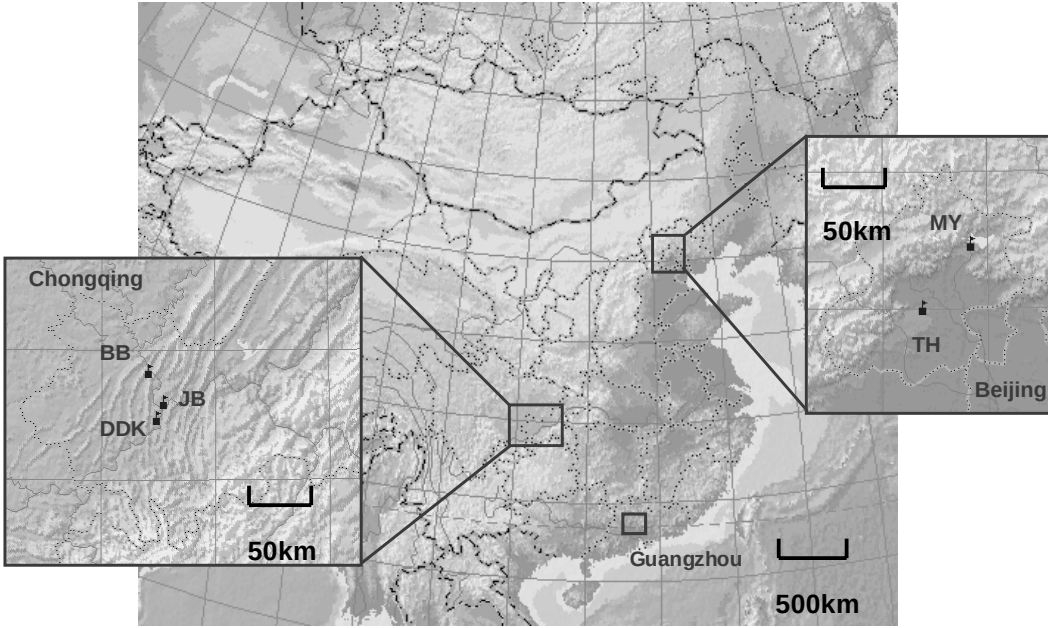

Fig. 1. Sampling sites in Beijing (TH and MY), Chongqing (JB, DDK, and BB), and Guangzhou (Wushan). The topography map was derived from the Microsoft Encarta® 2009 (1993–2008).

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

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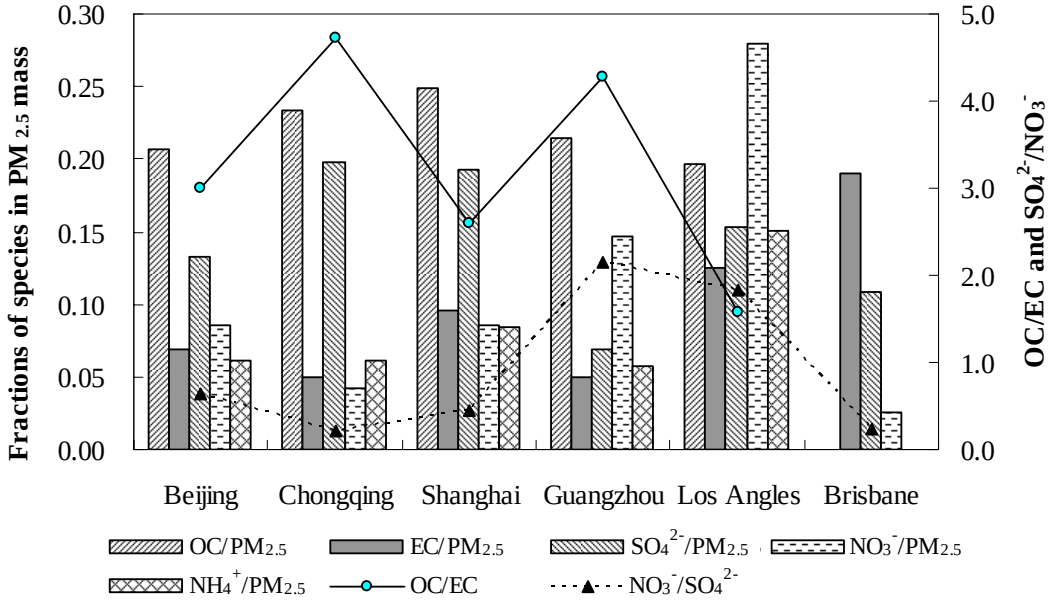

Fig. 2. Relative abundances of five major species in $PM_{2.5}$ and mass ratios of OC to EC and nitrate to sulfate in four Chinese mage cities, Los Angeles, and Brisbane.

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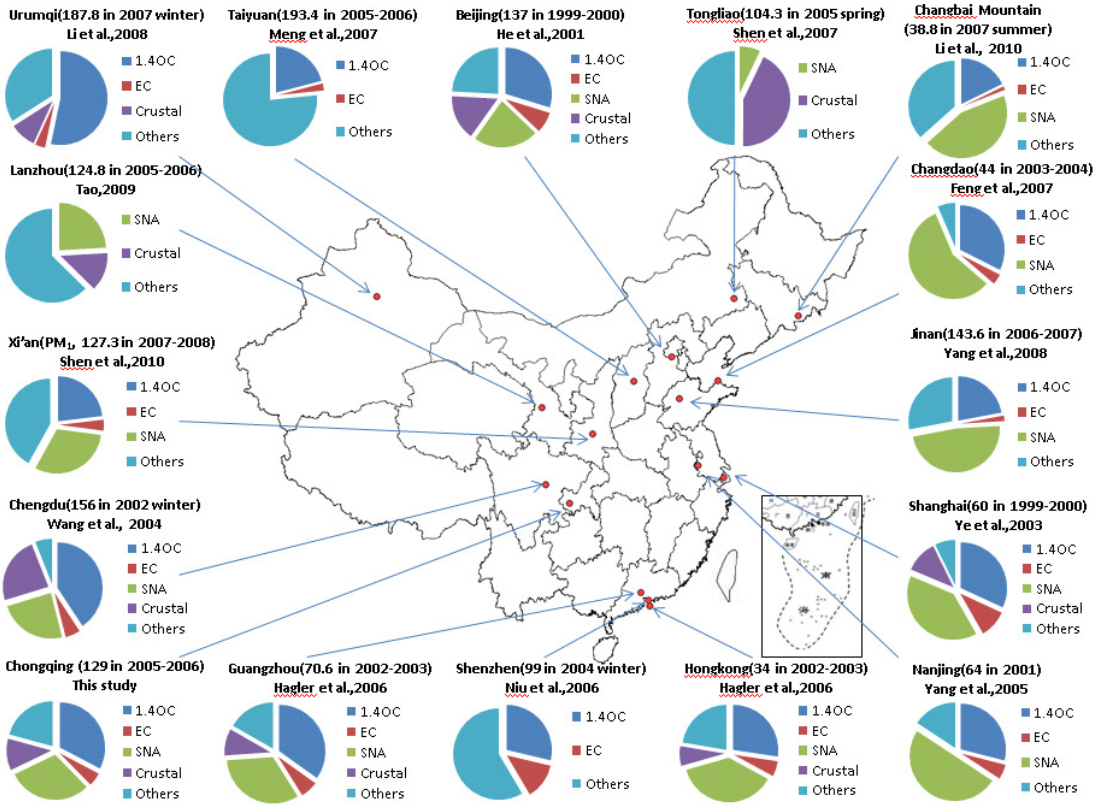

Fig. 3. $PM_{2.5}$ (except $PM_{1.0}$ in Xi'an) speciation at urban and rural locations in China. The rural sites are Changbai Mountain, Tongliao, and Changdao. Averaging periods, average $PM_{2.5}$ mass ($\mu g\,m^{-3}$), and references are indicated. A coefficient of 1.4 to convert OC to POM was adopted 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.

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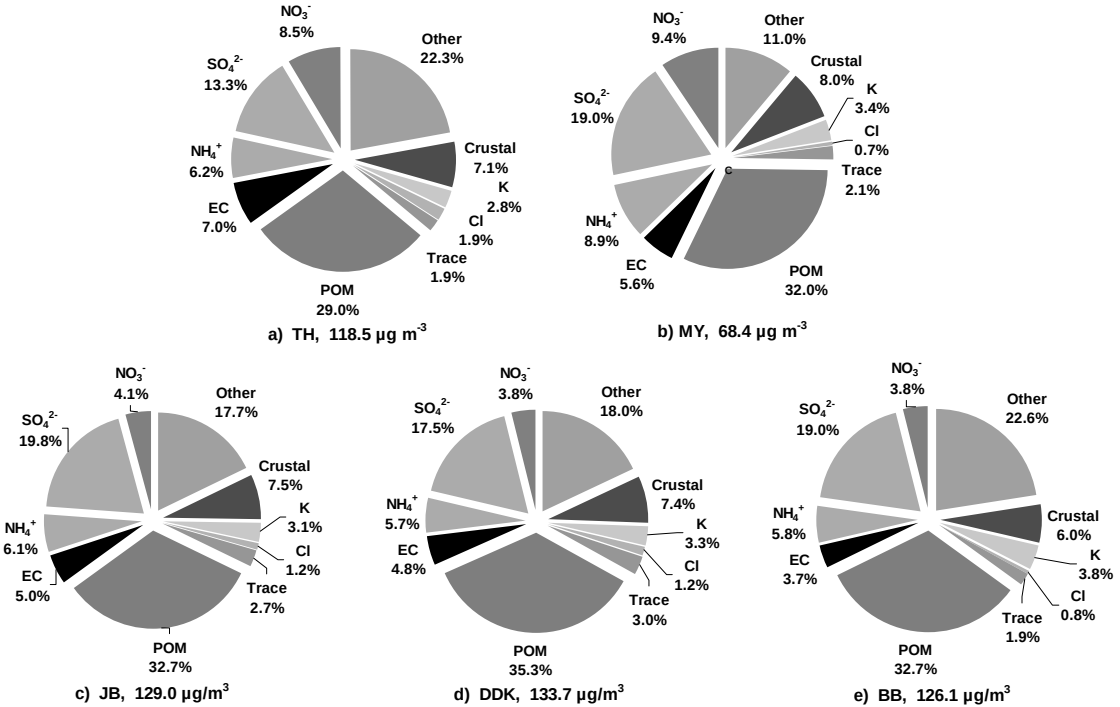

Fig. 4. Average $PM_{2.5}$ speciation at TH and MY in Beijing and at JB, DDK, and BB in Chongqing from March 2005 through February 2006.

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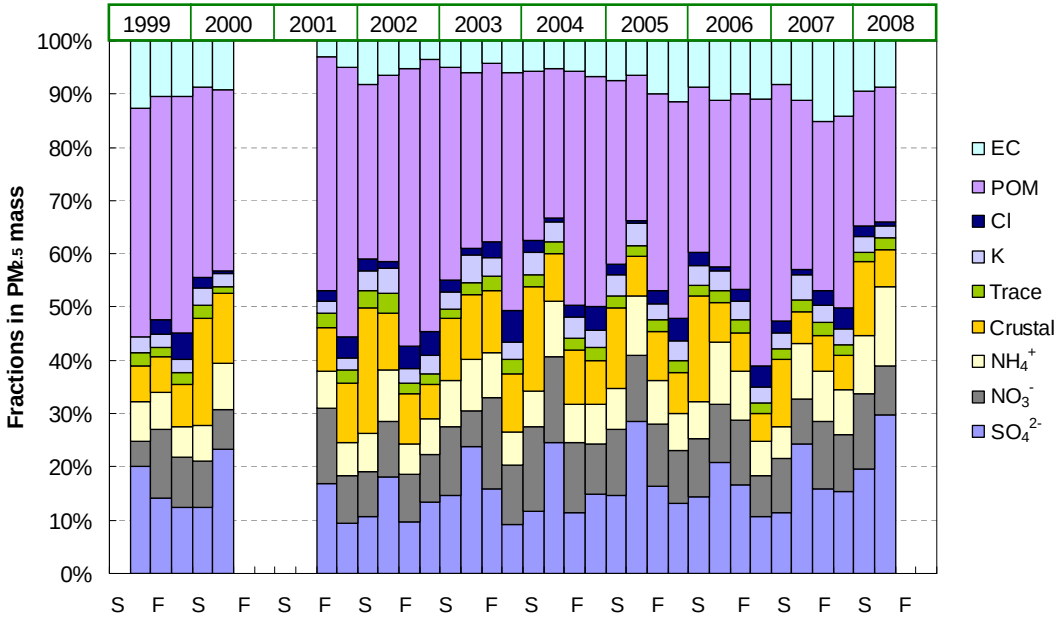

Fig. 5. Seasonal $PM_{2.5}$ speciation abundances at TH in Beijing from 1999 summer through 2008 summer. Sampling years and seasons ("S" means spring and "F" means fall) are indicated.

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