Heavy Particulate Matter Pollution during the 2014–2015 Winter in Tianjin, China

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ABSTRACT

Tianjin, a city located in North China, is heavily polluted with frequent haze, particularly in winter. In this study, continuous online field observations of the sulfate, nitrate, ammonium, PM_{2.5}, and gaseous pollutant concentrations in addition to the meteorological parameters were conducted in Tianjin during the 2014–2015 winter (December–January–February). The PM_{2.5} concentrations ranged from 5.6 to 495.6 $\mu\text{g m}^{-3}$, with an average value of $112.2 \pm 96.1 \mu\text{g m}^{-3}$. The worst pollution was observed in January, when levels on 10% of the days exceeded 250 $\mu\text{g m}^{-3}$, qualifying as severely polluted, and four haze episodes, each lasting 5–7 days, occurred in rapid succession (separated by ~1-day intervals). Back-trajectory and chemical composition analysis suggested that elevated levels of secondary ionic aerosol species were a primary cause of these episodes. Regional transport of PM_{2.5} also played a large role in the formation of haze. CO was selected as an inactive chemical tracer in studying the chemical process of PM_{2.5} formation. The results indicated that when high concentrations of PM_{2.5} were present, the formation of secondary PM_{2.5} increased while the photochemical production of O₃ ceased. The sulfur oxidation ratio [SOR = $n\text{SO}_4^{2-}/(n\text{SO}_4^{2-} + n\text{SO}_2)$; n refers to the molar concentration] and nitrate oxidation ratio [NOR = $n\text{NO}_3^-/(n\text{NO}_3^- + n\text{NO}_2)$] increased with the PM_{2.5} level, and heterogeneous processes on the surfaces of fine particles rather than photochemistry drove the haze events. This research elucidates haze formation mechanisms, which must be understood in order to create effective control policies in Tianjin.

Keywords: Aerosols; PM_{2.5}; Secondary formation; Tianjin; Winter haze.

INTRODUCTION

Epidemiological studies have reported that exposure to air pollution, especially fine particulate matter (PM_{2.5}), adversely affects human health, including contributing to respiratory and cardiovascular diseases (Peng *et al.*, 2009; Li *et al.*, 2017b). Environmental pollution by PM_{2.5} has become a serious problem in China, particularly in economically developed regions, such as the Yangtze River Delta region (Shen *et al.*, 2016; Zhang *et al.*, 2016), Pearl River Delta (Tan *et al.*, 2016a; Tan *et al.*, 2016b), and the Beijing–Tianjin–Hebei region (Ma *et al.*, 2017; Zhang *et al.*, 2018).

The city of Tianjin, located in the southeast area of the

Beijing–Tianjin–Hebei region, faces severe PM_{2.5} pollution (Tian *et al.*, 2016; Wang *et al.*, 2016; Zhou *et al.*, 2016a). A persistent dense fog event, with a minimum visibility of 117 m, occurred in Tianjin from November 28 to December 2, 2010 (Han *et al.*, 2015). The average PM_{2.5} concentration in Tianjin was $141.5 \pm 78.0 \mu\text{g m}^{-3}$ from April 2009 to February 2010 (Zhao *et al.*, 2013) and $148.9 \pm 91.1 \mu\text{g m}^{-3}$ over a year long period from 2012–2013 (Zhou *et al.*, 2016a), approximately 2–6 times higher than the National Ambient Air Quality Standards of China (NAAQS; GB-3095-2012) of 35 $\mu\text{g m}^{-3}$. The level of haze pollution over Tianjin increases in winter because of enhanced heating, traffic, and industrial emissions and stable synoptic conditions. However, the current understanding of the sources and formation mechanisms of such pollution haze events is limited. Therefore, assessing the PM_{2.5} pollution in Tianjin is an urgent requirement.

The purpose of this work was to investigate heavy aerosol pollution during the 2014–2015 winter in Tianjin. In this study, continuous measurements were performed, and the evolutions of PM_{2.5} and other related gas pollutants, such as SO₂, O₃, and CO, were explored under various

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meteorological conditions. Moreover, a back-trajectory model was developed to investigate the transport pathways and potential sources of $\text{PM}_{2.5}$. The aerosol chemical data were then characterized for four high-pollution episodes in January 2015. The relative contributions of meteorological and chemical processes to aerosol concentration during the haze events were discussed, and the formation mechanisms were investigated in detail.

EXPERIMENTAL METHODS

Sampling Site

Online ambient observations were performed during the winter of 2014–2015 (December–January–February) on the Nankai University campus (39.13°N , 117.15°E) in Tianjin. The sampling site is situated approximately 14 m above the ground level, on the roof of the School of Environment at Nankai University (Fig. 1). There are no major pollution sources near the sampling site.

Instrumentation

Continuous online observations were carried out for meteorological parameters, the mass concentration of $\text{PM}_{2.5}$, and the mass concentration of the main chemical species in the $\text{PM}_{2.5}$ with values averaged hourly. The mass concentration of $\text{PM}_{2.5}$ was detected using a dichotomous monitor (PM-712; Kimoto Electric, Ltd., Japan) (Duan *et al.*, 2016). The concentration of H_2O , water soluble organic carbon (WSOC), water-soluble inorganic ions (NO_3^- and SO_4^{2-}), and optical black carbon (BC) in the $\text{PM}_{2.5}$ were monitored on a dichotomous aerosol chemical speciation analyzer (ACSA-08; Kimoto Electric, Ltd., Japan). The ammonium in the $\text{PM}_{2.5}$ was calculated under the assumption that the ammonium existed as NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ and the particles were neutral (He *et al.*, 2012). The gaseous pollutants (O_3 , CO , and SO_2) were detected by a MCSAM-13 system (Kimoto Electric, Ltd., Japan).

Meteorological parameters, such as relative humidity (RH), temperature, pressure, wind direction (WD), and wind speed (WS), were monitored concurrently.

Trajectory Analysis

To calculate the backward trajectories of air flows, we used the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT4) model. The HYSPLIT4 model was developed by the National Oceanic and Atmospheric Administration's (NOAA) Air Resources Laboratory (Stein *et al.*, 2015).

RESULTS AND DISCUSSION

$\text{PM}_{2.5}$ Evolution in Winter

The primary atmospheric pollutant in Tianjin during the winter of 2015 (December–January–February) was $\text{PM}_{2.5}$, with concentrations ranging from 5.6 to $495.6 \mu\text{g m}^{-3}$ (averaging $112.2 \pm 96.1 \mu\text{g m}^{-3}$; Fig. 2). The mass concentrations of $\text{PM}_{2.5}$ and PM_{10} showed a positive correlation with R^2 near 0.87, the mass concentrations of $\text{PM}_{2.5}$ and PM_{10} showed a positive correlation with R^2 near 0.86 (Fig. S1), and the $\text{PM}_{2.5}/\text{PM}_{10}$ ratio went up as the pollution became more severe (Fig. 2). This suggests that a decrease in $\text{PM}_{2.5}$ levels is critical in reducing particulate matter pollution and improving air quality (Zhou *et al.*, 2016b). A haze episode was observed during the Chinese Spring Festival (January 31–February 7) when large amounts of fireworks were set off, increasing regional $\text{PM}_{2.5}$ pollution levels (Kong *et al.*, 2015). The mean $\text{PM}_{2.5}$ concentrations were 107.2 ± 102.6 , 124.0 ± 106.1 , and $103.9 \pm 73.4 \mu\text{g m}^{-3}$ in December, January, and February, respectively (Fig. 3). To better understand the pollution levels, we divided the $\text{PM}_{2.5}$ levels observed during the study period into six categories based on the Air Quality Index of China (Li *et al.*, 2017a): excellent air quality (I; $\text{PM}_{2.5} \leq 35 \mu\text{g m}^{-3}$), good air quality (II; $35 < \text{PM}_{2.5} \leq 75 \mu\text{g m}^{-3}$), light pollution

Fig. 1. (a) Google Earth map and (b) the location of the sampling site in Tianjin, China.

Fig. 2. Time series of PM_{10} , $\text{PM}_{2.5}$, $\text{PM}_{10}/\text{PM}_{2.5}$, and meteorological data (temperature (T), relative humidity (RH), wind speed (WS), and wind direction (WD)) in December 2014, January 2015, and February 2015 in Tianjin, China.

Fig. 3. Monthly average $\text{PM}_{2.5}$ and PM_{10} concentrations in Tianjin during the winter of 2014–2015. The inset pie charts represent the percentage composition of the $\text{PM}_{2.5}$ levels observed during the study period: excellent air quality (I; $\text{PM}_{2.5} \leq 35 \mu\text{g m}^{-3}$), good air quality (II; $35 < \text{PM}_{2.5} \leq 75 \mu\text{g m}^{-3}$), light pollution (III; $75 < \text{PM}_{2.5} \leq 115 \mu\text{g m}^{-3}$), moderate pollution (IV; $115 < \text{PM}_{2.5} \leq 150 \mu\text{g m}^{-3}$), heavy pollution (V; $150 < \text{PM}_{2.5} \leq 250 \mu\text{g m}^{-3}$), and very heavy pollution (VI; $250 \leq \text{PM}_{2.5} \mu\text{g m}^{-3}$).

(III; $75 < \text{PM}_{2.5} \leq 115 \mu\text{g m}^{-3}$), moderate pollution (IV; $115 < \text{PM}_{2.5} \leq 150 \mu\text{g m}^{-3}$), heavy pollution (V; $150 < \text{PM}_{2.5} \leq 250 \mu\text{g m}^{-3}$), and very heavy pollution (VI; $250 \leq \text{PM}_{2.5} \mu\text{g m}^{-3}$). A similar classification method was adopted by Guo et al. (2016). The inset in Fig. 3 shows the distributions

of the monthly $\text{PM}_{2.5}$ levels during the monitoring period; 81%, 90%, and 89% of the days in December, January, and February, respectively, had $\text{PM}_{2.5}$ levels exceeding the NAAQS threshold of $35 \mu\text{g m}^{-3}$ (Gao, 2013). Therefore, the most severe haze appeared in January during the 2014–

2015 winter in Tianjin with very heavy pollution on 10% of the days. The average $\text{PM}_{2.5}$ concentration observed in January in our study was $124 \mu\text{g m}^{-3}$, similar to the level observed in Tianjin ($144.6 \mu\text{g m}^{-3}$) during a severe haze event in January 2008 (Gu *et al.*, 2011).

Severe $\text{PM}_{2.5}$ pollution characterized by long-lasting and frequent pollution episodes (Fig. 4) was present for most of January. We define an episode as the average daily $\text{PM}_{2.5}$ exceeding $250 \mu\text{g m}^{-3}$ for a set of consecutive days. Four episodes were observed: January 1–6 (Episode I), January 7–12 (Episode II), January 13–17 (Episode III), and January 18–27 (Episode IV). The maximum episode-averaged $\text{PM}_{2.5}$ concentration was $168.5 \mu\text{g m}^{-3}$ during Episode II (Table 1). Additionally, the high average $\text{PM}_{2.5}$ concentrations were long-lasting (5–7 days) and occurred in rapid succession (i.e., intervals between the episodes of ~ 1 day). RH showed obvious diurnal cycles, with peaks at night, while temperature displayed the opposite trend, with

the highest values appearing during the daytime (Fig. 2). The increased $\text{PM}_{2.5}$ concentration was typically accompanied by increased concentrations of gaseous precursors, lower WS, and higher RH (Fig. 2 and Table S1). These relevancies have been reported in many previous studies (Xu *et al.*, 2011; Li *et al.*, 2017a).

Haze Events: Chemical Processes and Formation Mechanisms

To investigate potential sources and transport pathways of $\text{PM}_{2.5}$ in Tianjin, the NOAA HYSPLIT (ver. 4) model was used to calculate the 24-hour back-trajectories for the days with peak pollution values (January 4, 10, 15, and 23) and the relatively clean days between episodes (January 6, 12, 17, and 27) of the four pollution episodes in 2015 (Figs. 5(a)–5(d) and S2). For Episode I, II, and IV, particles originated from Hebei Province and Beijing and then moved through the western and southern regions of Tianjin

Fig. 4. Statistical results of the daily average $\text{PM}_{2.5}$ concentrations for January 2015. For each box plot, the rectangle spans the 1st quartile to the 3rd quartile, and the central division indicates the median. The whiskers above and below the box show the locations of the 10th and 90th percentiles, respectively. The points above and below the whiskers show the 5th and 95th percentiles, respectively.

Table 1. General information on the severe haze episodes in January 2015.

		Ep. I	Ep. II	Ep. III	Ep. IV	Average
Meteorological condition	WS (m s^{-1})	1.6	1.7	1.5	1.8	1.7
	Temp ($^{\circ}\text{C}$)	2.0	2.2	0.8	1.1	1.4
	RH (%)	32.6	32.3	52.7	37.7	38.8
PM concentration	$\text{PM}_{2.5}$ ($\mu\text{g m}^{-3}$)	168.5	134.3	158.8	89.5	124.3
	PM_{10} ($\mu\text{g m}^{-3}$)	266.6	192.4	208.1	137.4	182.6
	$\text{PM}_{2.5}/\text{PM}_{10}$	63.2	69.8	76.3	65.1	68.3
Gas pollutants	SO_2 ($\mu\text{g m}^{-3}$)	33.0	26.1	19.9	20.0	23.2
	O_3 ($\mu\text{g m}^{-3}$)	8.1	8.7	7.3	10.3	9.1
	NO_2 ($\mu\text{g m}^{-3}$)	52.8	57.8	49.9	52.8	52.6
SNA concentration in $\text{PM}_{2.5}$	SO_4^{2-} ($\mu\text{g m}^{-3}$)	14.6	9.5	39.9	23.9	19.6
	NO_3^- ($\mu\text{g m}^{-3}$)	21.8	18.8	25.4	16.2	17.7
	NH_4^+ ($\mu\text{g m}^{-3}$)	10.2	7.3	20.4	12.2	11.2

to the study area. For Episode III, particles predominantly originated from the southwestern region of Tianjin, passing over the eastern region and circling around the study area. The high levels of $\text{PM}_{2.5}$ observed on January 15 (averaging $361 \mu\text{g m}^{-3}$) could be due to whirling winds, a high RH of 52.7%, and a low WS of 1.5 m s^{-1} . The RH in this event was about 20% higher than in others (Table 1) as the movement of the air mass near Bohai Bay may have facilitated the secondary conversion of aerosols. Finally, the trajectory shifted sharply to the north (for Episode I, III, and IV) or south (for Episode II) with high wind speed and the haze abruptly disappearing. Approximately 23–58% of the $\text{PM}_{2.5}$ mass concentrations were measured by six components (Figs. 5(e)–5(l)). Three major secondary ionic species (sulfate, nitrate, and ammonium (SNA)) contributed 3–21%, 8–14%, and 4–11% of the total $\text{PM}_{2.5}$, respectively, while H_2O contributed 2–10%. BC and WSOC accounted for about 1–3% and 2–3% of $\text{PM}_{2.5}$, respectively. Correlations between chemical components of $\text{PM}_{2.5}$ were determined through regression analysis

(Table S3). The unidentified portion of the $\text{PM}_{2.5}$ mass might be organic matter (OM), crustal matter, and trace metal elements. As reported previously (Gu et al., 2011), OM was a predominant fraction of $\text{PM}_{2.5}$, accounting for ~32.7%. However, it was not measured in this study and deserves greater attention in future studies. In addition to OM, SNA was an important cause of the reduction in visibility and regional haze pollution and was the dominant component of $\text{PM}_{2.5}$ (Guo et al., 2014). Here we focus more on the measured SNA. The chemical composition varied with increasing severity of pollution, and the proportion of SNA was found to be increasing, especially in Episode III (Figs. 5(g) and 5(k)). Nitrate increased from 14% to 21%, from clean to heavily polluted; sulfate increased from 9% to 12%; and ammonium rose from 7% to 11%. The back-trajectories and chemical composition results indicated that the secondary ionic species of aerosols were one of the important causes of the haze episode. The regional transport of $\text{PM}_{2.5}$ also played a big role in haze formation.

To assess the contributions of chemical processes to

Fig. 5. 24-hour back-trajectories for air masses arriving at Tianjin on the days with the peak pollution values during the pollution episodes: (a) January 4, (b) January 10, (c) January 15, and (d) January 23 in 2015. Chemical composition of $\text{PM}_{2.5}$ on clean days ($\text{PM}_{2.5} \leq 75 \mu\text{g m}^{-3}$): (e) January 1, (f) January 6, (g) January 12, and (h) January 17; and on peak pollution days: (i) January 4, (j) January 10, (k) January 15, and (l) January 23 during the four pollution episodes in 2015 in Tianjin. Calculations begin at 100 m above ground and continue for 24 h.

Fig. 6. Measured ratios of (a) $\text{PM}_{2.5}/\text{CO}$, (b) SO_2/CO , (c) O_3/CO , and (d) NO_2/CO for different $\text{PM}_{2.5}$ levels. Variation in the (e) sulfur oxidation ratio (SOR) and (f) nitrate oxidation ratio (NOR) with pollution levels.

aerosol concentrations during haze events, CO was selected as a chemically inactive tracer. The chemical lifetime of CO, which is on the order of a few months, depends on OH concentrations (Brasseur, 1999; Zhang *et al.*, 2015). The ratios of $\text{PM}_{2.5}/\text{CO}$, O_3/CO , NO_2/CO , and SO_2/CO were analyzed at different $\text{PM}_{2.5}$ levels (Fig. 6). The results showed that the $\text{PM}_{2.5}/\text{CO}$ ratio (Fig. 6(a)) increased with increasing $\text{PM}_{2.5}$ levels, suggesting that secondary $\text{PM}_{2.5}$ aerosol levels increased during the haze episodes. The O_3/CO ratio (Fig. 6(b)) rapidly decreased when the $\text{PM}_{2.5}$ concentrations increased from 75 to $250 \mu\text{g m}^{-3}$ and remained at very low levels when the $\text{PM}_{2.5}$ concentration rose above $250 \mu\text{g m}^{-3}$, indicating that the photochemical production of O_3 ceased during the high $\text{PM}_{2.5}$ periods, similar to results reported in other studies (Bian *et al.*, 2007). SOR and NOR are often used as indicators of secondary transformation of SO_2 and NO_2 to form SO_4^{2-} and NO_3^- , respectively (Zheng *et al.*, 2015; Xu *et al.*, 2017). Higher SOR and NOR (Figs. 6(e)–6(f)) values were observed during the polluted periods than during clean periods, while the SO_2/CO and NO_2/CO rapidly decreased with increasing $\text{PM}_{2.5}$ levels (Figs. 6(c)–6(d)). The results further indicated that the secondary aerosol levels were elevated on haze days, and it was hypothesized that the transformation of enhanced secondary aerosols was most likely driven by heterogeneous processes because the photochemical production of ozone ceased concurrently.

RH is generally regarded as one of the main factors facilitating the formation of haze through heterogeneous reactions (Chen *et al.*, 2016). The heterogeneous reactions in the following discussion cover both aqueous-phase reactions and gas-particle partitioning. As shown in Fig. S3, as the RH increased from 12% to 86%, the SOR value

exhibited an increasing trend, with high correlation ($R^2 = 0.64$). The size and surface area of the particles was enlarged with the increased RH. Thus, the pre-existing SO_4^{2-} were able to absorb water, which facilitated their capacity to accommodate aqueous-phase reactions (Cheng *et al.*, 2015; Li *et al.*, 2017a). Meanwhile, the particle viscosity decreased due to high RH. The mass transfer limits for gaseous pollutants into particle phase were kinetically elevated. Consequently, more pollutants were transferred into the particle phase, which aided the heterogeneous reactions (George *et al.*, 2015). Therefore, enhanced secondary transformation during the haze events was mainly driven by heterogeneous processes, not the photochemistry.

CONCLUSIONS

During the winter of 2014–2015 in Tianjin, China, the most severe $\text{PM}_{2.5}$ pollution, comprising four haze episodes, was observed in January. The secondary formation of aerosols was a primary cause of these episodes, and regional transport of $\text{PM}_{2.5}$ also played a main role. When $\text{PM}_{2.5}$ levels were high, the formation of secondary $\text{PM}_{2.5}$ increased, and the photochemical production of O_3 ceased. This study's analysis of $\text{PM}_{2.5}$'s chemical signatures contributes to our understanding of the current air pollution in Tianjin and can be used to improve model validation and emission control.

ACKNOWLEDGEMENTS

We acknowledge the HYSPLIT transport and dispersion model provided by the NOAA Air Resources Laboratory. We acknowledge the financial support of the National

Science and Technology Program of China (grant nos. 2017YFC0211502, 2014BAC22B01, 2016YFC0202700, and 2017YFC0211601), the National Natural Science Foundation of China (grant nos. 21707077 and 81571130090), the Science Fund for Creative Research Groups (grant no. 21521064), and the China Postdoctoral Science Foundation (grant no. 2017M610923).

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

REFERENCES

- Bian, H., Han, S., Tie, X., Sun, M. and Liu, A. (2007). Evidence of impact of aerosols on surface ozone concentration in Tianjin, China. *Atmos. Environ.* 41: 4672–4681.
- Brasseur, G.P., Orlando, J.J. and Geoffrey, S. (1999). *Atmospheric chemistry and global change*. Oxford University Press.
- Chen, D., Liu, Z.Q., Fast, J. and Ban, J.M. (2016). Simulations of sulfate-nitrate-ammonium (SNA) aerosols during the extreme haze events over northern China in October 2014. *Atmos. Chem. Phys.* 16: 10707–10724.
- Cheng, Y., He, K.B., Du, Z.Y., Zheng, M., Duan, F.K. and Ma, Y.L. (2015). Humidity plays an important role in the PM_{2.5} pollution in Beijing. *Environ. Pollut.* 197: 68–75.
- Duan, F.K., He, K.B., Ma, Y.L., Ihozaki, T., Kawasaki, H., Arakawa, R., Kitayama, S., Tujimoto, K., Huang, T. and Kimoto, T. (2016). High molecular weight organic compounds (HMW-OCs) in severe winter haze: Direct observation and insights on the formation mechanism. *Environ. Pollut.* 218: 289–296.
- Gao, F. (2013). Evaluation of the Chinese New Air Quality Index (Gb3095-2012): Based on Comparison with the US AQI System and the WHO AQGs. Degree Thesis, Integrated Coastal Zone Management, Raseborg, Finland.
- George, C., Ammann, M., D'Anna, B., Donaldson, D.J. and Nizkorodov, S.A. (2015). Heterogeneous photochemistry in the atmosphere. *Chem. Rev.* 115: 4218–4258.
- Gu, J.X., Bai, Z.P., Li, W.F., Wu, L.P., Liu, A.X., Dong, H.Y. and Xie, Y.Y. (2011). Chemical composition of PM_{2.5} during winter in Tianjin, China. *Particuology* 9: 215–221.
- Guo, H., Cheng, T., Gu, X., Chen, H., Wang, Y., Zheng, F. and Xiang, K. (2016). Comparison of four ground-level PM_{2.5} estimation models using PARASOL aerosol optical depth data from China. *Int. J. Environ. Res. Public Health* 13: 180.
- Guo, S., Hu, M., Zamora, M.L., Peng, J., Shang, D., Zheng, J., Du, Z., Wu, Z., Shao, M., Zeng, L., Molina, M.J. and Zhang, R. (2014). Elucidating severe urban haze formation in China. *Proc. Natl. Acad. Sci. U.S.A.* 111: 17373–17378.
- Han, S.Q., Cai, Z.Y., Zhang, Y.F., Wang, P., Yao, Q., Li, P.Y. and Li, X.J. (2015). Long-term trends in fog and boundary layer characteristics in Tianjin, China. *Particuology* 20: 61–68.
- He, K., Zhao, Q., Ma, Y., Duan, F., Yang, F., Shi, Z. and Chen, G. (2012). Spatial and seasonal variability of PM_{2.5} acidity at two Chinese megacities: insights into the formation of secondary inorganic aerosols. *Atmos. Chem. Phys.* 11: 25557–25603.
- Kong, S.F., Li, X.X., Li, L., Yin, Y., Chen, K., Yuan, L., Zhang, Y.J., Shan, Y.P. and Ji, Y.Q. (2015). Variation of polycyclic aromatic hydrocarbons in atmospheric PM_{2.5} during winter haze period around 2014 Chinese Spring Festival at Nanjing: Insights of source changes, air mass direction and firework particle injection. *Sci. Total Environ.* 520: 59–72.
- Li, H., Ma, Y., Duan, F., He, K., Zhu, L., Huang, T., Kimoto, T., Ma, X., Ma, T. and Xu, L. (2017a). Typical winter haze pollution in Zibo, an industrial city in China: Characteristics, secondary formation, and regional contribution. *Environ. Pollut.* 229: 339–349.
- Li, H.M., Wu, H.F., Wang, Q.G., Yang, M., Li, F.Y., Sun, Y.X., Qian, X., Wang, J.H. and Wang, C. (2017b). Chemical partitioning of fine particle-bound metals on haze-fog and non-haze-fog days in Nanjing, China and its contribution to human health risks. *Atmos. Res.* 183: 142–150.
- Ma, Q., Wu, Y., Tao, J., Xia, Y., Liu, X., Zhang, D., Han, Z., Zhang, X. and Zhang, R. (2017). Variations of chemical composition and source apportionment of PM_{2.5} during winter haze episodes in Beijing. *Aerosol Air Qual. Res.* 17: 2791–2803.
- Peng, R.D., Bell, M.L., Geyh, A.S., Mcdermott, A., Zeger, S.L., Samet, J.M. and Dominici, F. (2009). Emergency admissions for cardiovascular and respiratory diseases and the chemical composition of fine particle air pollution. *Environ. Health Perspect.* 117: 957–963.
- Shen, L.J., Wang, H.L., Lu, S., Li, L., Yuan, J., Zhang, X.H., Tian, X.D. and Tang, Q. (2016). Observation of aerosol size distribution and new particle formation at a coastal city in the Yangtze River Delta, China. *Sci. Total Environ.* 565: 1175–1184.
- Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B., Cohen, M.D. and Ngan, F. (2015). NOAA's HYSPLIT atmospheric transport and dispersion modeling system. *Bull. Am. Meteorol. Soc.* 96: 2059–2077.
- Tan, H.B., Liu, L., Fan, S.J., Li, F., Yin, Y., Cai, M.F. and Chan, P.W. (2016a). Aerosol optical properties and mixing state of black carbon in the Pearl River Delta, China. *Atmos. Environ.* 131: 196–208.
- Tan, J.H., Duan, J.C., Ma, Y.L., He, K.B., Cheng, Y., Deng, S.X., Huang, Y.L. and Si-Tu, S.P. (2016b). Long-term trends of chemical characteristics and sources of fine particle in Foshan City, Pearl River Delta: 2008–2014. *Sci. Total Environ.* 565: 519–528.
- Tian, Y.Z., Chen, G., Wang, H.T., Huang-Fu, Y.Q., Shi, G.L., Han, B. and Feng, Y.C. (2016). Source regional contributions to PM_{2.5} in a megacity in China using an advanced source regional apportionment method. *Chemosphere* 147: 256–263.
- Wang, J., Zhou, M., Liu, B.S., Wu, J.H., Peng, X., Zhang,

- Y.F., Han, S.Q., Feng, Y.C. and Zhu, T. (2016). Characterization and source apportionment of size-segregated atmospheric particulate matter collected at ground level and from the urban canopy in Tianjin. *Environ. Pollut.* 219: 982–992.
- Xu, L.L., Duan, F.K., He, K.B., Ma, Y.L., Zhu, L.D., Zheng, Y.X., Huang, T., Kimoto, T., Ma, T., Li, H., Ye, S.Q., Yang, S., Sun, Z.L. and Xu, B.Y. (2017). Characteristics of the secondary water-soluble ions in a typical autumn haze in Beijing. *Environ. Pollut.* 227: 296–305.
- Xu, W.Y., Zhao, C.S., Ran, L. and Deng, Z.Z. (2011). Characteristics of pollutants and their correlation to meteorological conditions at a suburban site in the North China Plain. *Atmos. Chem. Phys.* 11: 4353–4369.
- Zhang, B., Wang, Y. and Hao, J. (2015). Simulating aerosol–radiation–cloud feedbacks on meteorology and air quality over eastern China under severe haze conditions in winter. *Atmos. Chem. Phys.* 15: 2387–2404.
- Zhang, H.F., Wang, S.X., Hao, J.M., Wang, X.M., Wang, S.L., Chai, F.H. and Li, M. (2016). Air pollution and control action in Beijing. *J. Clean Prod.* 112: 1519–1527.
- Zhang, Z., Ma, Z. and Kim, S.J. (2018). Significant decrease of $PM_{2.5}$ in Beijing based on long-term records and Kolmogorov-Zurbenko filter approach. *Aerosol Air Qual. Res.* 18: 711–718.
- Zhao, P.S., Dong, F., Yang, Y.D., He, D., Zhao, X.J., Zhang, W.Z., Yao, Q. and Liu, H.Y. (2013). Characteristics of carbonaceous aerosol in the region of Beijing, Tianjin, and Hebei, China. *Atmos. Environ.* 71: 389–398.
- Zheng, G.J., Duan, F.K., Su, H., Ma, Y.L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T. and Chang, D. (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, J.B., Xing, Z.Y., Deng, J.J. and Du, K. (2016a). Characterizing and sourcing ambient $PM_{2.5}$ over key emission regions in China I: Water-soluble ions and carbonaceous fractions. *Atmos. Environ.* 135: 20–30.
- Zhou, X.H., Cao, Z.Y., Ma, Y.J., Wang, L.P., Wu, R.D. and Wang, W.X. (2016b). Concentrations, correlations and chemical species of $PM_{2.5}/PM_{10}$ based on published data in China: Potential implications for the revised particulate standard. *Chemosphere* 144: 518–526.

Received for review, April 25, 2018

Revised, April 28, 2019

Accepted, May 5, 2019