Characteristics of PM$_{2.5}$ mass concentrations and chemical species in urban and background areas of China: emerging results from the CARE-China network

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Abstract: The “Campaign on atmospheric Aerosol REsearch” network of China (CARE-China) is a long-term project for the study of the spatiotemporal distributions of physical aerosol characteristics as well as the chemical components and optical properties of aerosols over China. This study presents the first long-term datasets from this project, including three years of observations of online PM$_{2.5}$ mass concentrations (2012-2014) and one year of observations of PM$_{2.5}$ compositions (2012-2013) from the CARE-China network. The average PM$_{2.5}$ concentrations at 20 urban sites is 73.2 $\mu$g/m$^3$ (16.8-126.9 $\mu$g/m$^3$), which was three times higher than the average value from the 12 background sites (11.2-46.5 $\mu$g/m$^3$). The PM$_{2.5}$ concentrations are generally higher in east-central China than in the other parts of the country due to their relative large particulate matter (PM) emissions and the unfavorable meteorological conditions for pollution dispersion. A distinct seasonal variability of the PM$_{2.5}$ is observed, with highs in the winter and lows during the summer at urban sites. Inconsistent seasonal trends were observed at the background sites. Bimodal and unimodal diurnal variation patterns were identified at both urban and background sites. The chemical compositions of PM$_{2.5}$ at six paired urban and background sites located within the most polluted urban agglomerations and cleanest regions of China were analyzed. The major PM$_{2.5}$ constituents across all the urban sites are organic matter (OM, 26.0%), SO$_4^{2-}$ (17.7%), mineral dust (11.8%), NO$_3^-$ (9.8%), NH$_4^+$ (6.6%), elemental carbon (EC) (6.0%), Cl$^-$ (1.2%) at 45% RH and residual matter (20.7%). Similar chemical compositions of PM$_{2.5}$ were observed at background sites but were associated with higher fractions of OM (33.2%) and lower fractions of NO$_3^-$ (8.6%) and EC (4.1%). Significant variations of the chemical species were observed among the sites. At the urban sites, the OM ranged from 12.6 $\mu$g/m$^3$ (Lhasa) to 23.3 $\mu$g/m$^3$ (Shenyang), the SO$_4^{2-}$ ranged from 0.8 $\mu$g/m$^3$ (Lhasa) to 19.7 $\mu$g/m$^3$ (Chongqing), the NO$_3^-$ ranged from 0.5 $\mu$g/m$^3$ (Lhasa) to 11.9 $\mu$g/m$^3$ (Shanghai) and the EC ranged from 1.4 $\mu$g/m$^3$ (Lhasa) to 7.1 $\mu$g/m$^3$ (Guangzhou). The PM$_{2.5}$
chemical species at the background sites exhibited larger spatial heterogeneities than those at urban sites, suggesting the different contributions from regional anthropogenic or natural emissions and from the long-range transport to background areas. Notable seasonal variations of PM$_{2.5}$ polluted days were observed, especially for the megacities in east-central China, resulting in frequent heavy pollution episodes occurring during the winter. The evolution of the PM$_{2.5}$ chemical compositions on polluted days was similar for the urban and nearby background sites, suggesting the significant regional pollution characteristics of the most polluted areas of China. However, the chemical species dominating the evolutions of the highly polluted events were different in these areas, indicating that unique mitigation measures should be developed for different regions of China. This analysis reveals the spatial and seasonal variabilities of the urban and background aerosol concentrations on a national scale and provides insights into their sources, processes, and lifetimes.

1. Introduction

Atmospheric fine particulate matter (PM$_{2.5}$) is a complex heterogeneous mixture, whose physical size distribution and chemical composition change in time and space and are dependent on the emission sources, atmospheric chemistry, and meteorological conditions (Seinfeld and Pandis, 2016). Atmospheric PM$_{2.5}$ has known important environmental impacts related to visibility degradation and climate change. Because of their abilities to scatter and absorb solar radiation, aerosols degrade visibility in both remote and urban locations and can have direct and indirect effects on the climate (IPCC, 2013). Fine atmospheric particles are also a health concern and have been linked to respiratory and cardiovascular diseases (Sun et al., 2010; Viana et al., 2008; Zhang et al., 2014a). The magnitudes of the effects of PM$_{2.5}$ on all these systems depend on their sizes and chemical compositions. Highly reflective aerosols, such as sulfates and nitrates, result in direct cooling effects, while aerosols with low single-scattering albedos absorb solar radiation and include light-absorbing carbon, humic-like substances, and some components of mineral soils (Hoffer et al., 2006). The health impacts of these particles may also differ with different aerosol compositions (Zimmermann, 2015); the adverse health effects specifically associated with organic aerosols have been reported by Mauderly and Chow (2008). Therefore, the uncertainties surrounding the roles of aerosols in climate, visibility, and health studies can be significant because chemical composition data may not be available for large spatial and temporal ranges.

Reducing the uncertainties associated with aerosol effects requires observations of aerosol mass concentrations and chemical speciation from long-term spatially extensive ground-based networks. Continental sampling using ground-based networks has been conducted in North America (Hand et al., 2012) and Europe (Putaud et al., 2010) since the 1980s, such as via the U.S. EPA's Chemical Speciation Network (CSN), the Interagency Monitoring of Protected Visual Environments (IMPROVE) network, the Clean Air Status and Trends Network (CASTNET) and the National Atmospheric Deposition Program (NADP). Previous studies suggest the spatial and temporal patterns of PM$_{2.5}$ mass concentrations and chemical species can vary significantly depending on species and location. For example, Malm et al. (2004) reported the 2001 monthly mean speciated aerosol concentrations from the IMPROVE monitors across the United States and demonstrated that ammonium sulfate concentrations were highest in the eastern United States and dominated the fine particle masses in the summer. Clearly decreasing gradients of the SO$_4^{2-}$ and NO$_3^-$ contributions to
PM$_{10}$ were observed in Europe when moving from rural to urban to kerbside sites (Putaud et al., 2010). Although large disparities of PM$_{2.5}$ pollution levels exist between those megacities in developing and developed countries, the PM$_{2.5}$ annual mass concentrations in the former are approximately 10 times greater than those of the latter (Cheng et al., 2016); however, ground-based networks that consistently measures PM$_{2.5}$ mass concentrations and chemical compositions remain rare in the densely populated regions of developing countries.

China is the world’s most populous country and has one of the fastest-growing economies. Fast urbanization and industrialization can cause considerable increases in energy consumption. China’s energy consumption increased 120% from 2000 to 2010. Coal accounted for most of the primary energy consumption (up to 70%) (Department of Energy Statistics, National Bureau of Statistics of China, 2001; 2011). Meanwhile, the emissions of high concentrations of numerous air pollutants cause severe air pollution and haze episodes. For example, a heavy air pollution episode occurred in northeastern China in January of 2013, wherein the maximum hourly averaged PM$_{2.5}$ exceeded 600 μg m$^{-3}$ in Beijing (Wang et al., 2014). This event led to considerable public concern. However, ground-based networks that consistently measure PM$_{2.5}$ mass concentrations and chemical compositions in China are limited. Although there were some investigations of the various aerosol chemical compositions in China (He et al., 2001; Huang et al., 2013; Li et al., 2012; Liu et al., 2015; Pan et al., 2013; Tao et al., 2014; Wang et al., 2013; Yang et al., 2011; Zhao et al., 2013a; Zhou et al., 2012), earlier studies were limited in their temporal and spatial scopes, with very few having data exceeding one year while covering various urban and remote regions of the country (Zhang et al., 2012; Wang et al., 2015). Indeed, before 2013, the Chinese national monitoring network did not report measurements of PM$_{2.5}$ or its chemical composition, and thus, ground-based networks for atmospheric fine particulate matter measurements at regional and continental scales are needed as these networks are essential for the development and implementation of effective air pollution control strategies and are also useful for the evaluation of regional and global models and satellite retrievals.

To meet these sampling needs, the “Campaign on atmospheric Aerosol REsearch” network of China (CARE-China) was established in late 2011 for the study of the spatiotemporal distributions of the physical and chemical characteristics and optical properties of aerosols (Xin et al., 2015). This study presents the first long-term dataset to include three years of observations of online PM$_{2.5}$ mass concentrations (2012-2014) and one year of observations of PM$_{2.5}$ compositions (2012-2013) from the CARE-China network. The purpose of this work is to (1) assess the PM$_{2.5}$ mass concentration levels, including the seasonal and diurnal variation characteristics at the urban, rural and regional background sites; to (2) obtain the seasonal variations of the PM$_{2.5}$ chemical compositions at paired urban/background sites in the most polluted regions and clean areas; and to (3) identify the occurrences and chemical signatures of haze events via an analysis of the temporal evolutions and chemical compositions of PM$_{2.5}$ on polluted days. These observations and analyses provide general pictures of atmospheric fine particulate matter in China and can also be used to validate model results and implement effective air pollution control strategies.

2 Materials and methods
2.1 An introduction to the PM$_{2.5}$ monitoring sites

The PM$_{2.5}$ data from 36 ground observation sites used in this study were obtained from the
CARE-China network (Campaign on the atmospheric Aerosol REsearch network of China), which was supported by the Chinese Academy of Sciences (CAS) Strategic Priority Research Program grants (Category A). Xin et al. (2015) provided an overview of the CARE-China network, the cost-effective sampling methods employed and the post-sampling instrumental methods of analysis. Four more ground observation sites (Shijiazhuang, Tianjin, Ji’nan and Lin’an) from the “Forming Mechanism and Control Strategies of Haze in China” group (Wang et al., 2014) were also included in this study to better depict the spatial distributions and temporal variations of the PM$_{2.5}$ in eastern China. A comprehensive 3-year observational network campaign from 2012 to 2014 was carried out at these 40 ground observation sites. Figure 1 and Table 1, respectively, show the geographic distribution and details of the network stations, which include 20 urban sites, 12 background sites and 8 rural/suburban sites. The urban sites, such as those at Beijing, Shanghai and Guangzhou, are locations surrounded by typical residential areas and commercial districts. The background sites are located in natural reserve areas or scenic spots, which are far away from anthropogenic emissions and are less influenced by human activities. Rural/suburban sites are situated in rural and suburban areas, which may be affected by agricultural activities, vehicle emissions and some light industrial activities. These sites are located in different parts of China and can provide an integrated insight into the characteristic of PM$_{2.5}$ over China.

2.2 Online instruments and data sets

A tapered element oscillating microbalance (TEOM) was used for the PM$_{2.5}$ measurements at thirty-four sites within the network (Table S1). This system was designated by the US Environmental Protection Agency (USEPA) as having a monitoring compliance equivalent to the National Ambient Air Quality standard for particulate matter (Patashnick and Rupprecht 1991). The measurement ranges of the TEOMs were 0-5 g/m$^3$, with a 0.1 μg/m$^2$ resolution and precisions of ±1.5 (1-hour average) and ±0.5 μg/m$^2$. The models used in the network are TEOM 1400a and TEOM 1405, and the entire system was heated to 50 °C; thus, a loss of semivolatile compounds cannot be avoided. Our previous study showed that up to 25%-lower mass concentrations were found for select daily means than those observed with gravimetric filter measurements, depending on the ammonium-nitrate levels and ambient temperatures (Liu et al., 2015). The errors of the TEOM measurements are systematic in that they are always negative. Thus, these errors may not be important for the study of the spatial distributions and temporal variations of PM$_{2.5}$. The other six sites of the network were equipped with beta gauge instruments (EBAM, Met One Instruments Inc., Oregon) (Table S1). The measurement range of EBAM is 0-1000 μg/m$^3$, with a precision of 0.1 μg/m$^3$ and a resolution of 0.1 μg/m$^3$. The filters were changed every week, and the inlet was cleaned every month. The flow rates were also monitored and concurrently calibrated.

2.3 Filter sampling and chemical analysis

In this study, filter sampling was conducted at the five urban sites of Beijing, Guangzhou, Lhasa, Shenyang and Chongqing as well as at the six background sites of Xinglong, Lin’an, Dinghu Mountain, Namsto, Changbai Mountain and Gongga Mountain. The Automatic Cartridge Collection Unit (ACCU) system of Rupprecht & Patashnick Co. with 47 mm diameter quartz fiber filters (Pall Life Sciences, Ann Arbor, MI, USA) was deployed in Beijing to collect the PM$_{2.5}$ samplers (Liu et al., 2016a). Similar to the ACCU system, a standard 47 mm filter holder with quartz fiber filters (Pall Life Sciences, Ann Arbor, MI, USA) was placed in the bypass line of TEOM 1400a and TEOM...
1405 using quick-connect fittings and was used to collect the PM$_{2.5}$ samplers of the other nine sites, excepting Guangzhou and Lin'an. Each set of the PM$_{2.5}$ samples was continuously collected over 48 h on the same days of each week, generally starting at 8:00 a.m. The flow rates were typically 15.6 L/min. For the Guangzhou site, the fine particles were collected on Whatman quartz fiber filters using an Andersen model SA235 sampler (Andersen Instruments Inc.) with an air flow rate of 1.13 m$^3$/min. The sampling lasted 24 or 48 h, generally starting at 8:00 a.m. For the Lin'an site, a medium volume PM$_{2.5}$ sampler (Model: TH-150CIII, Tianhong Instrument CO., Ltd. Wuhan, China) was used to collect 24 h of PM$_{2.5}$ aerosols on 90 mm quartz fiber filters (QMA, Whatman, UK) once every 6 days (Xu et al., 2017). The sampling periods of these 11 urban and background sites are shown in Table S1.

All the filters were heat treated at 500 °C for at least 4 h for cleaning prior to filter sampling. The PM$_{2.5}$ mass concentrations were obtained via the gravimetry method with an electronic balance with a detection limit of 0.01 mg (Sartorius, Germany) after stabilizing at a constant temperature (20±1 °C) and humidity (45%±5%). Three types of chemical species were measured using the methods described in Xin et al. (2015). Briefly, the OC and elemental carbon (EC) values were determined using a thermal/optical reflectance protocol using a DRI model 2001 carbon analyzer (Atomslytic, Inc., Calabasas, CA, USA). Eight main ions, including K$^+$, Ca$^{2+}$, Na$^+$, Mg$^{2+}$, NH$_4^+$, SO$_{4}^{2-}$, NO$_3^-$ and Cl$^-$, were measured via ion chromatography (using a Dionex DX 120 connected to a DX AS50 autosampler for anions and a DX ICS90 connected to a DX AS40 autosampler for cations), and 18 elements, including Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Ti and Pb, were determined by Agilent 7500a inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies, Tokyo, Japan).

3. Results and discussions

3.1 Characteristics of PM$_{2.5}$ mass concentrations at urban and background sites

3.1.1 Average PM$_{2.5}$ levels

The location, station information and average PM$_{2.5}$ concentrations from the 40 monitoring stations are shown in Fig. 1 and Table 1. The highest PM$_{2.5}$ concentrations were observed at the urban stations of Xi’an (125.8 μg/m$^3$), Taiyuan (111.5 μg/m$^3$), Ji’nan (107.5 μg/m$^3$) and Shijiazhuang (105.1 μg/m$^3$), which are located in the most polluted areas of the Guanzhong Plain (GZP) and the North China Plain (NCP). Several studies have revealed that the enhanced PM$_{2.5}$ pollutions of the GZP and NCP are not only due to the primary emissions from local sources such as the local industrial, domestic and agricultural sources but are also due to secondary productions (Huang et al., 2014; Guo et al., 2014; Wang et al., 2014). Furthermore, the climates of the GZP and NCP are characterized by stagnant weather with weak winds and relatively low boundary layer heights, leading to favorable atmospheric conditions for the accumulation, formation and processing of aerosols (Chan and Yao, 2008). Note that the averaged PM$_{2.5}$ concentrations in Beijing and Tianjin were approximately 70 μg/m$^3$, which is much lower than those of the other cities, including Ji’nan and Shijiazhuang in the NCP, possibly because Beijing and Tianjin are located in the northern part of the NCP, far from the intense industrial emission area that is mainly located in the southern part of the NCP. Interestingly, the average PM$_{2.5}$ concentrations at Yucheng (102.8 μg/m$^3$) and Xianghe (83.7 μg/m$^3$) were even higher than most of those from the urban stations. Although Yucheng is a
rural site, it is located in an area with rapid urbanization near Ji'nan and is therefore subjected to the associated large quantities of air pollutants. In addition, Xianghe is located between Beijing and Tianjin and is influenced by the regionally transported contributions from nearby megacities and the primary emissions from local sources. Yantai is a coastal city with relatively low PM concentrations compared to those of with inland cities on the NCP.

The PM$_{2.5}$ concentrations were also high in the Yangtze River Delta (YRD), which is another developed and highly-populated city cluster area like the NCP (Fu et al., 2013). The average PM$_{2.5}$ values of the three urban stations of Shanghai, Wuxi and Hefei were 56.2, 65.2 and 80.4 μg/m$^3$, respectively, which are comparable to those of the megacities of Beijing and Tianjin in the NCP. Due to the presence of fewer coal-based industries and dispersive weather conditions, the PM$_{2.5}$ concentrations of the Pearl River Delta (PRD) are generally lower than those of the other two largest city clusters in China, such as those from the NCP and YRD. The average PM$_{2.5}$ value at Guangzhou was 44.1 μg/m$^3$, which was similar to the PM$_{2.5}$ values of the background stations from the NCP and YRD. Shenyang, the capital of the province of Liaoning, is located in the Northeast China Region (NECR), which is an established industrial area. High concentrations of trace gases and aerosol scattering in the free troposphere have been observed via aircraft observations and are due to regional transports and heavy local industrial emissions (Dickerson et al., 2007). In the present study, the average PM$_{2.5}$ concentration of Shenyang was 77.6 μg/m$^3$. Meanwhile, Hailun, which is a rural site in northeastern China, had an average PM$_{2.5}$ concentration of 41.6 μg/m$^3$, which was much lower than that of the rural site of Yucheng in the NCP.

High aerosol optical depths and low visibilities have been observed in the Sichuan Basin (Zhang et al., 2012), which is located in the Southwestern China Region (SWCR). The poor dispersion conditions and heavy local industrial emissions make this another highly polluted area in China. In the present study, the average PM$_{2.5}$ concentration in Chengdu was measured as 102.2 μg/m$^3$, which is much higher than the averages from the megacities of Beijing, Shanghai and Guangzhou but is comparable to those of Ji'nan and Shijiazhuang. Chongqing, another megacity located in the SWCR, however, showed much lower PM$_{2.5}$ values than Chengdu. Urumqi, the capital of the Uighur Autonomous Region of Xinjiang, located in northwestern China, experiences air pollution due to its increasing consumption of fossil fuel energy and steadily growing fleet of motor vehicles (Mamtimin and Meixner, 2011). The average PM$_{2.5}$ concentration measured in Urumqi is 104.1 μg/m$^3$, which is comparable to those of the urban sites in the GZP and NCP. The similarity among the PM$_{2.5}$ values for Cele, Dunhuang and Fukang is due to their location, being far from regions with intensive economic development but strongly affected by sandstorms and dust storms due to their proximity to dust source areas. For example, the average PM$_{2.5}$ concentration in Cele during the spring (200.7 μg/m$^3$) was much greater than those of the other three seasons. Lhasa, the capital of the Tibet Autonomous Region (TAR), is located in the center of the Tibetan Plateau at a very high altitude of 3700 m. The PM$_{2.5}$ concentrations in Lhasa were low, with average values of 30.6 μg/m$^3$, because of its relatively small population and few industrial emissions.

Much lower PM$_{2.5}$ concentrations were observed at the background stations, the values of which ranged from 11.2 to 46.5 μg/m$^3$. The lowest concentration of PM$_{2.5}$ was observed in Namsto, a background station on the TAR with nearly no anthropogenic effects. The highest PM$_{2.5}$ concentration of the background stations was observed at Lin’an, a background station in the PRD.
The average PM$_{2.5}$ concentration at the urban and background sites in this study are shown as boxplots in Fig. S1a. The average PM$_{2.5}$ concentration of the background stations (a total of 12 sites) is 28.5 μg/m$^3$, and the average concentration of the PM$_{2.5}$ values from urban stations (a total of 20 sites) is 73.2 μg/m$^3$. The latter value is approximately three times the former, suggesting the large differences in fine particle pollution at urban and background sites across China. All values were much greater than the results from Europe and North America. Gehrig and Buchmann (2003) reported that average PM$_{2.5}$ concentrations from 1998 to 2001 at urban/suburban stations in Switzerland were 20.1 μg/m$^3$. The average PM$_{2.5}$ concentrations were 16.3 μg/m$^3$ for the period 2008-2009 in the Netherlands (Janssen et al., 2013). Between October 2008 and April 2011, the 20 study areas of the European ESCAPE project showed annual average concentrations of PM$_{2.5}$ ranging from 8.5 to 29.3 μg/m$^3$, with low concentrations in northern Europe and high concentrations in southern and eastern Europe (Eeftens et al., 2012). An average PM$_{2.5}$ value of 14.0 μg/m$^3$ was observed over the study period of 2000-2005 via measurements from 187 counties in the United States, with higher values in the eastern United States and California and lower values in the central regions and the northwest (Bell et al., 2007).

To further characterize these kinds of differences for different parts of China, six pairs of PM$_{2.5}$ values measured from urban and background stations were selected to represent the NCP, YRD, PRD, TAR, NECR and SWCR, respectively (Fig. S1). The first three areas (NCP, YRD and PRD) and the last two areas (NECR and SWCR) were the most industrialized and populated regions in China, while TAR is the cleanest area in China. The PM$_{2.5}$ concentrations of the background stations in the NCP, YRD and PRD are 39.8 μg/m$^3$ (Xinglong), 46.5 μg/m$^3$ (Lin’an) and 40.1 μg/m$^3$ (Dinghu Mountain) and are much higher than those of the background stations in other parts of China, which are usually below 25 μg/m$^3$. In addition, the background PM$_{2.5}$ concentrations in the NCP, YRD and PRD were comparable to those from nearby urban sites, especially for the PRD, as shown in Fig. S1. In contrast, the background PM$_{2.5}$ concentrations in TAR, NECR and SWCR were much lower than those of the nearby cities. These results suggest that the background sites in the NCP, YRD and PRD are more influenced by regional pollution, which will be further discussed in section 3.2.

### 3.1.2 Seasonal variations of PM$_{2.5}$ mass concentrations

Generally, the PM$_{2.5}$ concentrations in urban areas show distinct seasonal variabilities, with maxima during the winter and minima during the summer for most of China (Fig. 1), which is a similar pattern to that of the results reported by Zhang and Cao (2015). In northern and northeastern China, the wintertime peak values of PM$_{2.5}$ were mainly attributed to the combustion of fossil fuels and biomass burning for domestic heating over extensive areas, which emit large quantities of primary particulates as well as the precursors of secondary particles (He et al., 2001). In addition, new particle formation and the secondary production of both inorganic aerosols and OM could further enhance fine PM abundance (Huang et al., 2014; Guo et al., 2014). Furthermore, the planetary boundary layer is relatively low in the winter, and more frequent occurrences of stagnant weather and intensive temperature inversions cause very bad diffusion conditions, which can result in the accumulation of atmospheric particulates and lead to high-concentration PM episodes (Quan et al., 2014; Zhao et al., 2013b). In southern and eastern China, although the effect of domestic heating is not as important as that in northern China, the weakened diffusion and transport of pollutants from the north due to the activity of the East Asian Winter Monsoon reinforces the
pollution from large local emissions in the winter more than in any other season (Li et al., 2011; Mao et al., 2017). For northwestern and West Central China, the most polluted season is the spring instead of the winter due to the increased contribution from dust particles in this desert-like region (Zou and Zhai, 2004), suggesting that the current PM$_{2.5}$ control strategies (i.e., reducing fossil/non-fossil combustion derived VOCs and PM emissions) will only partly reduce the PM$_{2.5}$ pollution in western China. PM$_{2.5}$ is greatly decreased during the summer in urban areas, which is associated with the reduced anthropogenic emissions from fossil fuel combustion and biomass burning domestic heating. Further, the more intense solar radiation causes a higher atmospheric mixing layer, which leads to strong vertical and horizontal aerosol dilution effects (Xia et al., 2006). In addition, increased precipitation in most of China due to the summer monsoon can increase the wet scavenging of atmospheric particles. As a result, PM$_{2.5}$ minima are observed in the summer at urban sites.

The seasonal variations of PM$_{2.5}$ at the background sites varied in different parts of China (Fig. 3). Dinghu Mountain and Lin’an showed maximum values in the winter, while Zangdongnan, Qinghai Lake, Xishuangbanna and Mount Everest showed maximum values in the spring. In addition, a summer maximum of PM$_{2.5}$ was observed for Xinglong, and an autumn maximum was observed for Tongyu. Changbai Mountain, Gongga Mountain and Namsto showed weak seasonal variabilities. These results suggest the different contributions from regional anthropogenic and natural emissions and long-range transports to background stations. The monthly average PM$_{2.5}$ concentrations of the urban and background sites in the NCP, YRD, PRD, TAR, NECR and SWCR are further analyzed and shown in Fig. 2. The monthly variations of the PM$_{2.5}$ concentrations at the background sites in the YRD and PRD were consistent with those of the nearby urban sites, both of which showed maximum values in December (YRD) and January (PRD). The reasons for this similarity are primarily the seasonal fluctuations of emissions, which are already well known due to the similar variations of other parameters, including sulfur dioxide and nitrogen oxide, as shown in Fig. S2. In contrast, the monthly variations of PM$_{2.5}$ at Xinglong showed different trends than those of the nearby urban stations. The maximum value of PM$_{2.5}$ at this site was observed in July, while the maximum value in Beijing was observed in January. The reasons for this are not primarily the seasonal fluctuations of emissions, but rather meteorological effects (frequent inversions during the winter and strong vertical mixing during the summer). The Xinglong site is situated at an altitude of 900 m a.s.l., and therefore, during the wintertime, the majority of cases above the inversion layer are protected from the emissions of the urban agglomerations of the NCP. Furthermore, in the NCP area, northerly winds prevail in the winter, while southerly winds prevail in the summer. Thus, in the summer, more air masses from the southern urban agglomerations will lead to high PM$_{2.5}$ concentrations in Xinglong. Weak monthly variabilities were observed for Namsto, Changbai Mountain and Gongga Mountain, although remarkable monthly variabilities were found at the nearby cities of Lhasa, Shenyang and Chongqing. The reasons for this difference are mainly that these three sites are elevated remote stations that are far from human activities and show predominant meteorological influences.

### 3.1.3 Diurnal variations of PM$_{2.5}$ mass concentrations

To derive importance information to identify the potential emission sources and the times when the pollution levels exceed the proposed standards, hourly data were used to examine the
diurnal variabilities of PM$_{2.5}$ as well as those of the other major air pollutants. Fig. 3 illustrates the
diurnal variations of the hourly PM$_{2.5}$ concentrations in Beijing, Shanghai, Guangzhou, Lhasa,
Shenyang and Chongqing, in the largest megacities in the NCP, YRD, PRD, TPR, NECR and SWCR
and in the different climatic zones of China, respectively. Of the urban sites, Lhasa has the lowest
PM$_{2.5}$ concentrations, but the most significant pronounced diurnal variations of PM$_{2.5}$, with obvious
morning and evening peaks appearing at 10:00 and 22:00 (Beijing Time) due to the contributions of
enhanced anthropogenic activity during the rush hours. The minimum value occurred at 16:00,
which is mainly due to a higher atmospheric mixing layer, which is beneficial for air pollution
diffusion. This bimodal pattern was also observed in Shenyang and Chongqing, which show
morning peaks at 7:00 and 9:00 and evening peaks at 19:00 and 20:00, respectively. However, the
PM$_{2.5}$ values in Beijing, Shanghai and Guangzhou showed much weaker urban diurnal variation
patterns, and slightly higher PM$_{2.5}$ concentrations during the night than during the day were
observed, which can be explained by the enhanced emissions from heating and the relatively low
boundary layer. Note that the morning peaks in Beijing, Shanghai and Guangzhou were not as
obvious as those of other cities, although both the SO$_2$ and NO$_2$ values increased due to increased
anthropogenic emissions (Fig. S3). Alternatively, this decreasing trend may be the result of an
increasing boundary layer depth. At these three urban sites, the PM$_{2.5}$ levels started to increase in
the late afternoon, which could be explained by the increasing motor vehicle emissions as NO$_2$ is
also dramatically increased during the same period.

At the background area of the TPR, significant pronounced diurnal variations of PM$_{2.5}$ were
observed in Namsto, with a morning peak at 9:00 and an evening peak at 21:00 (Fig. 3d), which are
similar to those of the urban site of Lhasa. As there are hardly any anthropogenic activities near
Namsto, this kind of diurnal pattern of PM$_{2.5}$ may be influenced by the evolution of the planetary
boundary layer. Both Lin’an and Gongga Mountain showed the same bimodal pattern of PM$_{2.5}$ as
that in Namsto, which could also be influenced by the planetary boundary layer. For the background
site of the NCP, however, Xinglong showed smooth PM$_{2.5}$ variations. As mentioned before, the
Xinglong station is located on the mountain and has an altitude of 960 m a.s.l. The mixed boundary
layer of the urban area increases in height in the morning and reaches a height of approximately
1000 meters in the early afternoon. Then, the air pollutants from the urban area start to affect the
station as the vertical diffusion of the airflow and the PM$_{2.5}$ concentration reach their maxima at
18:00. Next, the concentration starts to decrease when the mixed boundary layer collapses in the
late afternoon, eventually forming the nocturnal boundary layer (Boyouk et al., 2010). Thus, PM$_{2.5}$
concentration decreased slowly during the night and morning, reaching a minimum at 10:00. At
Dinghu Mountain and Changbai Mountain, the daytime PM$_{2.5}$ greater than that of the nighttime,
with a maximum value occurring at approximately 11:00-12:00. This kind of diurnal pattern of
PM$_{2.5}$ is mainly determined by the effects of the mountain-valley breeze. Both the Dinghu Mountain
and Changbai Mountain stations are located near the mountain. Thus, during daytime, the valley
breeze from urban areas carries air pollutants that will accumulate in front of the mountain and cause
an increase of the PM concentration. Meanwhile, at night, the fresh air carried by the mountain
breeze will lead to the dilution of the PM, so low concentrations are sustained during the night.
Further support for this pattern comes from the much higher maximum values of PM$_{2.5}$ in the winter
than those in the summer, as enhanced air pollutant emissions in urban areas are expected in the
379 winter due to heating.

3.2 Chemical compositions of PM\textsubscript{2.5} in urban and background sites

3.2.1 Overview of PM\textsubscript{2.5} mass speciation

Figure 4 shows the annual average and seasonal average chemical compositions of PM\textsubscript{2.5} at six urban and six background sites, which represent the largest megacities and regional background areas of the NCP, YRD, PRD, TPR, NECR and SWCR. The chemical species of PM\textsubscript{2.5} in Shanghai were obtained from Zhao et al. (2015). The atmospheric concentrations of the main PM\textsubscript{2.5} constituents are also shown in Table 2. The EC, nitrate (NO\textsubscript{3}\textsuperscript{−}), sulfate (SO\textsubscript{4}\textsuperscript{2−}), ammonium (NH\textsubscript{4}\textsuperscript{+}) and chlorine (Cl\textsuperscript{−}) concentrations were derived directly from measurements. Organic matter (OM) was calculated assuming an average molecular weight per carbon weight, showing an OC of 1.6 at the urban sites and of 2.1 at the background sites, based on the work of Turpin and Lim (2001); however, these values are also spatially and temporally variable, and typical values could range from 1.3 to 2.16 (Xing, et al., 2013). The calculation of mineral dust was performed on the basis of crustal element oxides (Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, CaO, Fe\textsubscript{2}O\textsubscript{3}, MnO\textsubscript{2} and K\textsubscript{2}O). In addition, the Si content, which was not measured in this study, was calculated based on its ratio to Al in crustal materials; namely, [Si]=3.41×[Al]. Finally, the unaccounted-for mass refers to the difference between the PM\textsubscript{2.5} gravimetric mass and the sum of the PM constituents mentioned above.

The PM constituents’ relative contributions to the PM mass are independent of their dilutions and reflect differences in the sources and processes controlling the aerosol compositions (Putaud et al., 2010). When all the main aerosol components except water are quantified, they account for 73.6-84.8% of the PM\textsubscript{2.5} mass (average 79.2%) at urban sites and for 76.2-91.1% of the PM\textsubscript{2.5} mass (average 83.4%) at background sites. The remaining unaccounted-for mass fraction may be the result of analytical errors, a systematic underestimation of the PM constituents whose concentrations are calculated from the measured data (e.g., OM, and mineral dust), and aerosol-bound water (especially when mass concentrations are determined at RH >30%). For the urban sites, the mean composition given in descending concentrations is 26.0% OM, 17.7% SO\textsubscript{4}\textsuperscript{2−}, 11.8% mineral dust, 9.8% NO\textsubscript{3}\textsuperscript{−}, 6.6% NH\textsubscript{4}\textsuperscript{+}, 6.0% EC and 1.2% Cl\textsuperscript{−}. For the background sites, the mean composition given in descending concentrations is 33.2% OM, 17.8% SO\textsubscript{4}\textsuperscript{2−}, 10.1% mineral dust, 8.7% NH\textsubscript{4}\textsuperscript{+}, 8.6% NO\textsubscript{3}\textsuperscript{−}, 4.1% EC and 0.9% Cl\textsuperscript{−}. Generally, the chemical compositions of the PM\textsubscript{2.5} at background sites are similar to those of the urban sites, although they show a much higher fraction of OM and lower fractions of NO\textsubscript{3}\textsuperscript{−} and EC. Significant seasonal variations of the chemical compositions were observed at urban sites (Fig. 4c), with much higher fractions of OM (33.7%) and NO\textsubscript{3}\textsuperscript{−} (11.1%) in the winter and much lower fractions of OM (20.7%) and NO\textsubscript{3}\textsuperscript{−} (6.9%) in the summer. In contrast, the fraction of SO\textsubscript{4}\textsuperscript{2−} was consistent among the different seasons, although its absolute concentration in the winter (14.9 µg/m\textsuperscript{3}) was higher than that in the summer (11.7 µg/m\textsuperscript{3}). Compared with those at urban sites, different seasonal variation of OM were observed at the background sites, which showed summer maxima and winter/spring minima (Fig. 4d). While the wintertime peaks of OM at the urban sites were probably due to additional local emissions sources related to processes like heating, the summer peaks at the background sites were attributed to the enhanced biogenic emissions. Note that the seasonal variations of NO\textsubscript{3}\textsuperscript{−} were similar to those at urban sites; this seasonal phenomenon is due to the favorable conditions of cold temperature and high relative humidity conditions leading to the formation of particulate nitrate. The seasonal behaviors of SO\textsubscript{4}\textsuperscript{2−} at the
background sites were markedly different than those of the urban sites and indicate very different sources and atmospheric processing of SO$_2$\(^2\) which will be further discussed for specific regions of China.

There are significant variations of the absolute speciation concentrations at these urban and background sites (Table 2). For the urban sites, the OM concentrations span a 2-fold concentration range from 12.6 µg/m\(^3\) (Lhasa) to 23.3 µg/m\(^3\) (Shenyang), while these values range from 3.4 µg/m\(^3\) (Namtso) to 21.7 µg/m\(^3\) (Lin’an) at the background sites. The SO$_2$\(^2\) and NO$_3$\(^-\) concentrations exhibit larger spatial heterogeneities than those of the OM for both urban and background sites. The absolute values of SO$_2$\(^2\) have an approximately 25-fold range in urban sites, from 0.8 µg/m\(^3\) (Lhasa) to 19.7 µg/m\(^3\) (Chongqing), while this value has a 30-fold range at the background sites, from 0.4 µg/m\(^3\) (Namtso) to 11.2 µg/m\(^3\) (Lin’an). The corresponding mass fractions are 26.8% in Chongqing and below 3% in Lhasa. Much higher fractions of SO$_2$\(^2\) in the PM$_{2.5}$ were observed at the urban sites located in southern China than those in northern China, although the average concentration of PM$_{2.5}$ is greater in the north than in the south, suggesting that sulfur pollution remains a problem for southern China (Liu et al., 2016b). This problem may be attributed to higher sulfur contents of the coal in southern China, with 0.51% in the north vs. 1.32% in the south and up to >3.5% in Chongqing in southern China (Lu et al., 2010; Zhang et al., 2010). The absolute values of NO$_3$\(^-\) have an approximately 20-fold range in urban sites and a greater than 100-fold range in background sites.

This heterogeneity reflects the large spatial and temporal variations of the NOx sources. For the urban sites, the absolute EC values have a 5-fold concentration range, from 1.4 µg/m\(^3\) (Lhasa) to greater than 7.0 µg/m\(^3\) (Guangzhou), while this species has a 15-fold concentration range at the background sites and is mainly from anthropogenic sources. In comparison, the absolute concentrations of mineral dust exhibit much weaker spatial variations at the urban and background sites.

The characteristics of the PM$_{2.5}$ chemical compositions at individual site were discussed in more detail. In this section, six pairs of urban and background sites from each region of China were selected, and the differences in the chemical compositions of urban and background sites were analyzed.

### 3.2.2 North China Plain

Beijing is the capital of China and has attracted considerable attention due to its air pollution (Chen et al., 2013). Beijing is the largest megacity in the NCP, which is surrounded by the Yanshan Mountains to the west, north and northeast and is connected to the Great North China Plain to the south. The filter sampler is located in the courtyard of the Institute of Atmospheric Physics (IAP) (116.37°E, 39.97°N), 8 km northwest of the center of downtown. The PM$_{2.5}$ concentration during the filter sampling period was 71.7 µg/m\(^3\), which is close to the three-year average PM$_{2.5}$ value reported by TEOM (Table 1). PM$_{2.5}$ in Beijing is mainly composed by OM (26.6%), SO$_2$\(^2\) (16.5%) and NO$_3$\(^-\) (13.0%) (Fig. 5a), which compare well with previous studies (Yang et al., 2011; Oanh et al., 2006). However, the mineral dust fraction found in this study (6.5%) was much lower than that found in Yang et al. (2011) (19%) but was comparable to that found in Oanh et al. (2006) (5%), potentially due to difference in definitions. The annual concentration of OM (19.1 µg/m\(^3\)) in Beijing was comparable to those in Shanghai, Guangzhou and Chongqing, but was much lower than that in Shenyang. Higher fractions of OM were observed in the winter (34.2%) and autumn (30.5%) than...
in the summer (21.6%) and spring (20.9%). The annual concentration of SO$_4^{2-}$ (11.9 μg/m$^3$) was much lower than those of earlier years (15.8 μg/m$^3$, 2005-2006) (Yang et al., 2011), suggesting that the energy structure adjustment implemented in Beijing (e.g., replacing coal fuel with natural gas) has been effective in decreasing the particulate sulfate in Beijing. Further support for this comes from the SO$_4^{2-}$ concentration in the winter (16.5 μg/m$^3$) being comparable to that in the summer (13.4 μg/m$^3$). The significant NO$_3^{-}$ value (9.3 μg/m$^3$) reflects the significant urban NOx emissions in Beijing, which was greatest during the winter, as expected from ammonium-nitrate thermodynamics. The greater mineral component in the spring reflects the regional natural dust sources.

The filter sampling site in Xinglong (117.58°E, 40.39°N) was located at Xinglong Observatory, National Astronomical Observatory, Chinese Academy of Sciences, which is 110 km northeast of Beijing (Fig. 1). This site is surrounded by mountains and is minimally affected by anthropogenic activities. The PM$_{2.5}$ concentration during the filter sampling period was 42.6 μg/m$^3$, which is close to the three-year average PM$_{2.5}$ values reported by TEOM (Table 1). The annual chemical composition of the PM$_{2.5}$ in Xinglong was similar to that in Beijing, although relatively higher fractions of OM and sulfate were observed in Xinglong (Fig. 5a). Higher fractions of OM were found in the winter (36.7%), and higher fractions of sulfate were found in the summer (32.1%) than in any other season (OM: 23.0-30.4%; SO$_4^{2-}$: 15.7-20.1%). Interestingly, the summer SO$_4^{2-}$ concentration in Xinglong (14.4 μg/m$^3$) was even higher than that in Beijing, suggesting spatially uniform distributions of SO$_4^{2-}$ concentrations across the NCP. This result indicates that regional transport can be an important source of SO$_4^{2-}$ aerosols in Beijing, especially during the summer.

3.2.3 Yangtze River Delta

Shanghai is the economic center of China, lying on the edge of the broad flat alluvial plain of the YRD, with a few mountains to the southwest. The filter sampler was located at the top of a four-floor building of the East China University of Science and Technology (121.52°E, 31.15°N) (Zhao et al., 2015), approximately 10 km northwest of the center of downtown. The PM$_{2.5}$ concentration during the filter sampling period was 68.4 μg/m$^3$, which is greater than the three-year average PM$_{2.5}$ value reported by EBAM, likely due to the different sampling period (Table S1). The PM$_{2.5}$ in Shanghai mainly comprises OM (24.9%), SO$_4^{2-}$ (19.9%) and NO$_3^{-}$ (17.4%), which is comparable to the results of previous studies (Ye et al., 2003; Wang et al., 2016). This site had the highest NO$_3^{-}$ (11.9 μg/m$^3$) and the second-highest SO$_4^{2-}$ (13.6 μg/m$^3$) values of the urban sites, while its OM (17.1 μg/m$^3$) was comparable to those of Guangzhou and Chongqing. The SO$_4^{2-}$ and NO$_3^{-}$ values were highest during the autumn as expected based on the widespread biomass burning in the autumn in the YRD (Niu et al., 2013). However, the OM values were highest during the winter and mainly originated from secondary aerosol processes based on the highest OC/EC ratios (6.0) and the poor relationship of the OC and EC in this season.

Filter sampling was conducted at the Lin’an Regional Atmospheric Background Station (119.73°E, 30.30°N), which is a background monitoring station for the World Meteorological Organization (WMO) global atmospheric observation network. The Lin’an site was located at the outskirts of Lin’an County within Hangzhou Municipality, which was 200 km southwest of Shanghai (Fig. 1). This site is surrounded by agricultural fields and woods and is less affected by urban, industrial and vehicular emissions (Xu et al., 2017). The PM$_{2.5}$ concentration during the filter
sampling period was 66.3 μg/m³, which is higher than the three-year average PM\(_{2.5}\) values reported by TEOM, likely due to the different sampling period (Table S1). The annual chemical composition of the PM\(_{2.5}\) in Lin’an was different than that in Shanghai, with much higher fractions of OM (32.7%) and NH\(_4^+\) (11.0%). Furthermore, the absolute concentration of OM in Lin’an was much higher than that in Shanghai, especially in the summer (21.7 vs. 9.9 μg/m³), which may be attributed to the enhanced biomass burning at both local and regional scales as well as the higher concentration of summer EC in Lin’an than in Shanghai (2.2 vs. 1.4 μg/m³). In addition, the SO\(_4^{2-}\) and NO\(_3^-\) concentrations in Lin’an were comparable to those in Shanghai. These results suggest a spatially homogeneous distribution of secondary aerosols over the PRD and the transportation of aged aerosol and gas pollutants from city clusters has significant influence on the background area of this region.

### 3.2.4 Pearl River Delta

Guangzhou is the biggest megacity in south China located in the PRD and mainly consists of floodplains within the transitional zone of the East Asian monsoon system (Yang et al., 2011). The filter sampler was set up on the rooftop of a 15-m high building of the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (113.35°E, 23.12°N). This site was surrounded by heavily trafficked roads and dense residential areas, representing a typical urban location. The PM\(_{2.5}\) concentration during the filter sampling period was 75.3 μg/m³, which is much higher than the three-year average PM\(_{2.5}\) value reported by EBAM (Table 1), likely due to the different sampling period and location. The PM\(_{2.5}\) in Guangzhou mainly comprises OM (22.2%), SO\(_4^{2-}\) (17.3%) and mineral dust (9.7%), which have values comparable to previous studies conducted in the years of 2013-2014 (Chen et al., 2016; Tao et al., 2017). This site has the lowest OC/EC ratio (1.5) of all urban sites, which can be explained by the abundance of diesel engine truck in Guangzhou City (Verma et al., 2010). Obvious seasonal variations of OM, SO\(_4^{2-}\) and NO\(_3^-\) were observed, showing winter/autumn maxima and summer/spring minima. In addition, summer minima were also observed for EC and NH\(_4^+\). High mixing heights in the summer and clean air masses affected by summer monsoons from the South China Sea should lead to the minima of these species in summer, while the low wind speeds, weak solar radiation, relatively low precipitation (Tao et al., 2014) and relatively high emissions (Zheng et al., 2009) result in the much higher concentrations of OM and secondary inorganic aerosols (SO\(_4^{2-}\), NO\(_3^-\) and NH\(_4^+\)) in the winter and autumn.

Filter sampling was conducted at Dinghu Mountain Station (112.50°E, 23.15°N), which is located in the middle of Guangdong Province in southern China. This site was surrounded by hills and valleys, being approximately 70 km west of Guangzhou (Fig. 1). The PM\(_{2.5}\) concentration during the filter sampling period was 40.1 μg/m³, close to the three-year average PM\(_{2.5}\) values reported by TEOM. Distinct seasonal variations of OM, SO\(_4^{2-}\), NO\(_3^-\) and NH\(_4^+\) were observed, with the highest concentration of OM and NO\(_3^-\) occurring in the winter, while the highest concentrations of SO\(_4^{2-}\) and NH\(_4^+\) occurred in the autumn. In contrast, EC and mineral dust showed weak seasonal variations. Dinghu Mountain has the second-highest EC and SO\(_4^{2-}\) values of the background sites, being 2.0 μg/m³ and 10.1 μg/m³. In addition, the lowest OC/EC ratio was observed at Dinghu Mountain (2.8); the other background sites had values ranging from 3.5-8.3. These results indicate that this background site is intensely influenced by vehicular traffic, fossil fuel combustion and industrial emissions due to the advanced urban agglomeration in the PRD region. These results are
consistent with the finds from previous studies (Liu et al., 2011; Wu et al., 2016). Compared with those from Guangzhou, higher fractions of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ were observed at Dinghu Mountain, while the fractions of OM and mineral dust were similar at these two sites, possibly indicating that there was a significantly larger fraction of transported secondary aerosols or aged aerosols at the background site of the PRD.

### 3.2.5 Tibetan Autonomous Region

Located in the inland TAR, Lhasa is one of the highest cities in the world (at an altitude of 3700 m). The city of Lhasa is located in a narrow west-east oriented valley in the southern part of the TAR. The filter sampler was located on the roof of a 20-m high building on the campus of the Institute of Tibetan Plateau Research (Lhasa branch) (91.63°E, 29.63°N). This site is close to Jinzhu road, one of the busiest roads in the city (Cong et al., 2011). The $\text{PM}_{2.5}$ concentration during the filter sampling period was 36.4 $\mu$g/m$^3$, which is close to the three-year average $\text{PM}_{2.5}$ values reported by TEOM. The $\text{PM}_{2.5}$ in Lhasa mainly comprises OM (34.5%) and mineral dust (31.9%), and the secondary inorganic aerosols ($\text{SO}_4^{2-}$, $\text{NO}_3^-$ and $\text{NH}_4^+$) contributed little to the $\text{PM}_{2.5}$ (<5%). These results are comparable to those of a previous study conducted in the year of 2013-2014 (Wan et al., 2016). In addition, this site reports the lowest OM (12.6 $\mu$g/m$^3$), secondary inorganic aerosols (1.7 $\mu$g/m$^3$) and EC (1.4 $\mu$g/m$^3$) values of the urban sites in this study. Higher fractions of OM were observed in the winter (48.4%) and spring (43.1%), exceeding those in the summer (24.6%) and autumn (31.2%). Weak seasonal variations were found for the $\text{SO}_4^{2-}$ (1.5-3.0%) and $\text{NO}_3^-$ (1.1-1.7%) values, suggesting the negligible contributions from fossil fuel combustion in Lhasa.

Filter sampling was conducted at the Namtso Monitoring and Research Station for Multiphase Interactions (90.98°E, 30.77°N), a remote site located on the northern slope of the Nyainqen-tanglha Mountains, approximately 125 km northwest of Lhasa (Fig. 1). The $\text{PM}_{2.5}$ concentration during the filter sampling period was 9.5 $\mu$g/m$^3$, which is close to the three-year average $\text{PM}_{2.5}$ value reported by TEOM. The $\text{PM}_{2.5}$ in Namtso mainly comprises mineral dust (40.8%) and OM (36.3%), while $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ contributed less than 5% to the $\text{PM}_{2.5}$. This chemical composition is distinctly different from those of the other background sites in this study, but is comparable to the background site at Qinghai Lake in the TAR (Zhang et al., 2014b). Namtso has the lowest OM, EC, $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and $\text{NH}_4^+$ values of all the background sites in this study. Spring maxima and winter minima were observed for the OM and EC, while the $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and $\text{NH}_4^+$ values showed weak seasonal variations. The highest OC/EC ratio was observed (8.3) at this site, suggesting that the organic aerosols at Namtso mainly originated from secondary aerosol processes or aged organic aerosols from regional transports.

### 3.2.6 Northeast China Region

Shenyang is the capital city of Liaoning province and the largest city in northeastern China. The main urban area is located on a delta to the north of the Hun River. The filter sampler was located at the Shenyang Ecological Experimental Station of the Chinese Academy of Science (123.40°E, 41.50°N) and was surrounded by residential areas with no obvious industrial pollution sources around the monitoring station, representing the urban area of Shenyang. The $\text{PM}_{2.5}$ concentration during the filter sampling period was 81.8 $\mu$g/m$^3$, which is close to the three-year average $\text{PM}_{2.5}$ value reported by TEOM (Table 1). The $\text{PM}_{2.5}$ in Shenyang mainly comprises OM (28.5%), $\text{SO}_4^{2-}$ (16.1%) and mineral dust (11.3%). This site reports the highest OM (23.3 $\mu$g/m$^3$) and...
mineral dust (9.2 μg/m³) values as well as the second-highest EC (5.2 μg/m³) value of the urban sites. The NO³ concentration at this site, however, was the second-lowest of the urban sites (Table 2). Much higher fractions of OM were observed in the winter (40.5%) than in the other seasons (15.6-26.5%) (Fig. 5), possibly due to the enhanced coal burning for winter heating. Further support for this pattern comes from the high abundance of chlorine during the cold seasons, which is mainly associated with coal combustion. The contribution from sea-salt particles is not important since the sampling sites are at least 200 km from the sea. Note that the fraction of SO₄²⁻ in the PM₂.₅ during the winter was lower than that in the summer, although the absolute concentration was much higher in the winter (23.6 μg/m³) than in the summer (11.3 μg/m³). This result may be attributed to the reduced transformation of sulfur dioxide at low temperatures.

Filter sampling was conducted at the Changbai Mountain forest ecosystem station (128.01°E, 42.40°N), which was mostly surrounded by hills and forest and is located approximately 390 km northeast of Shenyang (Fig. 1). This site is situated 10 km from the nearest town, Erdaobaihe, which has approximately 45000 residents. The sources of PM were expected to be non-local. Hence, this site is considered a background site in the NECR. The PM₂.₅ concentration during the filter sampling period was 23.3 μg/m³, which is close to the three-year average PM₂.₅ value reported by TEOM (Table 1). The main contributions to the PM₂.₅ at Changbai Mountain were OM (38.1%), mineral dust (16.0%) and SO₄²⁻ (14.3%), similar to those in Shenyang. Note that the summer OM concentrations were quite similar at these two sites (8.0 vs. 9.0 μg/m³), but the OC/EC ratios were different (4.8 vs. 1.6), which may reflect the different origins of the OM at the urban (primary emissions) and background sites (secondary processes) of the NECR. The OM concentrations in the other seasons were much lower at Changbai Mountain than those from Shenyang city, especially during the winter (10.8 vs. 59.4 μg/m³). In fact, weak seasonal variations of chemical species (OM, EC, SO₄²⁻, NO₃⁻ and NH₄⁺) were observed at Changbai Mountain. This site reports the second-lowest values of OM, EC, SO₄²⁻ and Cl⁻ of the background sites. These results suggest that aerosols at Changbai Mountain were influenced by the regional transports alone.

### 3.2.7 Southwestern China Region

Chongqing is the fourth municipality near Central China, lying on the Yangtze River in mountainous southwestern China, near the eastern border of the Sichuan Basin and the western border of Central China. For topographic reasons, Chongqing has some of the lowest wind speeds in China (annual averages of 0.9-1.6 m s⁻¹ from 1979 to 2007; Chongqing Municipal Bureau of Statistics, 2008), which favors the accumulation of pollutants. The filter sampler was located on the rooftop of a 15-m high building on the campus of the Southwest University (106.54°E, 29.59°N). This site is located in an urban district of Chongqing with no obvious industrial pollution sources around the monitoring site, representing the urban area of Chongqing. The PM₂.₅ concentration during the filter sampling period was 73.5 μg/m³, of which 26.8% is SO₄²⁻, 23.5% OM, 10.0% mineral dust, 8.9% NO₃⁻, 8.2% EC and 6.5% NH₄⁺. The OM fraction is smaller than those measured by Yang et al. (2011) (32.7%) and Chen et al., 2017 (30.8%), while the SO₄²⁻ fraction is greater than the values reported in these two studies (19.8-23.0%). This site shows the highest SO₄²⁻ (19.7 μg/m³), the highest NH₄⁺ (6.1 μg/m³) and the third-highest EC (4.8 μg/m³) values of the urban sites. A weak seasonal variation in the chemical composition of PM₂.₅ was observed, although a much higher concentration of this species was found in the winter than in the other seasons.
Filter sampling was performed at the Gongga Mountain Forest Ecosystem Research Station (101.98°E, 29.51°N) in the Hailuogou Scenic Area, a remote site located in southeastern Ganzi in the Tibetan Autonomous Prefecture in Sichuan province. This site is mostly surrounded by glaciers and forests and is located approximately 450 km northwest of Chongqing (Fig. 1). The PM$_{2.5}$ concentration during the filter sampling period was 32.2 μg/m$^3$, close to the three-year average PM$_{2.5}$ value reported by TEOM (Table 1). The dominant components of PM$_{2.5}$ were OM (40.7%), SO$_4^{2-}$ (14.6%) and mineral dust (9.8%), similar to those at Changbai Mountain. This site has the second-highest OM (13.1 μg/m$^3$) value of the background sites, which may mainly be due to secondary processes, considering the high OC/EC ratio (5.6). In addition, distinct seasonal variations of OM were observed, which shows summer maxima (19.9 μg/m$^3$) and autumn minima (9.1 μg/m$^3$). Previous studies showed higher mixing ratios of VOCs during the spring and summer and lower mixing ratios during the autumn at Gongga Mountain (Zhang et al., 2014c), which may result in high concentrations of OM in the summer because the OC/EC ratio reaches its highest value in the summer (10.3). Second-lowest EC and NO$_3^-$ values of the background sites were observed here, suggesting the insignificant influence of human activities in this region.

### 3.3 Temporal evolution and chemical composition PM$_{2.5}$ in polluted days

Using the “Ambient Air Quality Standard” (GB3095-2012) of China (CAAQS), the occurrences of polluted days exceeding the daily threshold values during 2012-2014 were counted for each site (Fig. 6). Based on the number of polluted days exceeding the CAAQS daily guideline of 35 μg/m$^3$, substandard days of PM$_{2.5}$ account for more than 60% of the total period at the majority of urban sites, excepting Lhasa, Taipei and Sanya. Note that the ten most polluted cities (Ji'nan, Chengdu, Taiyuan, Hefei, Shenyang, Xi'an, Changsha, Shijiazhuang, Wuxi and Chongqing) experienced less than 20% clean days (daily PM$_{2.5}$<35 μg/m$^3$) during the three-year observation period. Interestingly, the occurrences of heavily polluted days (daily PM$_{2.5}$>150 μg/m$^3$) were different among these ten most polluted cities. While more than 15% of the total period comprised heavily polluted days in Ji'nan, Taiyuan, Chengdu, Xi'an and Shijiazhuang, heavily polluted days accounted for less than 5% of the total days in the other five cities, which mainly experienced slightly polluted (35-75 μg/m$^3$) and moderately polluted (75-115 μg/m$^3$) days. Due to the regional pollutant transports, the rural and background sites near the most polluted cities also showed high occurrences of polluted days. Polluted days accounted for more than 50% of the total period at Xin'long, Lin'an and Dinghu Mountain. In addition, an even higher occurrence of polluted days (>80%) was found for the rural areas of Yucheng and Xianghe. In contrast, the background sites in the TAR, NECR and SWCR rarely experienced polluted days, and over 80% of the total period comprised clean days at these sites.

The polluted days were not equally distributed throughout the year. The monthly distributions for the polluted days at each site are shown in Fig. 7. In terms of the occurrences of heavily polluted days, December, January and February were predominant months for the urban sites located in the most polluted areas of the GZP and NCP, where both the unfavorable dispersion conditions for pollutants and the additional emission enhancements from residential heating contributed to the heavy pollution in the winter. The heavy pollution occurring in April and November in Cele was primarily caused by sandstorms and dust storms. Heavily polluted days were rarely observed at the 12 background sites in this study. The moderately polluted and polluted days were still mainly...
concentrated in the winter in the megacities of the GZP and NCP and also occurred in the winter in the megacities of the YRD and SWCR. In addition, March to June and September to October were periods with high occurrences of polluted days. Dust storms from northern China (March to April), biomass burning after crop harvests (May to June and September to October) and worsening dispersion conditions after the summers likely accounted for the polluted days (Cheng et al., 2014; Fu et al., 2014). The majority of slightly polluted days occurred from June to September, except at several urban sites in southern China. The mass level of 35-75 μg/m³ was considered a low level of pollution for the entire year, illustrating that the summer and early autumn experienced cleaner conditions. The mean percentile compositions of the major components in PM$_{2.5}$ at different pollution levels from four paired urban-background sites are shown in Fig. 8. With the pollution level increased from clean to moderately polluted, the EC fraction in Beijing decreased slightly, the OM fraction decreased significantly, and the sulfate and nitrate contributions increased sharply (Fig. 8a). The same chemical evolution of the PM$_{2.5}$ was also observed at the background site of Xinglong, suggesting that regional transport plays a vital role in the formation of the slightly and moderately polluted days in the NCP. When the pollution level increased to heavily polluted, however, the OM fraction further increased and was accompanied by increases of the sulfate and nitrate contributions as well as decreases of the mineral dust contribution. This result indicates the enhanced secondary transformation of gaseous pollutants (etc. SO$_2$, NOx, VOCs) during heavily polluted periods, which is consistent with the findings of our previous study (Liu et al., 2016a), which stated that regionally transported aerosols contribute the most during slightly and moderately polluted days, while local origin secondary aerosols dominate the increases of fine particles during heavily polluted days in Beijing. Unlike in Beijing, the contributions of OM and EC were almost constant across the different pollution levels in Guangzhou, while the contribution of the secondary inorganic aerosols (SIA) increased slightly (Fig. 8b). Interestingly, the nitrate contribution increased faster than that of the sulfate when the pollution level increased from clean to heavily polluted, similar to the patterns of Beijing, which may suggest the enhanced contribution of local traffic emissions in these two cities during heavily polluted days. The chemical evolution of PM$_{2.5}$ at the background site of PRD was similar to that of the urban site at Guangzhou, although a significant contribution of SIA was observed when the pollution level increased from clean to moderately polluted (34% vs. 58%). Note that the contribution of sulfate increased sharply, suggesting that regional transports dominated the particle pollution during heavily polluted days. Compared with Beijing, a reversed chemical evolution of PM$_{2.5}$ for the different pollution levels was observed in Shenyang, with the OM fraction increasing sharply from 22% to 37%, while the SIA decreased slightly from 39% to 31% (Fig. 8c). Note that a steady increase of sulfate from slightly polluted days to heavily polluted days was observed. These results suggest that enhanced local emissions dominate the temporal evolution of PM$_{2.5}$ on polluted days in Shenyang. A similar chemical evolution of PM$_{2.5}$ was found at the background site of Changbai Mountain, which showed a significantly increased OM fraction and slightly decrease of SIA when the pollution level increased from clean to slightly polluted, indicating the enhanced contribution from local emissions like coal combustion for heating during slightly polluted days. Further support for this pattern is seen in the increase of the EC fraction (Fig. 8 g). Similar to that in Guangzhou, the contribution of OM was almost constant for different
pollution levels in Chongqing. In addition, a much higher contribution of SIA was observed, especially during the heavily polluted days, which suggests the importance of the formation of SIA in driving PM$_{2.5}$ pollution in Chongqing. The background site of Gongga Mountain shows decreased contributions of OM, EC, SIA and mineral dust when the pollution level increased from clean to slightly polluted days, similar to the pattern observed in Xinglong. Note that the unaccounted-for fraction was largely increased on slightly polluted days (33% vs. 10%), possibly due to the increase of aerosol-bound water related to the hygroscopic growth of aerosols at high RH values on slightly polluted days (Bian et al., 2014). These results suggest the different formation mechanisms of the heavy pollution in the most polluted city clusters, and unique mitigation measures should be developed for the different regions of China.

4. Conclusions

We have established a national-level network ("Campaign on atmospheric Aerosol REsearch" network of China (CARE-China)) that conducted continuous monitoring of PM$_{2.5}$ mass concentrations at 40 ground observation station, including 20 urban sites, 12 background sites and 8 rural/suburban sites. The average aerosol chemical composition was inferred from the filter samples from six paired urban and background sites, which represent the largest megacities and regional background areas in the five most polluted regions and the TAR of China. This study presents the first long-term dataset including three-year observations of online PM$_{2.5}$ mass concentrations (2012-2014) and one year observations of PM$_{2.5}$ compositions (2012-2013) from the CARE-China network. One of the major purposes of this study was to compare and contrast urban and background aerosol concentrations from nearby regions. The major findings include the following:

1. The average PM$_{2.5}$ concentration from 20 urban sites is 73.2 μg/m$^3$ (16.8-126.9 μg/m$^3$), which is three times greater than the average value of 12 background sites (11.2-46.5 μg/m$^3$). The highest PM$_{2.5}$ concentrations were observed at the stations on the Guanzhong Plain (GZP) and the NCP. The PM$_{2.5}$ pollution is also a serious problem for the industrial regions of northeastern China and the Sichuan Basin and is a relatively less serious problem for the YRD and the PRD. The background PM$_{2.5}$ concentrations of the NCP, YRD and PRD were comparable to those of the nearby urban sites, especially for the PRD. A distinct seasonal variability of the PM$_{2.5}$ is observed, presenting peaks during the winter and minima during the summer at the urban sites, while the seasonal variations of PM$_{2.5}$ at the background sites vary in different part of China. Bimodal and unimodal diurnal variation patterns were identified at both the urban and background stations.

2. The major PM$_{2.5}$ constituents across all the urban sites are OM (26.0%), SO$_{4}^{2-}$ (17.7%), mineral dust (11.8%), NO$_3^-$ (9.8%), NH$_4^+$ (6.6%), EC (6.0%), Cl$^-$ (1.2%) at 45% RH and residual matter (20.7%). Similar chemical compositions of PM$_{2.5}$ were observed for the background sites and were associated with higher fractions of OM (33.2%) and lower fractions of NO$_3^-$ (8.6%) and EC (4.1%). Analysis of filter samples reveals that several PM$_{2.5}$ chemical components varied by more than an order of magnitude between sites. For urban sites, the OM ranges from 12.6 μg/m$^3$ (Lhasa) to 23.3 μg/m$^3$ (Shenyang), the SO$_{4}^{2-}$ ranges from 0.8 μg/m$^3$ (Lhasa) to 19.7 μg/m$^3$ (Chongqing), the NO$_3^-$ ranges from 0.5 μg/m$^3$ (Lhasa) to 11.9 μg/m$^3$ (Shanghai) and the EC ranges from 1.4 μg/m$^3$ (Lhasa) to 7.1 μg/m$^3$ (Guangzhou). The PM$_{2.5}$ chemical species of the background
sites exhibit larger spatial heterogeneities than those of the urban sites, suggesting the different contributions from regional anthropogenic and natural emissions and from the long-range transport to background areas.

(3) Notable seasonal variations of PM$_{2.5}$ polluted days were observed, especially for the megacities in east-central China, resulting in frequent heavy pollution episodes occurring during the winter. The evolution of the chemical compositions of the PM$_{2.5}$ on polluted days was similar for the urban and nearby background sites, suggesting the significant regional pollution characteristics of the most polluted areas of China. However, the chemical species dominating the evolutions of heavily polluted events were different in these areas. While sharply increasing contributions of SIA and decreasing or constant contributions of OM during heavily polluted days were observed in Beijing, Guangzhou and Chongqing, the reverse contributions of secondary inorganic aerosol and OM were observed during the heavily polluted days of Shenyang. These results suggest that unique mitigation measures should be developed for different regions of China.

The seasonal and spatial patterns of urban and background aerosols emphasize the importance of understanding the variabilities of the concentrations of major aerosol species and their contributions to the PM$_{2.5}$ budget. Comparisons of PM$_{2.5}$ chemical compositions from urban and background sites of adjacent regions provided meaningful insights into aerosol sources and transport and into the role of urban influences on nearby rural regions. The integration of data from 40 sites from the CARE-China network provided an extensive spatial coverage of fine particle concentrations near the surface and could be used to validate model results and implement effective air pollution control strategies.

Acknowledgments

This study was supported by the Ministry of Science and Technology of China (Grant nos. 2017YFC0210000), the National Natural Science Foundation of China (Grant nos. 41705110) and the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant nos. XDB050200 & XDA05100100). We acknowledge the tremendous efforts of all the scientists and technicians involved in the many aspects of the Campaign on atmospheric Aerosol REsearch network of China (CARE-China).

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## Table 1 Geographic information and three-year mean PM$_{2.5}$ concentration of the monitor stations.

<table>
<thead>
<tr>
<th>Station/Code</th>
<th>Latitude, Longitude</th>
<th>Altitude(m)</th>
<th>Station type</th>
<th>Mean(μg/m$^3$)</th>
<th>N(day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing/BJC</td>
<td>39.97° N, 116.37° E</td>
<td>45</td>
<td>Northern city</td>
<td>69.4±54.8</td>
<td>1077</td>
</tr>
<tr>
<td>Cele/CLD</td>
<td>37.00° N, 80.72° E</td>
<td>1306</td>
<td>Northwestern country</td>
<td>126.9±155.4</td>
<td>600</td>
</tr>
<tr>
<td>Changbai Mountain/CM</td>
<td>42.40° N, 128.01° E</td>
<td>738</td>
<td>Northeastern background</td>
<td>17.6±12.6</td>
<td>807</td>
</tr>
<tr>
<td>Changsha/CSC</td>
<td>28.21° N, 113.06° E</td>
<td>45</td>
<td>Central city</td>
<td>77.9±45.4</td>
<td>1045</td>
</tr>
<tr>
<td>Chengdu/CDC</td>
<td>30.67° N, 104.06° E</td>
<td>506</td>
<td>Southwestern city</td>
<td>102.2±66.2</td>
<td>1008</td>
</tr>
<tr>
<td>Chongqing/CQC</td>
<td>29.59° N, 106.54° E</td>
<td>259</td>
<td>Southwestern city</td>
<td>65.1±35.8</td>
<td>972</td>
</tr>
<tr>
<td>Dinghu Mountain/DHM</td>
<td>23.17° N, 112.50° E</td>
<td>90</td>
<td>Pearl River Delta background</td>
<td>40.1±25.0</td>
<td>954</td>
</tr>
<tr>
<td>Dunhuang/DHD</td>
<td>40.13° N, 94.71° E</td>
<td>1139</td>
<td>Desert town</td>
<td>86.2±94.3</td>
<td>726</td>
</tr>
<tr>
<td>Fukang/FKZ</td>
<td>44.28° N, 87.92° E</td>
<td>460</td>
<td>Northwestern country</td>
<td>69.9±69.6</td>
<td>960</td>
</tr>
<tr>
<td>Gongga Mountain/GGM</td>
<td>29.51° N, 101.98° E</td>
<td>1640</td>
<td>Southwestern background</td>
<td>25.5±15.5</td>
<td>869</td>
</tr>
<tr>
<td>Guangzhou/GZC</td>
<td>23.16° N, 113.23° E</td>
<td>43</td>
<td>Southern city</td>
<td>44.1±23.8</td>
<td>772</td>
</tr>
<tr>
<td>Hailin/HILA</td>
<td>47.43° N, 126.63° E</td>
<td>236</td>
<td>Northeastern country</td>
<td>41.6±45.0</td>
<td>1076</td>
</tr>
<tr>
<td>Hefei/HFIC</td>
<td>31.86° N, 117.27° E</td>
<td>24</td>
<td>Eastern city</td>
<td>80.4±45.3</td>
<td>909</td>
</tr>
<tr>
<td>Ji’nan/JNC</td>
<td>36.65° N, 117.00° E</td>
<td>70</td>
<td>Northern city</td>
<td>107.8±57.4</td>
<td>701</td>
</tr>
<tr>
<td>Kunming/KMC</td>
<td>25.04° N, 102.73° E</td>
<td>1895</td>
<td>Southwestern city</td>
<td>47.0±25.2</td>
<td>967</td>
</tr>
<tr>
<td>Lhasa/LZS</td>
<td>29.67° N, 91.33° E</td>
<td>3700</td>
<td>Tibet city</td>
<td>30.6±21.3</td>
<td>600</td>
</tr>
<tr>
<td>Lin’an/LAZ</td>
<td>30.30° N, 119.73° E</td>
<td>139</td>
<td>Eastern background</td>
<td>46.5±27.2</td>
<td>1086</td>
</tr>
<tr>
<td>Mount Everest/ZFM</td>
<td>28.21° N, 86.56° E</td>
<td>4700</td>
<td>Tibet background</td>
<td>24.4±25.1</td>
<td>390</td>
</tr>
<tr>
<td>Namtso/NMT</td>
<td>30.77° N, 90.98° E</td>
<td>4700</td>
<td>Tibet background</td>
<td>11.2±6.9</td>
<td>499</td>
</tr>
<tr>
<td>Nagri/ALZ</td>
<td>32.52° N, 79.89° E</td>
<td>4300</td>
<td>Tibet background</td>
<td>19.5±12.4</td>
<td>72</td>
</tr>
<tr>
<td>Qiannianzhou/QYZ</td>
<td>26.75° N, 115.07° E</td>
<td>76</td>
<td>Southeastern country</td>
<td>52.1±28.4</td>
<td>927</td>
</tr>
<tr>
<td>Qinghai Lake/QHL</td>
<td>37.62° N, 101.32° E</td>
<td>3280</td>
<td>Tibet background</td>
<td>16.2±17.0</td>
<td>590</td>
</tr>
<tr>
<td>Sanya/SYB</td>
<td>18.22° N, 109.47° E</td>
<td>8</td>
<td>Southern island city</td>
<td>16.8±13.1</td>
<td>595</td>
</tr>
<tr>
<td>Shanghai/SHC</td>
<td>31.22° N, 121.48° E</td>
<td>9</td>
<td>Eastern city</td>
<td>56.2±59.4</td>
<td>822</td>
</tr>
<tr>
<td>Shapotou/SPD</td>
<td>37.45° N, 104.95° E</td>
<td>1350</td>
<td>Desert background</td>
<td>51.1±33.3</td>
<td>1016</td>
</tr>
<tr>
<td>Shenyang/SYC</td>
<td>41.50° N, 123.40° E</td>
<td>49</td>
<td>Northeastern city</td>
<td>77.6±41.2</td>
<td>926</td>
</tr>
<tr>
<td>Shijiazhuang/SIZ</td>
<td>38.03° N, 114.53° E</td>
<td>70</td>
<td>Northern city</td>
<td>105.1±92.7</td>
<td>1031</td>
</tr>
<tr>
<td>Taipei/TBC</td>
<td>25.03° N, 121.90° E</td>
<td>150</td>
<td>Island city</td>
<td>22.1±10.7</td>
<td>1083</td>
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<tr>
<td>Taiyuan/TYC</td>
<td>37.87° N, 112.53° E</td>
<td>784</td>
<td>Northern city</td>
<td>111.5±74.9</td>
<td>987</td>
</tr>
<tr>
<td>Tianjin/TJC</td>
<td>39.08° N, 117.21° E</td>
<td>9</td>
<td>Northern city</td>
<td>69.9±49.6</td>
<td>1034</td>
</tr>
<tr>
<td>Tongyu/TYZ</td>
<td>44.42° N, 122.87° E</td>
<td>160</td>
<td>Inner Mongolia background</td>
<td>24.5±24.5</td>
<td>757</td>
</tr>
<tr>
<td>Urumchi/URC</td>
<td>43.77° N, 87.68° E</td>
<td>918</td>
<td>Northwestern city</td>
<td>104.1±145.2</td>
<td>776</td>
</tr>
<tr>
<td>WuXi/WXC</td>
<td>31.50° N, 120.35° E</td>
<td>5</td>
<td>Eastern city</td>
<td>65.2±36.8</td>
<td>1003</td>
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<tr>
<td>Xi’An/XAC</td>
<td>34.27° N, 108.95° E</td>
<td>397</td>
<td>Central city</td>
<td>125.8±108.2</td>
<td>1077</td>
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<tr>
<td>Xianghe/XHZ</td>
<td>39.76° N, 116.95° E</td>
<td>25</td>
<td>North China suburbs</td>
<td>83.7±62.3</td>
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<td>Xinglong/XLZ</td>
<td>40.40° N, 117.58° E</td>
<td>900</td>
<td>North China background</td>
<td>39.8±34.0</td>
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</tr>
<tr>
<td>Xishuangbanna/BNF</td>
<td>21.90° N, 101.27° E</td>
<td>560</td>
<td>Southwestern rain forest</td>
<td>25.0±18.7</td>
<td>707</td>
</tr>
<tr>
<td>Yantai/YTZ</td>
<td>36.05° N, 120.27° E</td>
<td>47</td>
<td>East China sea coast city</td>
<td>51.1±36.7</td>
<td>915</td>
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<tr>
<td>Yucheng/YCA</td>
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<td>22</td>
<td>North China country</td>
<td>102.8±61.8</td>
<td>1008</td>
</tr>
<tr>
<td>Zangdongnan/ZDN</td>
<td>29.77° N, 94.73° E</td>
<td>2800</td>
<td>Southern Tibet forest</td>
<td>12.3±8.0</td>
<td>475</td>
</tr>
</tbody>
</table>
Table 2 Summary of the concentrations of PM$_{2.5}$ and its components (μg/m$^3$) in urban and background sites.

<table>
<thead>
<tr>
<th>Station</th>
<th>PM$_{2.5}$</th>
<th>OM</th>
<th>EC</th>
<th>NO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>NH$_4^+$</th>
<th>MD*</th>
<th>Cl</th>
<th>Un accounted</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Urban sites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beijing(n=88)</td>
<td>71.7</td>
<td>19.1</td>
<td>4.1</td>
<td>9.3</td>
<td>11.9</td>
<td>5.3</td>
<td>4.7</td>
<td>0.7</td>
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<tr>
<td>Shanghai(n=120)</td>
<td>68.4</td>
<td>17.1</td>
<td>2.0</td>
<td>11.9</td>
<td>13.6</td>
<td>5.8</td>
<td>7.3</td>
<td>1.0</td>
<td>18.1</td>
</tr>
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<td>Guangzhou(n=106)</td>
<td>75.3</td>
<td>16.7</td>
<td>7.1</td>
<td>7.2</td>
<td>13.1</td>
<td>4.8</td>
<td>7.3</td>
<td>1.0</td>
<td>18.1</td>
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<td>Lhasa(n=60)</td>
<td>36.4</td>
<td>12.6</td>
<td>1.4</td>
<td>0.5</td>
<td>0.8</td>
<td>0.4</td>
<td>11.6</td>
<td>0.3</td>
<td>8.8</td>
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<td>Shenyang(n=36)</td>
<td>81.8</td>
<td>23.3</td>
<td>5.2</td>
<td>4.6</td>
<td>13.2</td>
<td>4.5</td>
<td>9.2</td>
<td>1.4</td>
<td>20.4</td>
</tr>
<tr>
<td>Chongqing(n=56)</td>
<td>73.5</td>
<td>17.2</td>
<td>4.8</td>
<td>6.5</td>
<td>19.7</td>
<td>6.1</td>
<td>7.4</td>
<td>0.6</td>
<td>11.2</td>
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<td><strong>Background sites</strong></td>
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<td>Xinglong(n=42)</td>
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<td>1.5</td>
<td>3.7</td>
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<td>3.4</td>
<td>5.0</td>
<td>0.3</td>
<td>7.9</td>
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<td>Lin’an(n=60)</td>
<td>66.3</td>
<td>21.7</td>
<td>2.9</td>
<td>8.7</td>
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<td>2.0</td>
<td>0.6</td>
<td>11.9</td>
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<tr>
<td>Dinghu Mountain(n=36)</td>
<td>40.1</td>
<td>11.6</td>
<td>2.0</td>
<td>4.5</td>
<td>10.1</td>
<td>4.0</td>
<td>3.8</td>
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<td>Namsto(n=35)</td>
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<td>3.4</td>
<td>0.2</td>
<td>0.1</td>
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<td>0.4</td>
<td>3.9</td>
<td>0.1</td>
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</tr>
<tr>
<td>Changbai Mountain(n=52)</td>
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<td>0.9</td>
<td>1.1</td>
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<td>Gongga Mountain(n=36)</td>
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<td>0.4</td>
<td>4.7</td>
<td>1.7</td>
<td>3.2</td>
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<td>7.7</td>
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*MD: mineral dust
Fig. 1. Locations and the averaged PM$_{2.5}$ concentrations of the forty monitor stations during (a) the year of 2012-2014, (b) spring, (c) summer, (d) autumn and (e) winter.
Fig. 2. Monthly average PM$_{2.5}$ concentration (histogram, left coordinate) and the occurrence of substandard days in each month (dotted line, right coordinate) at urban and background sites in (a) North China plain, (b) Yangtze River delta, (c) Pearl River delta, (d) Tibetan Autonomous Region, (e) Northeast China Region and (f) Southwestern China Region. The error bar stands for the standard deviation.
Fig. 3 Diurnal cycles of PM$_{2.5}$ at six paired urban and background sites in (a) North China plain, (b) Yangtze River delta, (c) Pearl River delta, (d) Tibetan Autonomous Region, (e) Northeast China Region and (f) Southwestern China Region.
Fig. 4 Average chemical composition and its seasonal variations of PM$_{2.5}$ in (a, c) urban sites and (b, d) background sites.
Fig. 5 Average chemical composition of PM$_{2.5}$ in (a) urban sites and (b) background sites.
Fig. 6 Days separated by the threshold values of the “Ambient Air Quality Standard” (AAQS) (GB3095-2012) of China guideline. The threshold values of 35, 75, 115 and 150 μg/m$^3$ used for the daily concentration ranges are represented as clean (<35 μg/m$^3$), slightly polluted (35-75 μg/m$^3$), moderated polluted (75-115 μg/m$^3$), polluted (115-150 μg/m$^3$) and heavily polluted (>150 μg/m$^3$), which suggested by the guideline of the AAQS.
Fig. 7 Monthly distribution of the occurrence of the polluted days exceeding the “Ambient Air Quality Standard” (AAQS) (GB3095-2012) of China. The symbol size represents the occurrences of polluted days for the corresponding month. The symbol color represents the different mass range. The sites of Nagri and Mount Everest are excluded because of the small sample size.
Fig. 8 Average chemical composition of PM$_{2.5}$ with respect to pollution level. The C, SP, MP and HP is related to clean (daily PM$_{2.5}$ <35 μg/m$^3$), slightly polluted (35 μg/m$^3$<daily PM$_{2.5}$ <75 μg/m$^3$), moderated polluted (75 μg/m$^3$<daily PM$_{2.5}$ <150 μg/m$^3$) and heavily polluted (daily PM$_{2.5}$ >150 μg/m$^3$).