Spatial distributions and chemical properties of PM_{2.5} based on 21 field campaigns at 17 sites in China

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Abstract

Severe air pollution and its associated health impacts have become one of the major concerns in China. A detailed analysis of PM_{2.5} chemical compositions is critical for optimizing pollution control measures. In this study, daily 24-h bulk filter samples were collected and analyzed for totally 21 field campaigns at 17 sites in China between 2008 and 2013. The 17 sites were classified into four groups including six urban sites, seven regional sites, two coastal sites in four fast developing regions of China (i.e. Beijing-Tianjin-Hebei region, Yangtze River Delta, Pearl River Delta and Sichuan Basin), and two ship cruise measurements covered the East China Sea and Yellow Sea of China. The high average concentrations of PM_{2.5} and the occurrences of extreme cases at most sites imply the widespread air pollution in China. Fine particles were largely composed of organic matter and

secondary inorganic species at most sites. High correlation between the temporal trends of PM_{2.5} and secondary species of urban and regional sites highlights the uniformly distributed air pollutants within one region. Secondary inorganic species were the dominant contributors to the high PM_{2.5} concentration in Northern China. However in Southern China, the relative contributions of different chemical species kept constant as PM_{2.5} increased. This study provides us a better understanding of the current state of air pollution in diversified Chinese cities. Analysis of chemical signatures of PM_{2.5} could be a strong support for model validation and emission control strategy.

Key words

Air pollution; China; PM_{2.5}; Chemical properties; Secondary inorganic ions

1. Introduction

Air pollution is one of the most prominent environmental concerns in China due to its association with adverse effects on human health (Heal et al., 2012). High concentrations of gaseous pollutants such as sulfur dioxide (SO₂), ozone (O₃) and particulate matter (PM) from diverse sources coexist in the atmosphere, which far exceed the atmospheric self-purification capacity, and the complicate interactions among them lead to the formation of a complex air pollution that is difficult to disentangle (Shao et al., 2006). Air pollution comes from a complex mixture of sources such as traditional coal combustion, vehicular emissions, and secondary pollution (Kumar et al., 2011; Huang et al., 2014). In 2014, the annual average concentration of PM_{2.5} (PM with aerodynamic equivalent diameters less than 2.5 μm) in 161 cities reached 62 μg m⁻³, while only 11.2% of these cities met the Grade II of China National Ambient Air Quality Standard (Report on the state of the Environment in China, 2015). In recent years, severe and long-lasting haze affected China on many occasions. The pollution episodes which affected 1.3 million km² and 800 million people gained worldwide attention during the first quarter of 2013

(Huang et al., 2014).

Among all the air pollutants, ambient particles are of great interest to the scientific community and policy makers because of their ability to carry health risks, as well as influence air quality and global climate (Dusek et al., 2006; Kumar et al., 2010). The researches on chemical characteristics of particles remain key priorities since the mass and ratios of different components imply the various sources and formation mechanisms. It is crucial to develop detailed chemical databases of particles to precisely conduct source apportionment and evaluate environmental impacts. Significant efforts have been dedicated to understanding the characteristics and formation of fine particle pollution in megacities, especially for city clusters and megacities with high population density such as the Beijing, Tianjin and Hebei (BTH) region (He et al., 2001; Guo et al., 2010), Yangtze River Delta (YRD) region (Wang et al., 2006; Du et al., 2011), Pearl River Delta (PRD) region (Hu et al., 2008; Hu et al., 2012), and Sichuan Basin (Tao et al., 2013; Chen and Xie, 2014). However, most of the studies so far have focused on urban areas, ignoring the rural regions. Yang et al. (2011b) compiled chemical composition of PM_{2.5} for about 13 urban sites, 2 rural sites, and one mountain forest site. However, the different sampling and analytical techniques deployed by individual measurements may introduce a bias in comparative studies on air pollutants. Therefore, harmonized and systematic measurements are a key premise for characterizing the general mapping of air quality in China. In addition, pair studies of urban, regional sites of particle pollution need to be conducted to explore the influence of regional air pollution.

Here we present the mass concentrations and chemical compositions of fine particles based on the results from 21 field campaigns conducted at urban, regional, coastal sites and during two different ship cruise measurements. Chemical properties of PM_{2.5} at the particular sites and seasons are elucidated. Characteristics of regional air pollutions are also analyzed by urban-regional pair studies. The formation of heavy pollution episodes is also discussed. This article, therefore, provides

fundamental information for future studies that aim to evaluate the effects of air pollution on human health and climate change as well as to optimize the emission control strategies for the different regions in China and similar environmental conditions elsewhere.

2. Methodology

2.1. Sites description

Twenty one individual field campaigns were conducted at 17 different sites between 2008 and 2013. Each campaign lasted for around 30 days. According to the population density, geographic location (i.e. the distance between observation site and large pollution source), and energy structure, they were broadly classified into four different types (Table1). These included 6 urban sites, 7 regional sites, 2 coastal sites and 2 ship cruise measurements (see Supporting Information, SI, Section S1).

To highlight regional similarities and differences in particle characteristics, these sites were furtherly divided into 4 large regions according to their geographical location: BTH region (BJ_u, YF_r, WQ_r and CD_c) in Northern China, YRD Region (WX_u, JH_u, HZL_r and WL_{c/r}), PRD Region (GZ_u, SZ_u, JM_r, HS_r and CH_r), and Sichuan Basin (ZY_r) in Southern China. These four groups represented haze-affected regions with rapid industrialization and high population density, causing severe air pollution episodes. Among the 17 sites, three urban-regional site pairs were included: BJ_u-WQ_r in BTH region, JH_u-WL_{c/r} in YRD region and GZ_u-CH_r in PRD region. The regional sites are more than 50 km away from urban centers and have less local emissions compared to urban sites.

2.2. Sampling method

During each individual field campaign, a four-channel PM_{2.5} sampler (TH-16A, Tianhong, China) was deployed to collect samples on Teflon and Quartz filters. The time resolution was 12-h for the BJ_u, GZ_u (2008), YF_r, WQ_r, JM_r, ZY_r and CH_r sites. The samples were collected during daytime and nighttime separately. For the

remaining campaigns, the time resolution was 24-h. The sampling flow rate was 16.7 L min^{-1} . Each sample set consisted of one or two Teflon filters for the total mass and individual water-soluble ions measurement. Analyses of carbonaceous species were conducted with quartz filters. The quartz filters were pre-treated by heating at 550°C for 6 hours before each use. After sampling, the filters were stored in the refrigerator at -20°C until they were analyzed.

$\text{PM}_{2.5}$ mass concentration was obtained with an analytical balance by the gravimetric method (MettlerToledo AG285) (Yang et al., 2011b). As described in Guo et al. (2010; 2012), seven major water-soluble inorganic compounds (K^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , NO_3^- , SO_4^{2-} and Cl^-) were analyzed by ion-chromatograph (DIONEX, ICS-2500/2000). Organic carbon (OC) and elemental carbon (EC) of samples from all the sites except for SZ_u were analyzed via the thermal-optical transmission (TOT) method using a Sunset Laboratory-based instrument with NIOSH method (He et al., 2006). The OC and EC concentrations in samples from SZ_u were obtained by a DRI carbon analyzer, following the IMPROVE thermal optical reflectance (TOR) protocol (Cao et al., 2007). Comparison of EC concentrations in 27 samples showed EC results determined by TOR correction were about 35% higher than those by TOT correction (Fig. S1), which was close to the results obtained by Chow et al. (2004).

3. Results and discussion

3.1. Spatial distribution of chemical species in $\text{PM}_{2.5}$

3.1.1 $\text{PM}_{2.5}$ concentration

Total 1140 sets of $\text{PM}_{2.5}$ samples were collected at the 17 sites between 2008 and 2013. Descriptive statistics for all the valid observations are summarized in Table S2. In general, the mass concentrations of fine particles at different types of sites were 2-5 times higher than those of corresponding sites in European and American cities (Hidy, 2009; Putaud et al., 2010). As shown in Fig.1, high levels of $\text{PM}_{2.5}$ concentration

(exceeding $100 \mu\text{g m}^{-3}$) were observed at most of sites and covered from the urban to regional scale, indicating pollution episodes did not occur at or dependent on one particular season or site, but spread all over China. The average $\text{PM}_{2.5}$ concentrations were nearly identical at urban and regional pair sites of BTH, PRD and YRD regions, indicating the regional feature in the whole city cluster. The mean concentrations at two coastal sites (CD_c and $\text{WL}_{c/r}$) lie well above the median values due to the strong increases during injection of continental air mass with large amounts of air pollutants, which lead to skewed distributions of concentrations. The $\text{PM}_{2.5}$ concentrations measured during ship cruise measurements were relatively higher than that of Indian seas (Quinn and Bates, 2005), indicating that the East China sea and Yellow sea were strongly influenced by the inland anthropogenic activity.

3.1.2 Chemical speciation

Relative contributions of each species to $\text{PM}_{2.5}$ at different sites are plotted in Fig.2. The daily averaged chemical data sets for each individual field campaign are also presented in Table S2. Here we report organic matter (OM) concentration by scaling OC by a constant factor of 1.8 ($\text{OM} = 1.8 \times \text{OC}$) for all sites (Turpin and Lim, 2001). However it is possible that the actual scaling factor is inconstant and it might be higher at rural sites for organic aerosols due to a higher degree of aging (Zhang et al., 2011). The most abundant species in $\text{PM}_{2.5}$ in all campaigns were OM, sulfate, nitrate, ammonium, and EC. As shown in Fig.2, despite the dominant components were same in China, the fractions of each compound varied between different sites and sampling periods. The chemical speciations measured in China are similar to the European studies in the sense, that OM accounted for the highest fraction of $\text{PM}_{2.5}$ at urban sites and that sulfate contributed more at regional and background sites (Putaud et al., 2004).

Carbonaceous species: Carbonaceous aerosols in China are generated from the widespread use of coal, biomass burning, and petroleum products. Residential coal contributes significantly to black carbon in China (Bond et al., 2013).

Carbonaceous species represented a large fraction of PM_{2.5}, accounting for around 30%. The variations of OC/EC ratio may be used as an index reflecting emission sources and secondary organic aerosol (SOA) formation (Zeng and Wang, 2011). In this study, OC/EC ratios ranged from 2.74 to 7.46, within the ranges reported by the literatures of China (Table S3). Comparatively higher OC/EC ratios were observed during ship cruises measurements, due to the SOA formation during long-range transportation from inland to the ocean and biogenically driven OC's contribution to marine aerosol (O'Dowd et al., 2004).

For urban sites, the results were comparable to the concentrations of carbonaceous aerosols at other Chinese sites and some Asia urban sites (Table S3). The heating season with a greater consumption of coals in northern China is a plausible explanation for the high OC concentration in BJ_u. The OC concentration in the wintertime in ZY_r in Sichuan Basin ranked second after BJ_u wintertime. The stagnant dispersion conditions caused by mountain-basin topography in this region enhanced the accumulation of pollutants, leading to a high concentration of OC. In addition, biomass burning in this region also contributed to the high concentration of carbonaceous aerosol (Chen and Xie, 2014).

Relatively high concentrations of OC and EC were found at the regional sites (WL_{c/r}) compared to those of regional/background sites in other part of world (Table S3). This may be due to the strong anthropogenic influences from YRD region, respectively. The measurement at CD_c was comparable to the previous observation during the spring of 2003 (Feng et al., 2007). Asian continental flow carried pollutants to this downstream site.

Inorganic species: The anthropogenic emissions of precursors (SO₂, NO_x, and NH₃) strongly influence the concentration and compositions of SNA aerosol (sum of the mass concentration of NH₄⁺, SO₄²⁻ and NO₃⁻) (Wang et al., 2013). The high concentration of precursor gaseous pollutants can partially explain the high SNA

concentrations in China (Table S1). In this study, the contributions of sulfate were almost equal to those of OM in urban field campaigns, and higher contributions of sulfate were observed in regional sites. The concentrations of sulfate were 5-10 times the measured concentrations in Europe and United States (Putaud et al., 2004; Hidy, 2009).

Nitric acid is mainly formed by the reaction of NO₂ with OH radical during daytime or through hydrolysis of N₂O₅ during nighttime. The former pathway dominates HNO₃ formation (Alexander et al., 2009). Although the PRD region has higher NO_x emission intensity (Wang et al., 2013), the concentrations and the relative contributions of nitrate in this region were lower than those of other regions (below 10% of PM_{2.5}). The reason is partly attributed to the difficulties in precisely measuring particulate nitrate due to its volatilization under high temperatures.

In general, SNA contributed to more than 90% of the total inorganic ionic species mass and accounted for ~50% of PM_{2.5} during all field campaigns. Regional sites presented a comparatively higher percentage of SNA than urban sites, indicating relative higher contribution of secondary aerosol formation. It is consistent with European results that the regional background aerosol of Spain exhibited similar secondary characteristics (Salvador et al., 2012).

For the sites strongly influenced by biomass burning (i.e. ZY_r and HS_r), the concentrations of K⁺ could be more than 1 µg m⁻³, accounting for ~2% in PM_{2.5}. Higher chloride concentration at CD_c was mainly attributed to sea salt aerosols, for the coastal site was influenced by marine air masses (Wu et al., 2006). Relative higher concentrations of Ca²⁺ were observed at UR_u and WX_u. It has been reported that in spring, soil dust was transported from Jungger Basin and Guebantongute desert in the north of UR_u, resulting in a higher contribution of Ca²⁺ (Li et al., 2008). The neutralizing level of PM_{2.5} was determined by the equivalent charge ratio of major

cations to anions. The result shows the acidic aerosol can be neutralized at most of the sites (see Fig. S2).

The contribution of unidentified fraction (others) is estimated by taking the difference of the sum of OM, EC, and inorganic constituents from the $PM_{2.5}$, accounting for 2-40% among all the field campaigns. The unidentified matter mainly consists of crustal dust and sea salt. Crustal species tend to play a minor role in $PM_{2.5}$ (around 10%) (Zhou et al., 2016). But given their importance in source apportionment, detailed analysis of elements will be done in future analysis.

3.2. Chemical characterizations of fine particles

3.2.1 Characteristic of regional air pollution

The role of regional air pollution due to the rapid urbanization has been studied extensively in the past few years (Guo et al., 2010; Yang et al., 2011a; Li et al., 2014). Regional pollution is regarded as the regional scale elevated concentrations of air pollutants, which mainly due to the secondary formation and the horizontal and vertical homogeneity of the meteorological conditions of the whole region (Jia et al., 2008). Previous results revealed that persistent regional stagnation conditions favored the elevation of PM mass or SO_4^{2-} on a regional scale from the mid-western to northeastern of United States (Blanchard et al., 2013). Although several studies have been performed at urban/rural pair sites to investigate regional air pollution in BTH region (Guo et al., 2010; Yang et al., 2011a), a thorough analysis of the chemical components of fine particles for pair sites in China has not been conducted.

The comparison of chemical properties of fine particles at a pair sites supports the assessment of regional air pollution. For most chemical species, urban concentrations were similar to their regional counterparts, indicating the uniform distribution of regional pollution. For EC, the urban concentration reached 222% higher than that of regional sites, showing a stronger local contribution than other components (see Fig. 3). The linear correlations between temporal trends of each

species (e.g. concentration of $\text{PM}_{2.5}$, OC, SO_4^{2-} , NO_3^- , NH_4^+) of pair sites were analyzed here in terms of the Spearman correlation analysis, for example the correlation of $\text{PM}_{2.5}$ concentrations of BJ_u and WQ_r , to investigate the regional pollutions of fine particles during the observation periods. Table S4 summarizes the results of the correlation coefficient of each species. The temporal trends of $\text{PM}_{2.5}$ at the urban sites typically correlated well with those of corresponding regional sites. The regional wide elevated PM concentrations indicated the occurrence of regional air pollution. The analysis also showed generally high correlation values between the daily data of pair sites for the secondary inorganic species. The SO_4^{2-} correlations for BTH, YRD, and PRD region ranged from 0.74 to 0.78. This is consistent with a regional formation mechanism with SO_4^{2-} . For the primary traffic-related components, EC, the correlation coefficient decreased to around 0.5 for the three regions, indicating the influence of local emissions (see Fig.3). High correlations between the temporal trends of $\text{PM}_{2.5}$ and different chemical components of urban and regional sites highlighted the uniformly distributed air pollutants within one region. The regional influences were greater for secondary species than primary components.

3.2.2 Formation of heavy pollution episodes

Given the coupling interactions between complex meteorological conditions, pollution sources, and atmospheric transformation processes, characterization of formation mechanisms of severe haze with high $\text{PM}_{2.5}$ levels at different sites presents a major challenge (Guo et al., 2014). Fig.4 shows the relative contribution of OM, EC, SO_4^{2-} , NO_3^- , NH_4^+ and others to $\text{PM}_{2.5}$ as a function of $\text{PM}_{2.5}$ mass concentration. In Northern China (BTH region and CD_c), the fraction of OM in fine particle decreased with increasing $\text{PM}_{2.5}$ concentration, while the relative contributions of secondary inorganic species increased at the urban, regional, and coastal sites. When $\text{PM}_{2.5}$ concentration reached peak values, the fractions of SNA were around 60%-80%, indicating the importance of secondary formation in the

pollution episodes. Previous research with back trajectory analysis revealed that the clean air masses from the north had a larger contribution from primary aerosol emissions, characterized by a higher contribution of OM, while haze pollution occurred when stagnant air masses with secondary regional aerosols dominated (Huang et al., 2010; Sun et al., 2010). A broadly consistent pattern was also observed in Taiyuan, which is a heavily polluted city in Northern China (Meng et al., 2007). However in the Southern China (YRD and PRD region), the relative contributions of different chemical components remained relatively constant (the increase of secondary aerosols concentration was lower than 15%) as the $PM_{2.5}$ concentration increased. No significant increase of SNA fraction in $PM_{2.5}$ was also observed during a heavy polluted episode in the YRD region, with 42% on moderate days and 52% on the heavily polluted days (Fu et al., 2008).

Although secondary formation was a major cause of particulate pollution in the whole China, the discrepancy of relative contribution from different chemical components to $PM_{2.5}$ level implies diverse formation mechanisms of heavy air pollution at different sites of China. Comparatively stronger emissions of gas precursors (e.g SO_2 , NO_x) in Northern China would have a potential effect on SNA formation (Wang et al., 2013). It may be a plausible explanation for the dominant contribution of SNA. It is of interest to perform detail analyses on the relationship of geographical features with formation mechanisms of heavy pollution at specific sites in China.

4. Summary and conclusions

The paper presents comprehensive assessments of the chemical property of fine aerosol particles at different sites in China. Datasets of chemical characteristics of fine particles from 21 field campaigns at 17 sites are analyzed to understand the sources and transformation of $PM_{2.5}$ in the atmosphere.

Heavy pollution episodes with $PM_{2.5}$ higher than $100\mu g\ m^{-3}$ were observed

during most of the campaigns, independent of sites and seasons. High PM_{2.5} mass concentrations of coastal sites and during cruise measurements indicated offshore regions of China were strongly influenced by continental air pollutants. Organics and sulfate were the most abundant species in PM_{2.5}. SNA accounted for about 50% of the PM_{2.5} concentration.

Simultaneous measurements conducted at three urban-regional pairs of sites demonstrated the urban and regional sites had similar concentrations of pollutants. The similar variations of temporal trends of PM_{2.5} and secondary inorganic species of pairs sites indicated a uniform distribution of pollution.

Secondary inorganic species were the dominant contributors to high PM_{2.5} concentration in Northern China, indicating a high level of the secondary formation during haze days. The relative contributions of each species as a function of PM_{2.5} mass concentration demonstrated that Northern China and Southern China has different formation mechanisms of heavy pollution episode.

Our study presents a comprehensive picture of PM_{2.5} chemical composition at a numerous of different types of sites in China and evaluates air-pollutant compositional similarities and differences. This dataset can be further used for more in-depth research on source apportionment and secondary pollutants formation mechanisms, besides carrying out a thorough scientific assessment of health impacts.

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Table 1. Description of sampling sites and duration. Please note that the words in parenthesis against each site represent the short name of each site, and subscripts

u, r, c, b and s indicate urban, regional, coastal and cruise site types, respectively.

I and II refer to the first and second ship cruise measurement.

Type	Sites	Coordinates	Sampling period	Valid data ^{a*}
Urban	Beijing (BJ _u)	39.9°N, 116.4°E	16 July-31 August 2009 ^{b*}	92
			01 December 2009-28 February 2010 ^{b*}	115
			01 March-31 May 2010	86
	Guangzhou (GZ _u)	23.1°N, 113.3°E	15 October-16 November 2008 ^{b*}	64
			10-30 November 2010	20
	Shenzhen (SZ _u)	22.5°N, 113.9°E	31 December 2008-31 December 2009 ^{c*}	168
	Urumchi (UR _u)	87.6°N, 43.8°E	17 May-03 June 2008	18
	Wuxi (WX _u)	31.6°N, 120.3°E	21 April-05 May 2010	16
			21 July-07 August 2010	18
Regional	Jinhua (JH _u)	29.1°N, 119.7°E	29 October- 28 November 2011	21
	Yufa (YF _r)	39.5°N, 116.3°E	16 July-31 August 2008 ^{b*}	92
	Wuqing (WQ _r)	39.4°N, 117.0°E	16 July-25 August 2009 ^{b*}	81
	Jiangmen (JM _r)	22.6°N, 113.1°E	16 October-16 November 2008 ^{b*}	66
	Heshan (HS _r)	22.7°N, 112.9°E	13-30 November 2010	18
	Conghua (CH _r)	23.3°N, 113.1°E	16 October-17 November 2008 ^{b*}	64
	Hongze Lake (HZL _r)	33.2°N, 118.2°E	17 March-24 April 2011	31
	Ziyang (ZY _r)	30.2°N, 104.6°E	02 December 2012-05 January 2013 ^{b*}	67
Coastal/ regional	Wenling (WL _{c/r}) ^{d*}	28.4°N, 121.6°E	29 October-28 November 2011	25
	Changdao(CD _c)	38.0°N, 120.7°E	18 March-24 April 2011	34
Cruise	ES _s I		17 March-27 March 2011	33
	ES _s II		28 May-10 June 2011	11

^{a*}Valid data refers to the number of set of filter samples; ^{b*} 12-h aerosol samples were collected; ^{c*}Filter samples were collected every 2 days; ^{d*}Coastal site Wenlin

can be considered as a regional site of YRD region.

Fig. 1. Box-Whisker plot for PM_{2.5} mass concentration of each filed campaign. The box denotes the 25, 75 percentiles. The whiskers denote the 5th and 95th percentiles. The points represent max/min value. Crosses and horizontal lines represent the mean value and median value of PM_{2.5} concentration for entire study period, respectively.

Fig. 2. The mass concentration of PM_{2.5} and its major chemical speciation at different locations in China. (unit: $\mu\text{g m}^{-3}$)

Fig. 3. Comparison of mass concentration of PM_{2.5} and major chemical species for urban and regional sites in each region. Each color corresponds to a chemical species. The size of each circle is proportional to the correlation values between the temporal

trends of each species at urban and regional site.

Fig. 4. Relative contribution of each species (OM , SO_4^{2-} , NO_3^- , NH_4^+ , EC , and others) to $\text{PM}_{2.5}$ is shown as a function of total mass concentration of $\text{PM}_{2.5}$. The grey line denotes the trend of fraction of SNA as a function of $\text{PM}_{2.5}$ level.

Spatial distributions and chemical properties of PM_{2.5} based on 21 field campaigns at 17 sites in China

Supporting Information

S.1 Site description

S.1.1 Urban sites

The first urban site, Beijing (BJ_u; 39.9°N, 116.4°E), was located at the urban atmospheric environment monitoring station at Peking University. The observation site was located on the roof of a six-floor building on the campus of Peking University in the northwestern part of Beijing. It was about 600m away from one of major traffic lines of Beijing (Guo et al., 2010). The campaign included three parts, which were conducted from 16 July to 31 August 2009, 01 December 2009-28 February 2010, and 01 March- 31 May, 2010.

The second urban site, Guangzhou (GZ_u; 23.1°N, 113.3°E) was located on the top of the building (about 50m above street level) inside the Guangdong Provincial Environmental Monitoring Center (Yue et al., 2013). As the largest city in southern China and the central city of Pearl River Delta region, Guangzhou maintains a high development speed since the inception of reform and open up policy. The measurements of trace gases and particles were carried out from 15 October to 16 November, 2008, and 10 to 30 November, 2010 as part of PRD intensive campaign.

The third urban site, Shenzhen (SZ_u; 22.5°N, 113.9°E), was on the roof of an academic building (about 20m above the ground level) on the campus of Shenzhen Graduate School of Peking University. The campus was surrounded by vegetation, and no strong anthropogenic sources were present nearby. Shenzhen is also a fastest-developing city in the PRD region. The samples were collected during 2009.

The fourth urban site, Urumchi (UR_u; 87.6°N, 43.8°E), was located on roof of the Urumchi Environmental Monitoring Center in the center of Urumchi city.

Urumchi city is the capital of Xinjiang Uyghur Autonomous Region, with the biggest desert in China to the north and mountains to the south. Since it is located in the basin of Eurasia, the geographic location and meteorological conditions of Urumchi city is unfavorable for the dispersion of air pollutants. In additions, the city was often influenced by frequent sandstorms advected from the Gobi desert, resulting in high PM_{10} concentration (Li et al., 2008). The sampling inlet at UR_u site was located at ~20m above the street level. The sampling site was surrounded by residential and business buildings. The campaign lasted 18 days, from 17 May to 03 June, 2008.

The fifth and sixth urban site, Wuxi (WX_u; 31.6°N, 120.3°E) and Jinhua (JH_u; 29.1°N, 119.7°E), are both important cities in the well-developed regions in the Yangtze River Delta. The greater YRD area has over 140 million people. The detailed geographic description of both measurement sites are presented in Peng et al. (2014). The samples were collected in spring, from 21 April to 05 May, 2010, and summer, from 21 July to 07 August, 2010 at WX_u site. At JH_u site, the samples were collected from 29 October to 28 November, 2011.

S.1.2 Regional sites

The first regional sites, Yufa (YF_r, 39.5°N, 116.3°E), was a rural site that was located about 53 km to the south of Peking University. The sampling site was on top of a building (about 20 m above the ground level) on the campus of Huangpu College. During the campaign, the airmasses that arrived in Yufa were mainly from south and southwest. It was considered as an upwind rural site of BJ_u site. Given the relatively few industrial facilities and no major road locates nearby, YF_r had very few local emissions except domestic coal and biomass burning (Guo et al., 2010). The samples were collected during summer field campaign from 16 July to 31 August, 2008.

The second regional site, Wuqing (WQ_r, 39.4°N, 117.0°E), was located in the North China Plain (NCP) between the two megacities of Beijing (80km) and Tianjin

(30km). The site was inside the yard of the Wuqing Meteorological Administration of Tianjin and surrounded by farming land. No large local emission sources were located in the surrounding areas (Deng et al., 2011). The sampling inlet was about 2 meters above the ground. The campaign was conducted from 16 July to 25 August, 2009. Previous researches showed Wuqing can highly represent the regional air pollution in NCP (Xu et al., 2011).

The third regional site, Jiangmen (JM_r , 22.6°N, 113.1°E), was located in a mountainous areas with a spare pollution. Fruit trees were grown on the mountains surrounding this site. JM_r was a downwind site of GZ_u where the northerly or northwesterly winds prevailed during the observation period. The campaign was also a part of PRD intensive campaign, started from 16 October to 16 November, 2008.

The fourth regional site, Heshan (HS_r , 22.7°N, 112.9°E), was located on the top of a small hill (40m) and surrounded by farmlands and forests. It was 7 km from downtown areas of Heshan city and other strong industrial sources. As the observation period was autumn, biomass burning events were observed occasionally in the farmlands nearby. Since the wind was mainly from north and northeast during the campaign, Heshan was an urban outflow site of Guangzhou in the central PRD (Gong et al., 2012). The samples were collected simultaneously in GZ_u and HS_r , from 13 to 30 November, 2010.

The fifth regional site, Conghua (CH_r ; 23.3°N, 113.1°E), was located northwest of Guangzhou, which is in the center of Guangdong province. It was representative of the urban background atmosphere in the PRD region. Anthropogenic source in the surrounding area was relative spare. Since the wind mainly came from north or northwest (Zheng et al., 2010), the CH_r site can be considered as an upwind site of the megacity, Guangzhou. The campaign was carried from 16 October to 17 November, 2008, as a part of PRD intensive campaign.

The sixth regional site, Hongze Lake (HZL_r , 33.2°N, 118.2°E), was located in the Hongze Lake national wetland nature reserve. The observatory was on the 3rd

floor of a stationary ship, which was about 10m from the surface of the lake. The surrounding was mostly composed of farmland and reeds, with no industrial sources in the region. The campaign lasted 35 days, from 17 March to 24 April, 2011.

The seventh regional site, Ziyang (ZY_r, 30.2°N, 104.6°E), was located on the campus of a middle school. Ziyang was a small city located between two megacities in southwestern China, Chengdu and Chongqing. As a city located in the Sichan basin, Ziyang has complex topography, which promotes the accumulation of air pollutants. Hills covered with vegetation were located to the north of the site, with major road ways on the other three sides. Biomass burning events were observed occasionally from domestic heating and cooking. The campaign was conducted from 02 December 2012 to 05 January 2013.

S.1.3 Coastal site

Detailed geographic description of the coastal site Changdao (CD_c; 38.0°N, 120.7°E), is presented in Peng et al. (2014). Since during the campaign (from 18 March to 24 April, 2011) the air mass mainly came from west and south direction, Changdao was a downwind site of the BTH region and Shandong Peninsula. As a result, we were able to observe the long-range transport of air pollution from the central eastern China.

The description of the second coastal site Wenling (WL_{c/r}; 28.4°N, 121.6°E) is also presented in Peng et al. (2014). Since clean airmass from the sea and continental air mass from YRD region dominated this site alternatively, it could be consider as a regional site of YRD region. The campaign in WL_{c/r} was carried simultaneously with that in JH_u.

S.1.4 Ship cruise measurement

Ship cruise measurement (ES_s) was carried out on the Dong Fang Hong 2, which is a multi-functional marine research vessel (<http://eweb.ouc.edu.cn/4b/61/c4169a19297/page.htm>). The observatory was located on the 6th floor of the Dong Fang Hong 2. The ship cruise measurement was divided

into two parts, ES_sI started from Qingdao in the Shandong province (24.5°N, 118.1°E) on 17 March 2011, reached the southernmost area of near Wenzhou of Zhejiang province on 27 March 2011, and returned to Qingdao (24.5°N, 118.1°E) on 9 April 2011. ES_sII started from Fujian province (24.6°N, 119.0°E) on 28 May 2011, and arrived at Shandong province (36.0°N, 121.4°E) on 10 June 2011. These two cruise studies covered the East China Sea and Yellow Sea of China, respectively. Contamination from ship exhaust were determined by wind direction (wind and the vessel were in same direction), wind speed (contamination suspected if wind speed was lower than running speed of the vessel), concentration of NO and SO₂. Those samples influenced by ship emission were excluded from filter results presented below.

S.2 Levels of gaseous pollutants

Continuous measurements of SO₂, CO, O₃, NO, and NO₂ were measured at 16 different sites during 18 individual campaigns. The SO₂ concentration was measured by an online SO₂ analyzer either by a Thermo-Fisher Inc., USA (43C/ 43i) or an Ecotech Inc., AU (EC9850T). Concentrations of CO were measured by an enhanced trace level CO analyzer (48C, Thermo Environment Inc. (TEI), US) or an online CO analyzer (EC9830, Ecotech Inc., AU). O₃ concentrations were measured by a UV absorption ozone analyzer (49C, Thermo Environment Inc. (TEI), US) or an online O₃ analyzer (EC9810, Ecotech Inc., AU) at different sites. Concentrations of NO, NO₂, and NO_x were measured by either an online NO-NO₂-NO_x analyzer (42i, Thermo-Fisher, USA) or the instrument EC9841T from Ecotech Inc., AU. The time resolution of gas measurements were 1 min. Multipoint calibrations and zero checks of SO₂, CO, and NO-NO₂-NO_x analyzer were performed throughout the individual campaigns to ensure the quality of the data (Dong et al., 2012). The O₃ analyzer was calibrated by an O₃ calibrator at the beginning and at the end of each campaign.

S.3 Aerosol acidity

Acidity is an important chemical property to measure because it governs the aerosol phase reactions in terms of catalyzation of the secondary organic aerosol formation reaction (Surratt et al., 2007). Aerosol acidity is assessed by ion-balanced method. The neutralizing levels of PM_{2.5} was determined by the equivalent charge ratio of the cations to anions which are shown in Eq. (1) and (2), respectively (He et al., 2012). The square brackets refer to the molar concentration of the species inside.

$$\text{Cation equivalence } (\mu\text{M m}^{-3}) = [\text{NH}_4^+] + 2[\text{Ca}^{2+}] \quad (1)$$

$$\text{Anion equivalence } (\mu\text{M m}^{-3}) = [\text{NO}_3^-] + 2[\text{SO}_4^{2-}] \quad (2)$$

A ratio of cation versus anion ($R_{C/A}$) less than one indicates a partial neutralization of acidic aerosols. At most sites, this ratio was near 1, ranging from 0.89-1.10 (see Fig.S2). In contrast, for UR_u samples and ES_sI samples in spring, the ratio was much higher than one, indicating that the aerosols were in alkaline mode at these two sites. It is reliably due to the high concentrations of Ca²⁺ at UR_u transported from Jungger Basin and Guebantongute desert (Li et al., 2008). Ca²⁺ also played an important role in neutralizing the aerosol acidity during ship cruise measurements. For SZ_u site, since the concentrations of Ca²⁺ were not quantified, their contributions as well as neutralizing levels could not be calculated in our study.

Table S.1. Concentration of SO₂, NO, NO₂, CO, and O₃ during measurements at each site.

Type	Sites	Season	SO ₂ (ppb)	NO (ppb)	NO ₂ (ppb)	CO (ppb)	O ₃ (ppb)
Urban	BJ _u	Spring	7.31	15.09	27.71	960	22.84
		Summer	2.89	6.7	24.31	1180	36.03
		Winter	27.05	34.9	29.41	1940	12.07
	SZ _u	Spring	2.88	7.69	16.91	420	28.34
		Summer	3.02	10.42	15.31	400	18.25
		Autumn	3.83	11.94	19.87	580	30.09
		Winter	4.54	14.65	29.32	960	23.92
	WX _u	Spring	12.67	20.87	32.95		
		Summer	17.91	13.15	15.61	1833	23.41
	JH _u	Autumn	14.54	12.5	28.74	863	18.23
Regional	YF _r	Summer	4.84	1.5	9.52	760	43.97
	WQ _r	Summer	4.44	2.56	18.29	1247	45.39
	JM _r	Autumn	12.41	6.69	12.13	1248	37.7
	HS _r	Autumn	18.19	3.97	26.02	1200	39.13
	CH _r	Autumn	11.53	6.72	5.74	1130	47.74
	HZL _r	Spring	7.7	1.2	19.2	640	49.1
	ZY _r	Winter	6.85	8.16	12.25	817	15.34
Coastal/	WL _{c/r}	Autumn	4.09	2.12	10.49	499	25.78
Regional	CD _c	Spring	9.31	1.02	15.3	570	42.96
Cruise	ES _s I	Spring	3.52	0.96	4.84	370	54.55
	ES _s II	Spring	1.04	0.3	2.12	276	50.33

Table S.2. Comparison of PM_{2.5} mass concentrations and chemical compositions ($\mu\text{g m}^{-3}$) of different field campaigns.

Type	Site	Season	PM _{2.5}	OC	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Urban	BJ _u	Spring	65.2±65.1	9.6±9.6	1.9±1.9	11.1±10.1	11.1±11.0	1.9±1.9	6.8±6.7	1.1±1.1	0.1±0.1	0.6±0.4
		Summer	88.9±39.1	10.4±9.6	2.7±0.9	23.0±13.9	16.2±11.8	1.0±0.8	11.8±6.8	0.9±0.7	0.2±0.1	1.0±0.3
		Winter	84.0±66.6	16.5±12.9	2.7±2.5	8.1±8.3	8.0±9.6	3.6±3.4	5.9±7.1	1.9±3.3	0.3±0.4	0.5±0.7
	GZ _u	Autumn_08	53.9±18.7	12.1±4.7	2.9±1.7	13.8±5.6	2.7±2.1	0.5±0.4	5.6±2.3	1.0±0.3	0.04±0.02	0.3±0.1
		Autumn_10	73.3±16.5	14.0±3.8	3.6±1.2	16.6±4.0	5.7±3.8	0.6±0.3	6.2±2.0	1.3±0.4	0.04±0.02	0.3±0.1
	SZ _u	Spring	34.7±14.8	6.3±2.9	3.7±1.8	10.6±4.7	1.5±0.6	0.2±0.1	3.3±1.3	0.4±0.2	-	-
		Summer	25.9±15.0	5.0±2.8	3.8±2.3	7.1±5.0	1.0±0.5	0.2±0.2	2.0±1.6	0.3±0.2	-	-
		Autumn	47.2±24.7	10.4±6.9	5.4±3.4	16.4±4.9	3.4±3.6	0.6±0.5	3.9±1.7	0.7±0.5	-	-
		Winter	64.6±24.7	12.9±6.3	5.8±3.0	20.6±3.5	4.9±3.5	0.5±0.5	4.6±1.0	1.1±0.7	-	-
	UR _u	Spring	45.8±15.2	11.1±3.3	4.0±0.8	4.2±1.2	1.1±0.3	1.3±1.0	1.0±0.5	0.3±2.8	0.1±0.01	2.1±1.2
	WX _u	Spring	82.1±27.0	11.3±4.4	3.4±1.9	12.8±3.8	9.9±6.3	1.5±1.0	7.0±2.0	0.9±0.3	0.1±0.1	1.6±1.3
		Summer	46.2±20.3	8.2±3.3	2.2±1.2	12.9±9.0	2.2±3.2	0.4±0.3	5.4±3.5	0.5±0.2	0.05±0.01	0.5±0.1
	JH _u	Autumn	81.9±26.2	11.4±4.0	5.2±1.8	18.3±6.7	12.6±7.0	2.1±0.6	10.4±4.1	1.1±0.4	0.13±0.13	0.3±0.1
Region-a ₁	YF _r	Summer	65.3±32.3	9.0±2.6	2.3±0.9	24.7±16.8	7.7±4.4	1.0±0.6	11.4±7.3	0.8±0.3	0.04±0.02	0.3±0.1
	WQ _r	Summer	82.7±38.1	7.2±3.1	2.8±1.0	26.9±16.9	14.1±7.9	2.5±1.2	14.5±7.4	0.8±0.6	0.06±0.03	0.2±0.1
	JM _r	Autumn	54.0±26.1	8.8±2.1	1.7±0.7	15.7±6.6	3.8±2.8	0.5±0.3	6.6±3.0	1.1±0.4	0.03±0.01	0.2±0.1
	HS _r	Autumn	98.2±20.8	15.7±4.6	5.8±1.8	20.6±3.5	9.7±3.8	2.4±1.1	10.5±2.1	1.6±0.4	0.04±0.02	0.3±0.1
	CH _r	Autumn	31.1±12.9	5.6±2.1	0.9±0.4	10.8±4.9	0.7±0.5	0.1±0.1	4.0±1.8	0.7±0.3	0.02±0.01	0.1±0.1
	HZL _r	Spring	74.7±26.2	6.3±2.1	1.5±0.5	13.4±8.0	13.7±8.2	0.9±0.7	8.2±4.7	0.9±0.3	0.1±0.1	0.7±0.5
	ZY _r	Winter	94.1±44.8	16.5±7.9	5.4±2.1	15.6±7.5	13.2±9.9	2.7±1.8	9.8±5.2	1.2±0.8	0.04±0.02	0.2±0.2
Coastal	WL _{c/r}	Autumn	52.2±32.8	8.1±4.8	2.1±1.6	12.1±9.2	7.2±6.5	1.7±1.1	6.4±4.5	0.7±0.5	0.05±0.03	0.2±0.1

	CD _c	Spring	84.7±44.5	6.9±2.3	1.9±0.8	12.5±9.5	18.2±16.3	2.2±2.0	8.3±7.6	1.0±0.7	0.1±0.1	1.2±1.0
Cruise	ES _s I	Spring	36.6±16.2	4.7±1.6	0.8±0.5	5.7±3.1	2.7±2.2	0.2±0.2	3.6±1.8	0.3±0.1	0.02±0.03	0.1±0.1
	ES _s II	Spring	26.0±11.7	2.4±1.6	0.5±0.5	7.8±3.9	0.1±0.1	0.1±0.1	2.8±1.4	0.3±0.4	0.01±0.02	0.1±0.1

Table S.3. Comparisons of carbonaceous aerosol concentrations with other studies in

Location	Station types	period	OC ($\mu\text{g m}^{-3}$)	EC ($\mu\text{g m}^{-3}$)	OC/EC	Reference
BJ _u , China	Urban	Jul-06	10	2.2	4.6	Lin et al. (2009)
GZ _u , China	Urban	Jul-06	8.9	4.7	1.9	Verma et al. (2010)
Xiamen, China	Peri-urban	Summer 2009	9.7	2.2	4.4	Zhang et al. (2012)
		Autumn 2009	14	3	4.7	
		Winter 2009	23.6	4.2	5.6	
		Spring 2010	13.6	2.3	5.9	
Seoul, Korea	Urban	Mar 2003 – Feb 2005	10.2	4.1	2.5	Kim et al. (2007)
Gwangju, Korea	Urban	Mar–May 2001	15.7	5.7	2.8	Park et al. (2005)
Zografou, Greece	Urban	Feb–Dec 2010	2.43	0.99	2.5	Remoundaki et al. (2013)
BangGuang, China	Regional	Jul 2001– Aug 2002	5.7	3.3	1.7	Hu et al. (2012)
CH _r , China	Regional	Oct, Dec 2002; Mar, Jun 2003	8.1	1.4	5.8	Hagler et al. (2006)
Pittsburgh, USA	Regional	Jul 2001 – Aug 2002	2.8	0.9	3.1	Polidori et al. (2006)
T1, Mexico	Suburb	Mar 2006	6.4	2.1	3.1	Yu et al. (2009)
T2, Mexico	Non-urban	Mar 2006	5.4	0.6	9	
Barcelona, Spain	Urban background	Summer 2004	3.6	1.5	2.4	Viana et al. (2007)
CD _c , China	Coastal	Spring 2003	7.8	1.5	5.2	Feng et al. (2007)

China and other countries.

Table S.4. Spearman correlation analysis of daily data from pair sites in three regions for PM_{2.5} and different chemical components.

Spearman Correlations	PM _{2.5}	OC	EC	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺
BTH (BJ _u -WQ _r)	0.71**	0.73**	0.64**	0.78**	0.72**	0.73**
PRD (GZ _u -CH _r)	0.55**	0.60**	0.26	0.78**	0.68**	0.76**
YRD (JH _u -WL _{c/r})	0.66**	0.77**	0.54*	0.74**	0.46*	0.59**

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)

Fig. S1. Comparisons between TOR- and TOT-corrected EC. Note that the dashed line indicates the 1:1 correspondence.

Fig. S2. $R_{C/A}$ of different field campaigns.

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