

A comparison study of carbonaceous aerosols in a typical North China Plain urban atmosphere: Seasonal variability, sources and implications to haze formation



Shengzhen Zhou ^{a,b}, Lingxiao Yang ^{a,c,*}, Rui Gao ^d, Xinfeng Wang ^a, Xiaomei Gao ^e, Wei Nie ^{c,f}, Pengju Xu ^g, Qingzhu Zhang ^a, Wenxing Wang ^a

^a Environment Research Institute, Shandong University, Jinan, 250100, PR China

^b School of Atmospheric Sciences, Sun Yat-Sen University, Guangzhou, 510275, PR China

^c Jiangsu Collaborative Innovation Center for Climate Change, Nanjing, 210093, PR China

^d Shandong Academy of Environmental Science, Jinan, 250013, PR China

^e School of Resources and Environment, University of Jinan, Jinan, 250022, PR China

^f Institute for Climate and Global Change Research & School of Atmospheric Sciences, Nanjing University, Nanjing, 210093, PR China

^g College of Geography and Environment, Shandong Normal University, Jinan, 250014, PR China

HIGHLIGHTS

- Strong seasonal variability for carbonaceous aerosols in the NCP urban area.
- Coal and biomass combustion and secondary formations are important carbonaceous aerosol sources.
- RH and aqueous-phase chemical reactions contributed to the formation of regional haze.

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ABSTRACT

For a better understanding of the formation of regional haze in the North China Plain (NCP) region, aerosol concentrations and compositions, trace gases and meteorological factors were comprehensively measured for 1 year in Jinan, a typical city in the NCP. Through comparison studies between hazy & non-hazy days, and five years of changes, this paper presents the characterisation of seasonal variations and sources of carbonaceous aerosol, and their implications to haze formation in the NCP region. The contributions of carbonaceous aerosols ($OC \times 1.8 + EC$) to $PM_{2.5}$ ranged from 17.2 to 30.4% on hazy days and 20.5–29.7% on non-hazy days. The annual trends of organic carbon (OC) and elemental carbon showed obvious seasonality, with the lowest and highest concentrations in spring and winter, respectively. The ratio of secondary OC to OC on hazy days during all four seasons ranged from 43.8 to 63.4%, which was higher than that on non-hazy days. Different types of haze events are identified (e.g., combustion of coal and biomass), and the sources and formation mechanisms of carbonaceous aerosols are discussed. In winter, coal combustion and secondary formation were the main sources of carbonaceous aerosols. Biomass combustion contributed to the rapid enhancement of carbonaceous aerosols during summer and autumn. We found that the OC and secondary OC concentrations on haze-fog days during the winter of 2012–2013 in Jinan were much higher than those during the winter of 2007–2008, which was consistent with the ambient relative humidity. These results suggest that aqueous reaction played a significant role in the formation of secondary organic aerosols and contributed to regional haze formation in the NCP region.

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1. Introduction

Carbonaceous aerosols comprise elemental carbon (EC) and organic aerosols (OAs), which are the main components of $PM_{2.5}$,

* Corresponding author. Environment Research Institute, Shandong University, Jinan, 250100, PR China.

E-mail address: yanglingxiao@sdu.edu.cn (L. Yang).

making up over one third of PM_{2.5} mass loading (Yang et al., 2011; Zhang et al., 2007; Zhou et al., 2014). EC is emitted directly from incomplete combustion of fossil fuels and biomass, whilst OAs can be either directly emitted from numerous sources such as fossil fuel combustion, motor vehicles and biomass burning or produced via conversion of its precursor gases into particles. EC can absorb sunlight, heat the atmosphere and produce a net warming effect (Bond et al., 2013; Jacobson, 2001), and some organic matter, such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls, are of major health concern due to their carcinogenic and mutagenic properties. In addition, carbonaceous aerosols are the main sunlight extinction components that degrade ambient visibility (Cao et al., 2013; Li et al., 2013). Therefore, carbonaceous aerosols have strong implications in visibility degradation, human health and global radiative forcing, which has attracted concern (IPCC, 2013; Seinfeld and Pandis, 2006). However, our understanding of the sources and formation mechanisms of carbonaceous aerosols and their roles in haze formation and climate change are still limited (Hallquist et al., 2009; IPCC, 2013; Jimenez et al., 2009).

Along with rapid urbanisation and industrialisation, China has a severe atmospheric pollution problem (Chan and Yao, 2008). The most noticeable is regional haze, a weather phenomenon defined as atmospheric visibility of less than 10 km at a relative humidity (RH) of less than 80%. Haze is intrinsically caused by a high load of fine particulate matter. Water soluble inorganic ions (e.g. sulphate, ammonia, and nitrate), organics and element carbon are the dominant PM_{2.5} chemical components leading to the decreasing of visibility (Malm et al., 1994; Tao et al., 2009). Sulfates and organics are responsible for visibility degradation through scattering the sunlight, while element carbon is primarily responsible for aerosol absorption (Horvath, 1993; Malm et al., 1994). Satellite retrieval results show that China is one of the world's largest sources of PM_{2.5}, with annual mean PM_{2.5} concentration that exceeds 80 $\mu\text{g m}^{-3}$ over eastern China, especially in the North China Plain (NCP) region (Van Donkelaar et al., 2010). Mitigation of regional haze in China requires a fundamental understanding of the sources, formation mechanisms and physical and chemical properties of ambient aerosol particles and their gaseous precursors (Lee, 2015; Zhuang et al., 2014). Previous studies have shown that carbonaceous aerosols contribute significantly to haze formation in the NCP (Wang et al., 2014; Yang et al., 2012; Zhao et al., 2013). Therefore, more information on the sources and formation mechanisms of carbonaceous aerosols are needed to reduce regional haze events.

To investigate the particulate matter pollution and haze formation in the NCP, aerosol chemical components, including carbonaceous aerosols, inorganic water soluble ions and elements, pollution gases and meteorology were measured for 1 year in Jinan during 2007–2008. Jinan (26°01'–37°32' N, 116°11'–117°44' E), an industrial city and the capital of Shandong Province, is representative of the cities in the North China Plain. This region is characterized by a high population density, many heavy industries and power plants, and a terrain with mountains surrounded that hinder air pollutants dispersion, all of which caused the frequent occurrence of severe haze episodes, particularly in winter. The characteristics and formation mechanisms of inorganic water-soluble ions, PM_{2.5} source apportionment and an assessment of its human health risks have been reported in separate papers (Wang et al., 2012; Yang et al., 2013, 2014). In this study, we focus on seasonal variability and the sources and formation of carbonaceous aerosols and discuss their implications on haze formation. In January 2013, unprecedented severe haze-fog episodes occurred over central and eastern China, with the highest hourly PM_{2.5} concentrations over 1000 $\mu\text{g m}^{-3}$; these events attracted concern from the government and the public. Many studies have attempted to elucidate these

pollution episodes (He et al., 2014; Huang et al., 2014; Sun et al., 2014; Zheng et al., 2015). The second aim of this study was to compare the characteristics of carbonaceous aerosols in winter 2007 and January 2013, which will deepen our understanding of haze formation in the NCP region.

2. Methodology

2.1. Sampling site and collection

PM_{2.5} samples were collected in selected four seasons from December 2007 to October 2008 on the central campus of Shandong University, Jinan (Fig. 1). We defined the four seasons as follows: December 3, 2007, to February 26, 2008, as winter; March 1 to April 19, 2008, as spring; June 2 to 24, 2008, as summer; September 12 to October 14, 2008, as autumn. The sampling site was located on the rooftop of a seven-floor teaching building in the campus of Shandong University (36.67°N, 117.05°E; 50 m above sea level) and is a representative urban area in Jinan under the effects of vehicle emissions and residential activities. The PM_{2.5} samples were collected with a four-channel sampler (RAAS, Model RAAS2.5-400, Thermo Anderson). Quartz microfiber filters (Pall Corp.; pre-fired at 600 °C for 6 h) were used for determination of OC and EC, and aerosols collected on Teflon-membrane filters (Pall Corp.) were applied for the determination of the mass concentrations of water-soluble ions. Generally, the sampling period was 23.5 h, from 9:30 A.M. on one day to 9:00 A.M. the next day. After collection, the samples were stored in the refrigerator at –4 °C before being weighed and analysed. In total, 138 valid PM_{2.5} samples were obtained with two sets of field blanks at the start and end of each campaign. The filter samples were weighed with a Sartorius ME-5F balance (readability, 1 μg) before and after sampling at a constant temperature (20 °C \pm 0.5 °C) and RH (50% \pm 2%) to determine their mass concentrations.

2.2. Instrumentation

2.2.1. OC and EC analyses

A thermal-optical carbon aerosol analyser (Sunset Laboratory) based on the thermal-optical transmittance method (Birch and Cary, 1996) was used to determine the abundance of OC and EC with a modified NIOSH-5040 (National Institute of Occupational Safety and Health) protocol. The principles and a schematic of the instrument were depicted by Wang et al. (2011). To ensure the accuracy of the OC and EC analysis, the analyser was calibrated with a multipoint external standard calibration using the sucrose standard solution (slope, 1.03; $R^2 = 0.9998$), and CH₄ gas standard validations were performed periodically during the analysis. Oven cleaning procedures were implemented before analysis of the samples with the aim of checking the instrument blanks (acceptance criteria, value \pm 0.3 μgC). Two ambient blank filters were also analysed to correct the real ambient samples. The detection limit for OC and EC was 0.3 $\mu\text{g m}^{-3}$ (Wang et al., 2011), and the reproducibility was assessed by replicate analysis of samples, with uncertainty of less than 5% for total carbon and 8% for OC and EC.

2.2.2. Water soluble ions analyses

Inorganic water-soluble ions (including F⁻, Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) were determined with an ion chromatograph (ICs, ICS-90, Dionex). The anions were analysed with an AS14A Column with an AMMS 300 Suppressor and were eluted with 3.5 mmol L⁻¹ Na₂CO₃ and 1.0 mmol L⁻¹ NaHCO₃. The cations were analysed with a CS12A Column with a CSRS Ultra II Suppressor and were eluted with 20 mmol L⁻¹ methanesulfonic acid. A detailed introduction to ion chromatograph can be found in Zhou

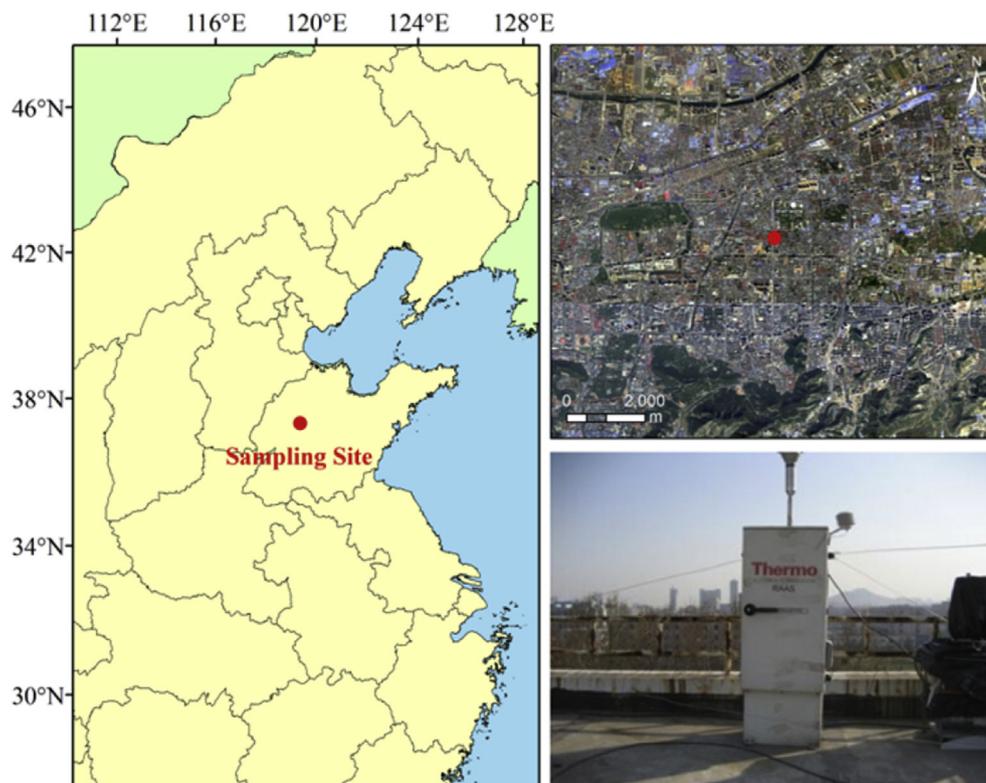


Fig. 1. Map showing the location of Jinan and the sampling site.

et al. (2009).

2.2.3. Meteorological data

The ambient temperature, RH and wind speed and direction were measured with a portable automatic meteorological station (Jinzhou Yangguang Corp., China). The visibility data were obtained from visual inspection during sampling, which was performed three times per day in the morning (9:00), noon (12:30) and afternoon (17:00), respectively. Here we define hazy days as days with atmospheric visibility of less than 10 km and an RH of less than 80% and with no rain, fog, snow and other adverse weather. The remainder were classified as non-hazy days.

3. Result and discussion

3.1. Seasonal variations of carbonaceous aerosols

The seasonal variations in OC and EC and their contribution to $PM_{2.5}$ on hazy and non-hazy days are compared in Fig. 2. Distinct seasonal variation was observed in the OC and EC concentrations; the highest concentrations were seen in winter and the lowest in spring. The OC concentrations on hazy days were 34.35 ± 18.76 (average \pm standard deviation), 13.88 ± 4.71 , 24.55 ± 8.42 and $20.31 \pm 10.20 \mu\text{g m}^{-3}$ in winter, spring, summer and autumn, which were approximately double those seen on non-hazy days. The EC concentrations on hazy days were 5.09 ± 3.54 (average \pm standard deviation), 1.86 ± 0.31 , 3.53 ± 1.14 and $2.48 \pm 1.18 \mu\text{g m}^{-3}$ in winter, spring, summer and autumn, which were 2.2, 1.4, 1.5 and 1.1 times higher, respectively, than those on non-hazy days. The percentage of OC's contribution to $PM_{2.5}$ ranged from 10.4 to 14.9%, with the high contribution in winter and autumn. The percentage of EC's contribution to $PM_{2.5}$ ranged from 1.9 to 2.5%, with the highest contribution in autumn, which may be due to intensive biomass

burning events, as shown in section 3.4. Fig. 2c and d depicts the OC and EC contributions to $PM_{2.5}$. It is interesting to notice that the contributions of OC and EC to $PM_{2.5}$ on hazy days were lower than those on non-hazy days, possibly because the concentrations of inorganic ions increased much more rapidly than those of OC and EC during hazy days, which was also found in Beijing (Han et al., 2015).

3.2. Relationship between OC and EC

EC is emitted from incomplete combustion and is relatively stable in the atmosphere, whilst OC can be emitted from primary sources (POC) or formed by conversion from gas to particle (i.e., secondary OC, SOC). The correlation between OC and EC has often been applied to investigate the origins of carbonaceous aerosols. Fig. 3 presents the correlations of OC and EC on hazy and non-hazy days in all four seasons. Strong correlations were found between OC and EC on both hazy and non-hazy days in winter, which suggest that OC and EC likely have common sources, e.g., coal combustion. Good correlations were also found between OC and EC in summer ($R^2 = 0.75$, $p < 0.01$), which indicate that OC and EC have similar sources in summer, e.g., biomass burning, as shown in Fig. 4. In autumn, the correlation between OC and EC was relatively lower than that in winter and summer, which suggests additional sources of OC, such as the SOC formed by intensified photochemical reactions in autumn. Furthermore, the slopes of EC and OC regression were higher on hazy days than on non-hazy days, which suggest that more secondary OAs were formed on hazy days.

3.3. Estimation of SOC formation

The SOC concentrations in all four seasons were estimated with the EC-tracer method (Turpin and Huntzicker, 1995). The key step

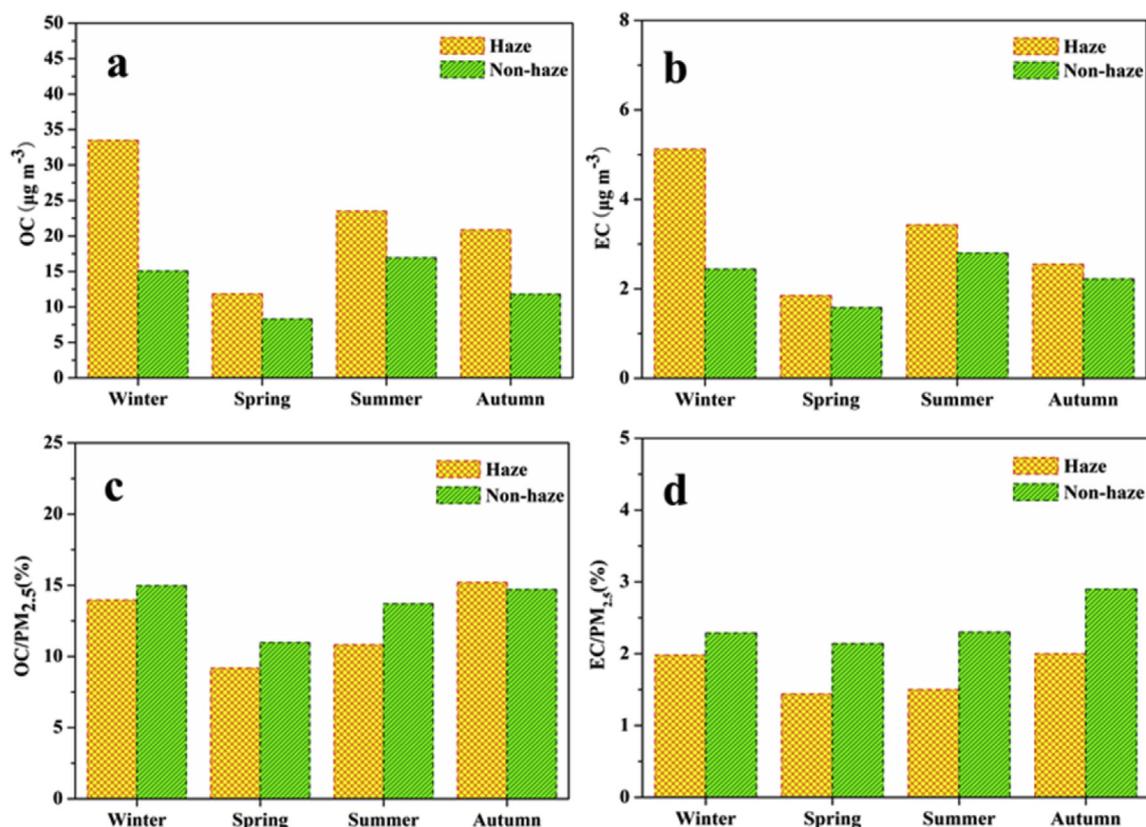


Fig. 2. Seasonal variations of OC and EC concentrations and the contributions of OC and EC to $PM_{2.5}$ on hazy days and non-hazy days in Jinan.

of this method is to obtain the representative primary OC/EC ratio. In this study, we used the minimum measured OC/EC ratio in each season as the ratio from primary OC and EC emissions, as proposed by Castro et al. (1999), which has been widely used in other studies (Cao et al., 2004; Tao et al., 2009; Zhang et al., 2008). The minimum OC/EC ratios in winter, spring, summer and autumn were 4.04, 3.43, 3.96 and 2.62, respectively. The EC-tracer method has an intrinsic drawback when a constant primary OC/EC ratio (e.g. minimum OC/EC ratio) is adopted. Some chemical production of SOC may still occur when the minimum OC/EC ratio was selected. Thus, the minimum OC/EC ratio is likely to be an upper limit of the “average” ratio of primary emissions in the region. As a result, the estimated SOC concentration using this method may represent a lower bound of the abundance of SOC.

The mean SOC concentrations and their contributions to OC and $PM_{2.5}$ are listed in Table 1. The SOC concentration showed the highest value in autumn, followed by winter, summer and spring. The high SOC concentrations in autumn and winter were ascribed to intensive coal combustion and the enhancement of secondary formation. The SOC concentrations on hazy days were obviously much higher than those on non-hazy days. The SOC to OC ratios varied from 43.8 to 63.4% on hazy days over the four seasons, which were also much higher than those on non-hazy days, suggesting strong SOC formation on hazy days.

3.4. Sources and formation of carbonaceous aerosols

Fig. 4 shows the daily variations in $PM_{2.5}$, sulphate, nitrate, potassium, carbonaceous aerosols, RH and visibility. Several haze episodes were observed during the 1-year field study. Based on the $PM_{2.5}$ concentrations, water-soluble ions and carbonaceous aerosols, we identified the main possible sources of $PM_{2.5}$ and estimated

the implications of carbonaceous aerosols on the formation of haze in Jinan.

3.4.1. Type I: coal combustion and secondary formation

High concentrations of $PM_{2.5}$, carbonaceous aerosols, sulphate, nitrate and chloride can be detected during these episodes, which are common in winter due to primary emissions and secondary formation from coal combustion (Fig. 4). There were three typical pollution episodes during the winter campaign: Dec. 8–12, Dec. 17–23 and Dec. 24–28, 2007. The pollution episodes normally lasted about 4–7 days in a saw-tooth pattern, as suggested by Jia et al. (2008).

The daily average $PM_{2.5}$ mass concentrations also presented drastic variations from $150 \mu\text{g m}^{-3}$ to $505.7 \mu\text{g m}^{-3}$ during the three pollution episodes. The secondary aerosols, including SOA, sulphate, nitrate and ammonium, comprised 41–73% of the $PM_{2.5}$, with an average concentration of $144 \mu\text{g m}^{-3}$ for the three pollution episodes. It can be seen from the results that primary aerosols, such as POA, EC, chloride and potassium, also played important roles in the formation of haze due to the intensified coal combustion.

Fig. 5a shows the daily variations of $PM_{2.5}$ concentrations and RH during the winter of 2007–2008. The fluctuations of $PM_{2.5}$ and secondary aerosols (e.g. sulphate, nitrate and SOC) were tracking the variations of RH. Similar results can also be found in Beijing, another city in the NCP (Cheng et al., 2015; Sun et al., 2013), and in the Yellow river delta region (Fu et al., 2008), indicating that RH can have a great influence on $PM_{2.5}$ formation in China. Fig. 5b presents the average composition of $PM_{2.5}$ at different levels of RH. As shown, the $PM_{2.5}$ concentrations were $83.7 \mu\text{g m}^{-3}$, $311.0 \mu\text{g m}^{-3}$ and $238.8 \mu\text{g m}^{-3}$ at $RH < 30\%$, $30\% < RH < 90\%$ and $RH \geq 90\%$, respectively. Most $PM_{2.5}$ components increased by a factor of 3 or above from low RH to high RH. It is interesting to notice that

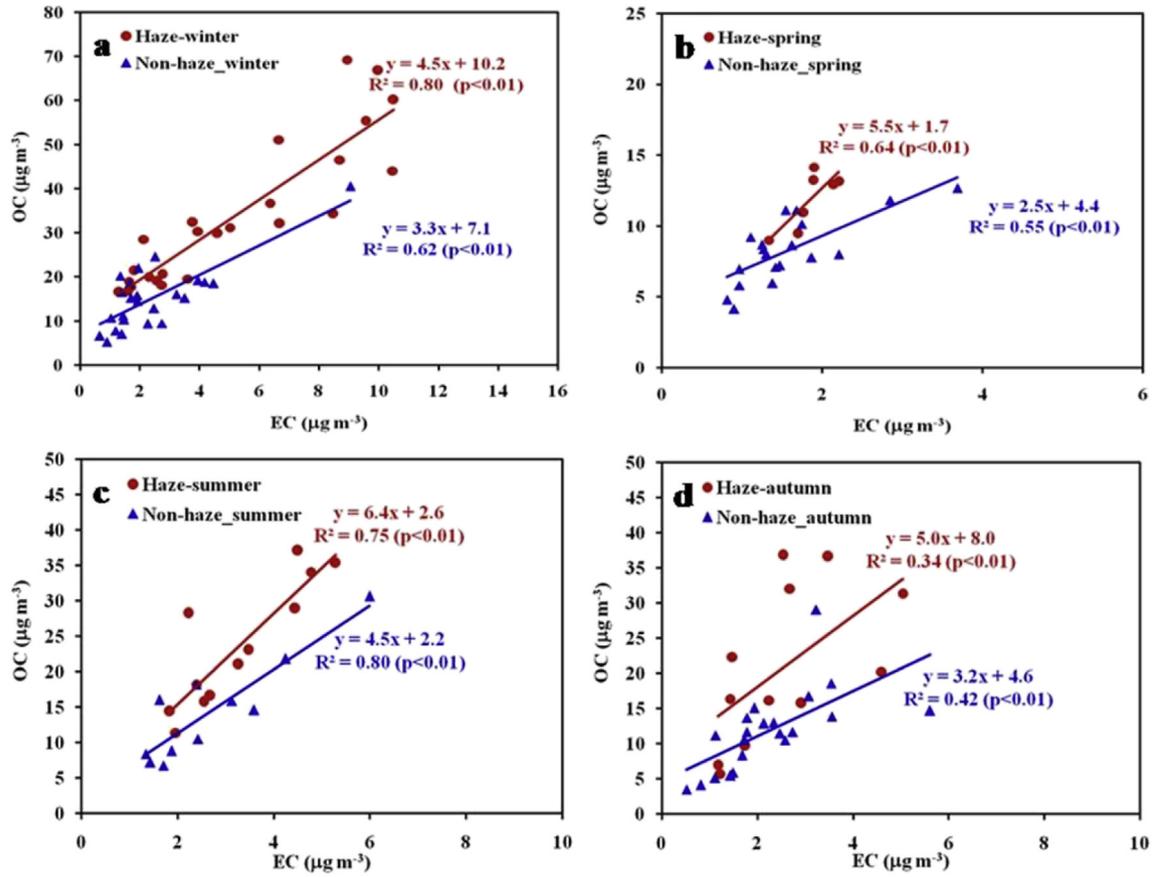


Fig. 3. Relationship between OC and EC on hazy and non-hazy days in four seasons in 2007–2008, Jinan.

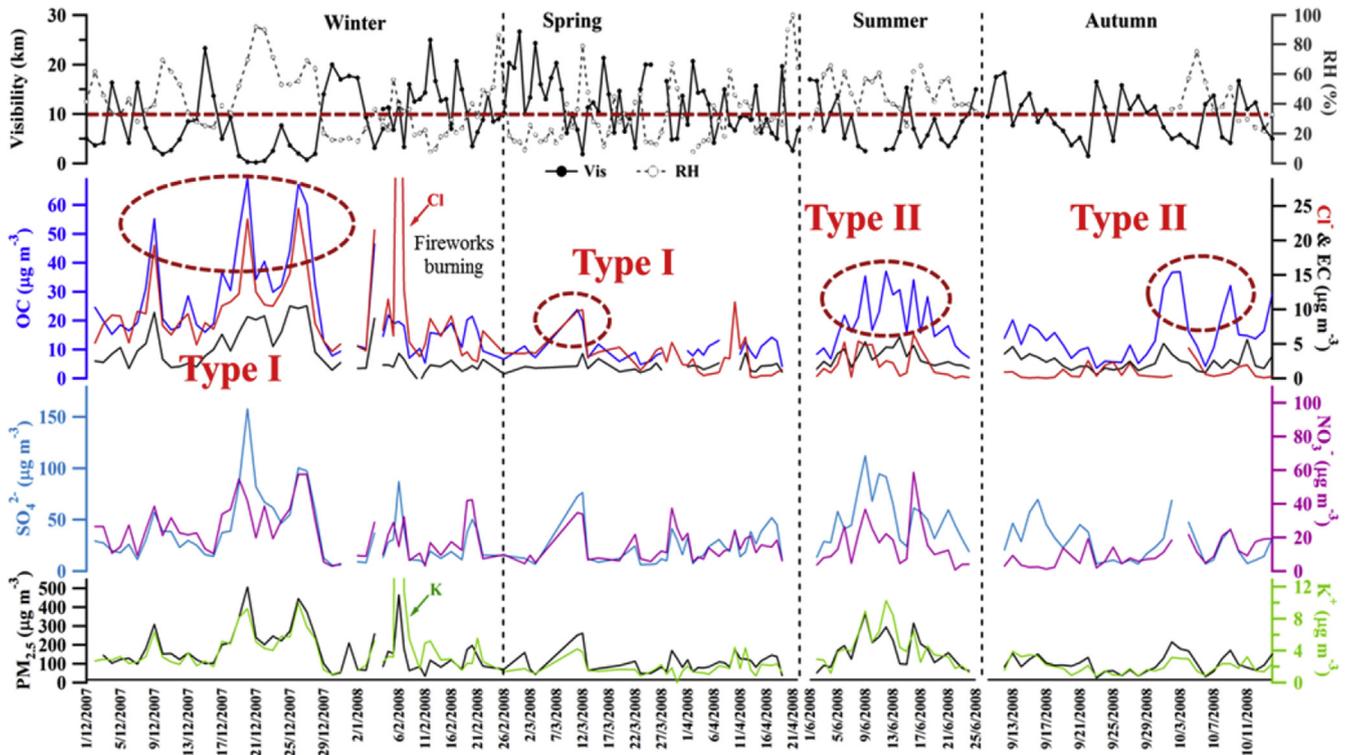


Fig. 4. Temporal variations in PM_{2.5}, sulphate, nitrate, potassium, carbonaceous aerosols, RH and visibility in 2007–2008 in Jinan.

Table 1
Mean SOC concentrations and their contributions to OC and PM_{2.5} over the four seasons.

Seasons	(OC/EC) _{min}	SOC ($\mu\text{g m}^{-3}$)		SOC/OC (%)		SOC/PM _{2.5} (%)	
		Haze	Non-haze	Haze	Non-haze	Haze	Non-haze
Winter	4.04	13.68 ± 6.92	5.81 ± 4.88	45.13 ± 17.89	40.45 ± 22.75	6.45 ± 2.38	5.97 ± 3.54
Spring	3.43	5.50 ± 1.36	2.87 ± 1.71	46.18 ± 5.48	36.97 ± 14.87	4.23 ± 0.75	3.83 ± 1.46
Summer	3.96	10.69 ± 5.29	4.11 ± 3.33	43.83 ± 9.91	26.10 ± 17.51	4.94 ± 2.31	3.79 ± 2.59
Autumn	2.62	14.19 ± 9.54	6.26 ± 4.35	63.39 ± 15.14	51.10 ± 12.90	10.05 ± 4.87	7.44 ± 2.75

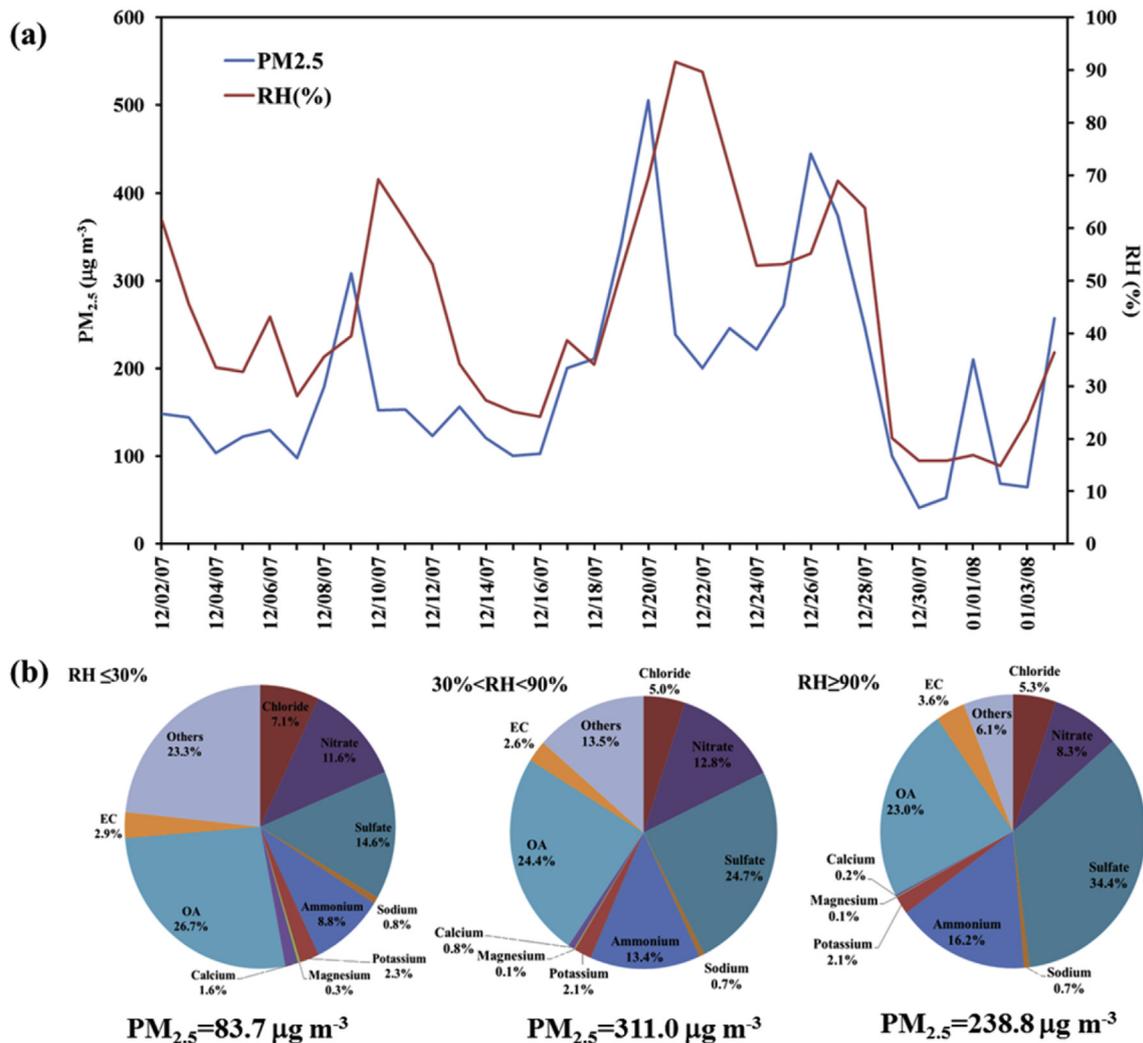


Fig. 5. (a) Daily variations of PM_{2.5} and RH during the winter of 2007–2008; (b) Average chemical compositions of PM_{2.5} at different levels of RH, i.e., RH \leq 30%, 30% < RH < 90% and RH \geq 90%.

sulphate showed the greatest enhancement amongst all the PM_{2.5} components elevated by RH, by a factor of nearly 7, and the highest sulphate concentration and proportion in PM_{2.5} were found when the RH exceeded 90%. This result confirms the significant influence of the aqueous-phase reaction on sulphate production. OAs are the dominant component of PM_{2.5} when RH is below 30%, whilst the proportion of organics in PM_{2.5} decreased as the RH increased due to the intensive enhancement of inorganic ions, such as sulphate.

3.4.2. Type II: biomass burning

Biomass burning (BB), the world's largest source of EC and primary OC, has great effects on air quality and the global climate (Andreae and Merlet, 2001; Cheng et al., 2013; Hobbs et al., 1997).

BB events are common in northern China, especially during the summer and autumn harvest seasons (Gao et al., 2011; Xu et al., 2011). Table 2 lists the K⁺ and OC concentrations, OC/EC, K⁺/OC and K⁺/Cl⁻ on the selected days during the summer and autumn of 2008. Water-soluble K⁺ is commonly used as a tracer to estimate BB (Reid et al., 2005). A typical summer haze event occurred from June 6 to 25. During this episode, the K⁺ concentration increased from 1.2 $\mu\text{g m}^{-3}$ before BB (June 4) to 10.3 $\mu\text{g m}^{-3}$ during BB (June 12), which indicates that BB contributed to the K⁺ concentration. The OC concentrations were almost five times higher during BB episodes than on clean days. The K⁺/OC ratio was also applied as the indicator of a BB event. Duan et al. (2004) investigated BB episodes in Beijing and found that the K⁺/OC ratios ranged from 0.19 to 0.21

Table 2

K^+ and OC concentrations, potassium to chloride ratio, OC/EC ratio and potassium to OC ratio in one clean day (June 4 in summer, September 28 in autumn) and three hazy days (June 9, 12 and 13 in summer; October 1, 2, 3 in autumn) during summer and autumn of 2008 in Jinan.

Date	K^+ ($\mu\text{g m}^{-3}$)	OC ($\mu\text{g m}^{-3}$)	EC ($\mu\text{g m}^{-3}$)	OC/EC	K^+/OC	K^+/Cl^-
Summer						
06/04/08	1.2	6.8	1.7	4.0	0.17	1.47
06/09/08	9.0	35.4	5.3	6.7	0.25	1.87
06/12/08	10.3	37.1	4.5	8.3	0.28	4.08
06/13/08	8.6	28.9	4.4	6.6	0.30	3.80
Autumn						
09/28/08	0.8	5.2	1.1	4.7	0.16	1.76
10/01/08	1.8	31.4	5.1	6.2	0.06	11.86
10/02/08	3.2	36.6	3.5	10.5	0.09	8.13
10/03/08	No data	36.9	2.5	14.7	No data	No data

during the BB periods, which could represent on-field wheat straw open fires. The K^+/OC ratios in Beijing were comparable with our observations. We also observed much higher OC/EC ratios during the BB events in this study, as in previous studies (Cao et al., 2005; Engling et al., 2010; Zhou et al., 2012). We found distinct differences in the OC/EC and K^+/OC ratios between the summer and autumn BB events shown in Table 2, possibly due to the combustion of different types of biomass. Winter wheat is harvested and the residues are burnt in June, whilst corn and soybeans are harvested and the residues burnt in autumn in the NCP region.

Fig. 6 shows the agricultural fire spots over China derived from MODIS remote sensing retrieval from June and October 2008 (<https://earthdata.nasa.gov/earth-observation-data/near-real-time/firms>). Combined with the MODIS fire spots map, air mass trajectories and K^+/Cl^- ratios, two types of BB events were identified in summer: BB-1, aerosols from biomass combustion near the Jinan sampling site; and BB-2, aerosols from biomass combustion transported over long distances (Fig. 6). One of the former cases occurred between June 9 and 11, and the latter occurred between June 12 and 13. BB-1 came from sources near the sampling site and was much younger smoke with many KCl particles (Li et al., 2003, 2010; Reid et al., 2005), whilst BB-2 consisted of aged biomass

burning smoke transported from the junctional zone of Shandong, Anhui, Henan and Jiangsu Provinces. We noted that the K/Cl ratio in BB-1 was much lower than that in BB-2 because KCl particles in the BB-2 smoke were converted to K_2SO_4 and KNO_3 via reaction with HNO_3 and H_2SO_4 gases during long-range transport, resulting in the loss of Cl (Li et al., 2003). The BB events that occurred in autumn were mainly the BB-1 type, with sources near the sampling site (Fig. 6b).

3.5. Comparisons of carbonaceous aerosols between winter 2007–2008 and winter 2012–2013

In winter 2012–2013, extremely severe regional haze-fog pollution occurred in central and eastern China, especially in January 2013, which affected approximately 800 million people and shrouded 1.3 million km^2 (Huang et al., 2014). We also collected daily $PM_{2.5}$ samples from January 12 to February 4, 2013 on the central campus of Shandong University, Jinan city (Zhang et al., 2014). The methods applied for chemical analysis of $PM_{2.5}$ samples were the same as described in section 2.2. The details can be found in Zhang et al. (2014). In order to compare the results with Zhang et al. (2014), we redefined the criteria for differentiating the haze-fog (HF) and non-haze-fog (NHF) periods in this section: a haze episode was characterized by RH and Vis less than 80% and 5 km, respectively, and a fog episode (which includes mist events because mist persists for a short time and cannot be clearly distinguished from fog in China) by RH over 90% and Vis less than 1 km (Zhang et al., 2014; WMO No. 782, 2005). Non-haze-fog days were characterized by Vis > 10 km.

We compared the characteristics of carbonaceous aerosols between winter 2007–2008 and winter 2012–2013. Table 3 summarises the results. First, the RH in winter 2012–2013 was much higher than that in winter 2007–2008, especially on HF days with an average RH of 84%. Zhang et al. (2015) examined surface meteorological data in Beijing for January from 2000 to 2014 and found that the average RH in January 2013 was the highest amongst the 15 years. The high RH favoured the formation of secondary OAs and sulphate (Cheng et al., 2015; Sun et al., 2014). Second, the OC and SOC concentrations on HF days in winter 2012–2013 were much

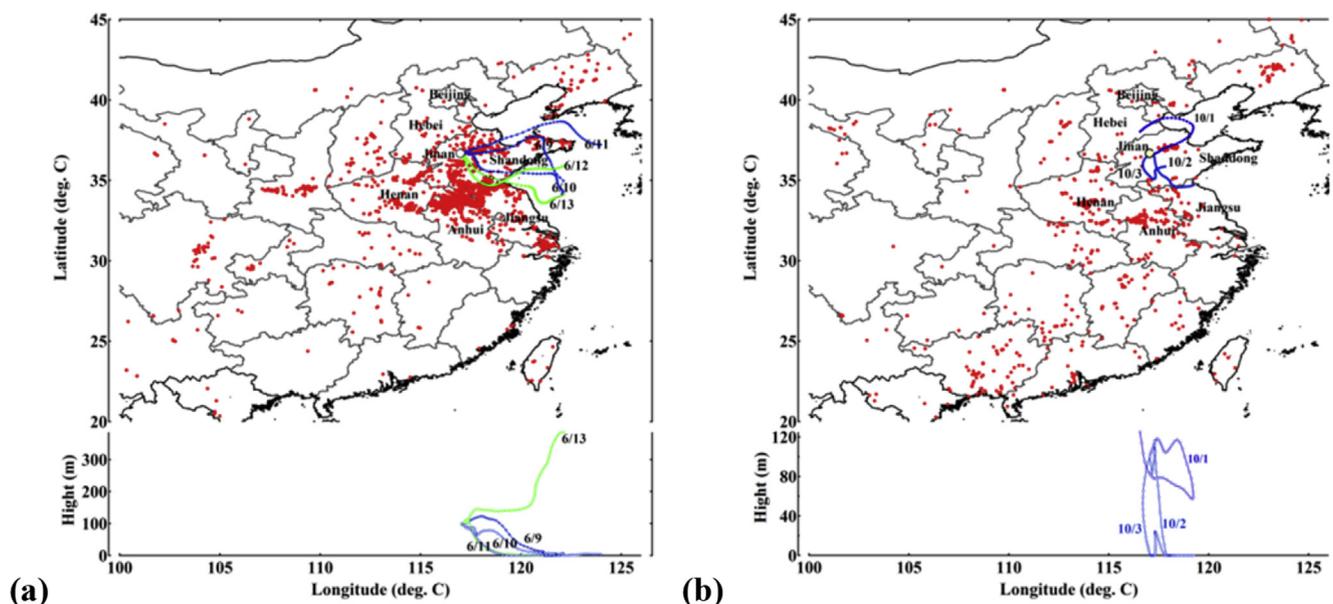


Fig. 6. Maps of agricultural fire spots over China derived from MODIS remote sensing retrieval from (a) June 6 to 15 and 48-h air mass trajectories from June 9 to 13 and (b) October 1 to 15 and 48-h air mass trajectories from October 1 to 3 ending at Jinan.

Table 3
Comparisons of RH, temperature and carbonaceous aerosols in winter 2007–2008 and winter 2012–2013.

		RH (%)		T (°C)		OC ($\mu\text{g m}^{-3}$)	EC ($\mu\text{g m}^{-3}$)	OC/EC /	SOC/OC (%)
		Range	Mean	Range	Mean				
12/3–2/26, 07–08	HF ^b	35.0 to 91.5	55.7	0.6 to 12.5	4.0	37.7	5.9	7.2	42.7%
	NHF ^c	7.8 to 52.5	24.5	–2.6 to 7.5	2.8	13.3	2.2	7.1	37.7%
1/12–2/4, 13 ^a	HF	60.0 to 100	84.0	–5 to 3	–0.4	47.5	7.0	7.2	60%
	NHF	44.3 to 93	66.5	–1 to 1.3	0.3	13.5	2.5	3.9	28%

^a Data obtained from Zhang et al. (2014).

^b HF: haze-fog.

^c NHF: non-haze-fog.

higher than those in 2007. SOC accounted for 60% of the OC concentration in the haze-fog days in winter 2012–2013, which was much higher than that in 2007. One reason is that the aqueous-phase reaction of volatile organic compounds can contribute to the formation of secondary OAs. Another reason may be the stagnant meteorological conditions and regional transport that favour the formation of secondary OAs (Sun et al., 2014; Zhang et al., 2015).

4. Conclusions

One year of intensive field study was carried out in 2007–2008 in Jinan, northern China. The main chemical components of PM_{2.5} and meteorological factors were determined. The characteristics of carbonaceous aerosols were examined in detail in this study. OC and EC concentrations on hazy days were one to three times higher than those in non-hazy days in all four seasons. Carbonaceous aerosols were the most abundant components in PM_{2.5} in winter, which suggests that carbonaceous aerosols were the key contributors to haze formation. Obvious seasonal variations were observed in OC and EC, with the highest concentrations in winter, followed by summer, autumn and spring. The SOC to OC ratios on hazy days in all four seasons ranged from 43.8 to 63.4%, whilst those ratios ranged from 26.1 to 51.1% on non-hazy days. Two types of haze events were identified, and the sources and formation of carbonaceous aerosols were discussed. In winter, coal combustion and secondary formation are the main sources of carbonaceous aerosols, while RH plays an important role in the formation of SOC, along with sulphate. Biomass burning is also a triggering factor in haze formation and contributed to the rapid enhancement of carbonaceous aerosols in summer and autumn.

We found that the OC and SOC concentrations on HF days were higher during winter 2012–2013 than during winter 2007–2008. One of the most prominent features in winter 2012–2013 was a much higher RH, which favoured the formation of secondary aerosols via aqueous reaction. Some other reasons may be stagnant meteorological conditions and regional transport. However, more information is needed, and more studies, including modelling, should be done in the future to better understand the mechanisms by which carbonaceous aerosols are formed and their contribution to regional haze.

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References

- Andreae, M., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. *Glob. Biogeochem. Cy* 15, 955–966.
- Birch, M., Cary, R., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol. Sci. Technol.* 25, 221–241.
- Bond, T.C., Doherty, S.J., Fahey, D.W., Forster, P.M., Berntsen, T., DeAngelo, B.J., Flanner, M.G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P.K., Sarofim, M.C., Schultz, M.G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S.K., Hopke, P.K., Jacobson, M.Z., Kaiser, J.W., Klimont, Z., Lohmann, U., Schwarz, J.P., Shindell, D., Storelvmo, T., Warren, S.G., Zender, C.S., 2013. Bounding the role of black carbon in the climate system: a scientific assessment. *J. Geophys. Res. Atmos.* 118, 5380–5552.
- Cao, J., Lee, S., Ho, K., Zou, S., Fung, K., Li, Y., Watson, J., Chow, J., 2004. Spatial and seasonal variations of atmospheric organic carbon and elemental carbon in Pearl River Delta Region, China. *Atmos. Environ.* 38, 4447–4456.
- Cao, J., Wu, F., Chow, J., Lee, S., Li, Y., Chen, S., An, Z., Fung, K., Watson, J., Zhu, C., 2005. Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China. *Atmos. Chem. Phys.* 5, 3127–3137.
- Cao, J.J., Wang, Q.Y., Chow, J.C., Watson, J.G., Tse, X.X., Shen, Z.X., Wang, P., An, Z.S., 2013. Impacts of aerosol compositions on visibility impairment in Xi'an, China. *Atmos. Environ.* 59, 559–566.
- Castro, L., Pio, C., Harrison, R., Smith, D., 1999. Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations. *Atmos. Environ.* 33, 2771–2781.
- Chan, C.K., Yao, X., 2008. Air pollution in mega cities in China. *Atmos. Environ.* 42, 1–42.
- Cheng, Y., Engling, G., He, K.B., Duan, F.K., Ma, Y.L., Du, Z.Y., Liu, J.M., Zheng, M., Weber, R.J., 2013. Biomass burning contribution to Beijing aerosol. *Atmos. Chem. Phys.* 13, 7765–7781.
- Cheng, Y., He, K.B., Du, Z.Y., Zheng, M., Duan, F.K., Ma, Y.L., 2015. Humidity plays an important role in the PM_{2.5} pollution in Beijing. *Environ. Pollut.* 197, 68–75.
- Duan, F., Liu, X., Yu, T., Cachier, H., 2004. Identification and estimate of biomass burning contribution to the urban aerosol organic carbon concentrations in Beijing. *Atmos. Environ.* 38, 1275–1282.
- Engling, G., Zhang, Y.-N., Chan, C.-Y., Sang, X.-F., Lin, M., Ho, K.-F., Li, Y.-S., Lin, C.-Y., Lee, J.J., 2010. Characterization and sources of aerosol particles over the southeastern Tibetan Plateau during the Southeast Asia biomass-burning season. *Tellus B* 63, 117–128.
- Fu, Q., Zhuang, G., Wang, J., Xu, C., Huang, K., Li, J., Hou, B., Lu, T., Streets, D.G., 2008. Mechanism of formation of the heaviest pollution episode ever recorded in the Yangtze River Delta, China. *Atmos. Environ.* 42, 2023–2036.
- Gao, X., Yang, L., Cheng, S., Gao, R., Zhou, Y., Xue, L., et al., 2011. Semi-continuous measurement of water-soluble ions in PM_{2.5} in Jinan, China: temporal variations and source apportionments. *Atmos. Environ.* 45, 6048–6056.
- Hallquist, M., Wenger, J., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N., George, C., Goldstein, A., 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* 9, 5155–5236.
- Han, T., Liu, X., Zhang, Y., Qu, Y., Zeng, L., Hu, M., Zhu, T., 2015. Role of secondary aerosols in haze formation in summer in the Megacity Beijing. *J. Environ. Sci.* 27, 51–60.
- He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., Tang, G., Liu, C., Zhang, H., Hao, J., 2014. Mineral dust and NO_x promote the conversion of SO₂ to sulfate in heavy pollution days. *Sci. Rep.* 4 (4172), 1–4.
- Hobbs, P.V., Reid, J.S., Kotchenruther, R.A., Ferek, R.J., Weiss, R., 1997. Direct radiative forcing by smoke from biomass burning. *Science* 275, 1777–1778.
- Horvath, H., 1993. Atmospheric light absorption - a review. *Atmos. Environ. Part A. General Top.* 27 (3), 293–317.
- Huang, R.J., Zhang, Y., Bozzetti, C., Ho, K.F., Cao, J.J., Han, Y., Daellenbach, K.R., Slowik, J.G., Platt, S.M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S.M., Bruns, E.A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., Haddad, I.E., Prevot, A.S.H., 2014. High secondary aerosol contribution to

- particulate pollution during haze events in China. *Nature* 514, 218–222.
- IPCC, 2013. Summary for Policymakers Climate Change 2013: the Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press.
- Jacobson, M., 2001. Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature* 409, 695–697.
- Jia, Y., Rahn, K.A., He, K., Wen, T., Wang, Y., 2008. A novel technique for quantifying the regional component of urban aerosol solely from its sawtooth cycles. *J. Geophys. Res. Atmos.* 113.
- Jimenez, J., Canagaratna, M., Donahue, N., Prevot, A., Zhang, Q., Kroll, J.H., DeCarlo, P.F., Allan, J.D., Coe, H., Ng, N., 2009. Evolution of organic aerosols in the atmosphere. *Science* 326, 1525–1529.
- Lee, A.K.Y., 2015. Haze formation in China: importance of secondary aerosol. *J. Environ. Sci.* 33, 261–262.
- Li, J., Pósfai, M., Hobbs, P.V., Buseck, P.R., 2003. Individual aerosol particles from biomass burning in southern Africa: 2, compositions and aging of inorganic particles. *J. Geophys. Res. Atmos.* 108.
- Li, W., Shao, L., Buseck, P., 2010. Haze types in Beijing and the influence of agricultural biomass burning. *Atmos. Chem. Phys.* 10, 8119–8130.
- Li, X., He, K., Li, C., Yang, F., Zhao, Q., Ma, Y., Cheng, Y., Ouyang, W., Chen, G., 2013. PM_{2.5} mass, chemical composition, and light extinction before and during the 2008 Beijing Olympics. *J. Geophys. Res. Atmos.* 118, 12158–12167.
- Malm, W.C., Sisler, J.F., Huffman, D., Eldred, R.A., Cahill, T.A., 1994. Spatial and seasonal trends in particle concentration and optical extinction in the United States. *J. Geophys. Res. Atmos.* 99 (D1), 1347–1370.
- Reid, J.S., Koppmann, R., Eck, T.F., Eleuterio, D.P., 2005. A review of biomass burning emissions part II: intensive physical properties of biomass burning particles. *Atmos. Chem. Phys.* 5, 799–825.
- Seinfeld, J., Pandis, S., 2006. Atmospheric Chemistry and Physics: from Air Pollution to Climate Change. John Wiley & Sons, New York.
- Sun, Y., Jiang, Q., Wang, Z., Fu, P., Li, J., Yang, T., Yin, Y., 2014. Investigation of the sources and evolution processes of severe haze pollution in Beijing in January 2013. *J. Geophys. Res. Atmos.* 119, 4380–4398.
- Sun, Y., Wang, Z., Fu, P., Jiang, Q., Yang, T., Li, J., Ge, X., 2013. The impact of relative humidity on aerosol composition and evolution processes during wintertime in Beijing, China. *Atmos. Environ.* 77, 927–934.
- Tao, J., Ho, K., Chen, L., Zhu, L., Han, J., Xu, Z., 2009. Effect of chemical composition of PM_{2.5} on visibility in Guangzhou, China, 2007 spring. *Particuology* 7, 68–75.
- Turpin, B., Huntzicker, J., 1995. Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. *Atmos. Environ.* 29, 3527–3544.
- Van Donkelaar, A., Martin, R.V., Brauer, M., Kahn, R., Levy, R., Verduzco, C., Villeneuve, P.J., 2010. Global estimates of ambient fine particulate matter concentrations from satellite-based aerosol optical depth: development and application. *Environ. Health Persp.* 118, 847–855.
- Wang, X., Wang, W., Yang, L., Gao, X., Nie, W., Yu, Y., Xu, P., Zhou, Y., Wang, Z., 2012. The secondary formation of inorganic aerosols in the droplet mode through heterogeneous aqueous reactions under haze conditions. *Atmos. Environ.* 63, 68–76.
- Wang, Y., Yao, L., Wang, L., Liu, Z., Ji, D., Tang, G., Zhang, J., Sun, Y., Hu, B., Xin, J., 2014. Mechanism for the formation of the January 2013 heavy haze pollution episode over central and eastern China. *Sci. China Earth Sci.* 57, 14–25.
- Wang, Z., Wang, T., Gao, R., Xue, L., Guo, J., Zhou, Y., Nie, W., Wang, X., Xu, P., Gao, J., 2011. Source and variation of carbonaceous aerosols at Mount Tai, North China: results from a semi-continuous instrument. *Atmos. Environ.* 45, 1655–1667.
- WMO-No. 782, 2005. Aerodrome Reports and Forecasts: a User's Handbook to the Codes.
- Xu, Z., Li, W., Yu, Y., Wang, X., Zhou, S., Wang, W., 2011. Characteristics of aerosol optical properties at haze and non-haze weather during autumn at Jinan city. *China Environ. Sci.* 31 (4), 546–552 (in Chinese).
- Yang, F., Tan, J., Zhao, Q., Du, Z., He, K., Ma, Y., Duan, F., Chen, G., 2011. Characteristics of PM_{2.5} speciation in representative megacities and across China. *Atmos. Chem. Phys.* 11, 5207–5219.
- Yang, L., Cheng, S., Wang, X., Nie, W., Xu, P., Gao, X., Yuan, C., Wang, W., 2013. Source identification and health impact of PM_{2.5} in a heavily polluted urban atmosphere in China. *Atmos. Environ.* 75, 265–269.
- Yang, L., Gao, X., Wang, X., Nie, W., Wang, J., Gao, R., Xu, P., Shou, Y., Zhang, Q., Wang, W., 2014. Impacts of firecracker burning on aerosol chemical characteristics and human health risk levels during the Chinese new year celebration in Jinan, China. *Sci. Total Environ.* 476–477, 57–64.
- Yang, L., Zhou, X., Wang, Z., Zhou, Y., Cheng, S., Xu, P., Gao, X., Nie, W., Wang, X., Wang, W., 2012. Airborne fine particulate pollution in Jinan, China: concentrations, chemical compositions and influence on visibility impairment. *Atmos. Environ.* 55, 506–514.
- Zhang, J., Chen, J., Yang, L., Sui, X., Yao, L., Zheng, L., Wen, L., Xu, C., Wang, W., 2014. Indoor PM_{2.5} and its chemical composition during a heavy haze-fog episode at Jinan, China. *Atmos. Environ.* 99, 641–649.
- Zhang, L., Wang, T., Lv, M., Zhang, Q., 2015. On the severe haze in Beijing during January 2013: unraveling the effects of meteorological anomalies with WRF-Chem. *Atmos. Environ.* 104, 11–21.
- Zhang, Q., Jimenez, J., Canagaratna, M., Allan, J., Coe, H., Ulbrich, I., Alfarra, M., Takami, A., Middlebrook, A., Sun, Y., 2007. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern hemisphere midlatitudes. *Geophys. Res. Lett.* 34, 13.
- Zhang, X., Wang, Y., Zhang, X., Guo, W., Gong, S., 2008. Carbonaceous aerosol composition over various regions of China during 2006. *J. Geophys. Res. Atmos.* 113, D14111.
- Zhao, X., Zhao, P., Xu, J., Meng, W., Pu, W., Dong, F., He, D., Shi, Q., 2013. Analysis of a winter regional haze event and its formation mechanism in the North China Plain. *Atmos. Chem. Phys.* 13, 5685–5696.
- Zheng, G.J., Duan, F.K., Su, H., Ma, Y.L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Poschl, U., Cheng, Y.F., He, K.B., 2015. Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions. *Atmos. Chem. Phys.* 15, 2969–2983.
- Zhou, S., Wang, T., Wang, Z., Li, W., Xu, Z., Wang, X., Yuan, C., Poon, C., Louie, P.K., Luk, C.W., 2014. Photochemical evolution of organic aerosols observed in urban plumes from Hong Kong and the Pearl River Delta of China. *Atmos. Environ.* 88, 219–229.
- Zhou, S., Wang, Z., Gao, R., Xue, L., Yuan, C., Wang, T., Gao, X., Wang, X., Nie, W., Xu, Z., 2012. Formation of secondary organic carbon and long-range transport of carbonaceous aerosols at Mount Heng in South China. *Atmos. Environ.* 63, 203–212.
- Zhou, Y., Wang, T., Gao, X., Xue, L., Wang, X., Wang, Z., Gao, J., Zhang, Q., Wang, W., 2009. Continuous observations of water-soluble ions in PM_{2.5} at Mount Tai (1534 m asl) in central-eastern China. *J. Atmos. Chem.* 64, 107–127.
- Zhuang, X., Wang, Y., He, H., Liu, J., Wang, X., Zhu, T., Ge, M., Zhou, J., Tang, G., Ma, J., 2014. Haze insights and mitigation in China: an overview. *J. Environ. Sci.* 26, 2–12.