Typical winter haze pollution in Zibo, an industrial city in China: Characteristics, secondary formation, and regional contribution

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ABSTRACT

Heavy haze pollution occurs frequently in northern China, most critically in the Beijing-Tianjin-Hebei area (BTH). Zibo, an industrial city located in Shandong province, is often listed as one of the top ten most polluted cities in China, particularly in winter. However, no studies of haze in Zibo have been conducted, which limits the understanding of the source and formation of haze pollution in this area, as well as mutual effects with the BTH area. We carried out online and continuous integrated field observation of particulate matter in winter, from 11 to 25 January 2015. SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ (SIA) and organics were the main constituents of PM$_{2.5}$, contributing 59.4% and 33.6%, respectively. With the increasing severity of pollution, the contribution of SIA increased while that of organics decreased. Meteorological conditions play an important role in haze formation; high relative humidity (RH) and low wind speed increased both the accumulation of pollutants and the secondary transition from gas precursors (gas-particle phase partitioning). Since RH and the presence of O$_3$ can indicate heterogeneous and photochemistry processes, respectively, we carried out correlation analysis and linear regression to identify their relative importance to the three main secondary species (sulfate, nitrate, and secondary organic carbon (SOC)). We found that the impact of RH is in the order of SO$_4^{2-}$ > NO$_3^-$ > SOC, while the impact of O$_3$ is reversed, in the order of SOC > NO$_3^-$ > SO$_4^{2-}$, indicating different effect of these factors on the secondary formation of main species in winter. Cluster analysis of backward trajectories showed that, during the observation period, six directional sources of air masses were identified, and more than 90% came from highly industrialized areas, indicating that regional transport from industrialized areas aggravates the haze pollution in Zibo. Inter-regional joint prevention and control is necessary to prevent further deterioration of the air quality.

1. Introduction

Air pollution, particularly fine particles with aerodynamic diameter less than 2.5 μm (PM$_{2.5}$), has become a major international environmental problem that has caused adverse impacts on climate (Tai et al., 2010), visibility (Zhang et al., 2010), and human health (Lee et al., 2015). Haze, a typical synoptic phenomenon mainly caused by PM$_{2.5}$, in which visibility is below 10 km and relative humidity (RH) is less than 90%, has been reported more and more frequently in both developing and developed countries (Tan et al., 2009). The study of haze has drawn the public’s attention, and, to date, many scientists worldwide have carried out investigations of various aspects of PM$_{2.5}$, including source identification (Duan et al., 2007; Han et al., 2016), chemical characterization (Murillo et al., 2013), and particle formation...
process (Guo et al., 2014). Wang et al. (2012a) and Zhu et al. (2011) also discussed and emphasized the importance of heterogeneous reactions in the formation of haze. Meanwhile, the role of photochemistry on particle pollution requires attention, especially during the hot season (Wang et al., 2016a; Zhang et al., 2011). In China, many studies have mainly focused on the North China Plain (NCP) (Du et al., 2014; Hu et al., 2014), the Yangtze River Delta (YRD) (Zhang et al., 2015), and the Pearl River Delta (PRD) (Hu et al., 2012; Zhou et al., 2014). In addition, the Beijing-Tianjin-Hebei (BTH) region (Zhao et al., 2013a), and in particular Beijing (Cheng et al., 2015; He et al., 2012; Zhang et al., 2014; Zheng et al., 2016), are hotspots for these studies considering their political position, pollution severity, and technology availability. To call for more attention on the climate change worldwide, the Paris Agreement was signed in April 4th, 2016, and China faces more serious status and pollution conditions in Zibo can affect BTH through regional transportation of pollutants. Therefore, an investigation of pollution in Zibo would provide a comprehensive understanding of the pollution characterization and pollution control needs in Zibo itself, BTH, and even the NCP. Studies have rarely been reported regarding haze pollution in Zibo, which therefore spurred this current investigation.

In this study, we carried out continuous field investigation of pollution in Zibo from 11 to 25 January 2015, when serious particulate pollution frequently occurred. The pollution conditions in Zibo were further divided into three levels in the following discussion; the chemical composition during each pollution condition was analyzed, and the characteristics of species with increasing severity of pollution were investigated. Moreover, we also explored the relative importance of photochemistry and heterogeneous processes on three main secondary species: sulfate, nitrate, and SOC (secondary organic carbon). Based on our results, a conceptual model has been proposed. Finally, we analyzed the regional transport effect on Zibo by performing a cluster analysis of backward trajectories.

2. Experimental methods

Our observation site was located on the roof of a building on the campus of Shandong University of Technology in Zibo, Shandong province (Fig. 1). The inlet was approximately 20 m above ground level. Our observations included continuous monitoring of hourly averaged concentration of PM$_{2.5}$, its main chemical species, and meteorological parameters. The mass concentration of PM$_{2.5}$ was monitored using a dichotomous monitor (PM-712, Kimoto Electric, Ltd., Japan) at a flow rate of 16.7 L min$^{-1}$. A detailed description of this equipment has been presented in previous work (Duan et al., 2016). In addition, water-soluble inorganic ions ($\text{SO}_4^{2-}$, $\text{NO}_3^-$), water-soluble organic carbon (WSOC), and acidity were detected simultaneously by a continuous dichotomous aerosol chemical speciation analyzer (Model ACSA-08; Kimoto Electric, Ltd., Japan). To better describe the pollution in Zibo, we carried out offline estimation of different chemical species with a sample collected daily by quartz membrane from January 11 at 12:00 to January 25 at 12:00 to in parallel with the on-line data. We used ion chromatography (IC) to analyze water-soluble anions and cations; a more detailed description can be found in the work of Duan et al. (2016). The total ions included $\text{SIA} (\text{SO}_4^{2-}, \text{NO}_3^-, \text{NH}_4^+)$, $\text{Cl}^-$, $\text{Na}^+$, $\text{K}^+$, $\text{Mg}^{2+}$, and $\text{Ca}^{2+}$. For the online observation, it should be noted that ammonium was predicted based on the assumption that the main species present are (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ (Cheng et al., 2011; He

Fig. 1. Map showing the position of Zibo. The map shows the relative position of Beijing and Shandong province, and the inset shows the specific location of Zibo (bigger red dot) and Jinan (smaller dot) in Shandong. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
et al., 2012). As such, the hourly data for NH₄⁺ may be overestimated (Sun et al., 2014), but the overestimation of hourly data for ammonium can be lessened by offline correction. Noting all data in this paper were hourly averaged except for Cl⁻, and metal ions (Na⁺, K⁺, Mg²⁺, and Ca²⁺), which were daily averaged. The off-line data of sulfate, nitrate and ammonium were used to correct corresponding on-line data, the calculation of their average value were based on the corrected hourly data. To better guarantee the data quality, we performed regular off-line measurements corresponding to the on-line periods as mentioned in our previous study (Duan et al., 2016). It should be noted that the online data showed slight underestimations as shown in Fig. S1 in Support Information (SI), especially for sulfate. It might be due to the turbidimetric method after addition of BaCl₂ dissolved in polyvinyl pyrrolidone solution for sulfate measurement. Therefore, it is necessary to strengthen the equipment maintenance so as to guarantee the normal work status of the operation, adjust the measurement internal of the water-soluble ions to avoid overloading in the solution especially during heavy pollution periods. In addition, a useful measure for the data quality assurance is to carry out inter-comparison between the online data and the offline data by traditional methods such as ion chromatography. In this work, since the strong correlations can be found between the online data and off-line data for sulfate, nitrate and ammonium, we considered that the on-line data was acceptable although they might produce systematic errors for the data analysis to some extent.

We applied an online and continuous particulate carbon monitor APC-710 (Kimoto Electric, Ltd., Japan) with optical transmittance and reflectance methods to measure the hourly organic carbon (OC) and elemental carbon (EC). This analyzer collects aerosol samples on the PFTE filter tape, and then performs optical analysis in different wavelengths as being introduced in the previous patent of Kimoto Electric, Ltd., Japan (application number: 2015-039568, Japan Patent Office, https://www.j-platpat.inpit.go.jp/web/all/top/BTmTopPage). The detector schematic diagram is shown in SI (Fig. S2). For data quality assurance, we carried out a comparison between online data from the APC-710 with the data from the traditional method IMPROVE-A that has been mentioned in our previous work (Duan et al., 2016). Although our online data showed a slight overestimation on OC and underestimation on EC, respectively, a good correlation can be seen between the two methods (Fig. S3), suggesting that the online data from the APC-710 were acceptable. It should be noticed that the online method for OC and EC measurements has its limitations especially at low concentration levels. However, since there is no standard measurement of carbonaceous aerosols to current, a better way for data quality assurance and quality control is to carry out inter-comparison between different laboratories, different methods especially with the traditional method such as IMPROVE A protocol. Organic matter (OM) was estimated as 1.6 times OC, which was based on a previous study conducted in Beijing due to the lack of a previous study in Zibo (Zhang et al., 2014). In addition, the hourly average concentrations of gaseous pollutants such as NOₓ, SO₂, CO, and O₃ were monitored using a MCSAM-13 system (Kimoto Electric, Ltd., Japan). Hourly meteorological parameters such as wind speed (WS), wind direction (WD), pressure, temperature, and relative humidity (RH) were also monitored concurrently.

3. Results and discussion

3.1. Characteristics of PM₂.₅ in January

Fig. 2 presents the hourly series of PM₂.₅ measurements, concentrations of gaseous pollutants, and meteorological conditions from 11 to 25 January 2015. The range of PM₂.₅ was large, ranging from 21.9 to 358.0 μg m⁻³. The highest value of PM₂.₅ was recorded at 9:00 on January 16, when RH was high (80.4%) and O₃ was low (4.5 μg m⁻³). Conversely, the minimum value of PM₂.₅ was recorded at lower RH (22.0%) and higher concentration of O₃ (40.9 μg m⁻³). The temporal trend of the main chemical species, including SIA and carbonaceous species, was consistent with that of PM₂.₅. Specifically, sulfate peaked at 5:00 on January 16 with value of 92.6 μg m⁻³, accompanied by a high RH (71.1%), low WS (1.0 m s⁻¹), and low O₃ level (6.0 μg m⁻³), and nitrate reached its highest concentration at 63.1 μg m⁻³ one hour later under similar conditions; however, OM soared to 104.8 μg m⁻³ at 12:00 on January 24, when RH was relatively low (35.1%) and the level of O₃ was higher (29.6 μg m⁻³). Gaseous pollutants such as SO₂, CO, and NO₂ also showed similar variations in their concentrations, while O₃ presented the opposite trend. The similar trend of SO₂, CO and NO₂ was easily accepted considering they were both primary emission from similar sources including coal combustion, industrial process, etc. The reversed trend between NO₂ and O₃ was caused by the basic photochemical cycle between NO₃ and O₃ (Cruzen, 1979). Temperature had clear diurnal cycles with the highest values in daytime; in contrast, RH showed an opposite trend, peaking in nighttime. During the observation period, the temperature ranged from −3.0 to 10.5 °C, with an average of 3.7 ± 3.2 °C. Relative humidity varied from 14.6 to 90.5%, averaging 45.5 ± 20.2%. Wind speed varied between 0.3 and 3.6 m s⁻¹, with an average of 1.3 ± 0.7 m s⁻¹. The occurrence of higher PM₂.₅ concentration was typically accompanied by higher RH, lower wind speed, and increased concentration of gaseous precursors. These phenomena have been documented by many previous investigations (Sun et al., 2013b; Tai et al., 2010; Xu et al., 2011; Yang et al., 2007). To better understand the levels of pollution, we classified the observation period into three different levels (based on the Air Quality Index: http://kis.mep.gov.cn/hjbhz/bzwb/dqhjb/zj/ffhzbb/201203/t20120302_224166.htm?COLLCC=2906016564&t): clean periods (C, PM₂.₅ ≤ 75 μg m⁻³), polluted periods (P, 75 < PM₂.₅ ≤ 250 μg m⁻³), and highly polluted periods (H, PM₂.₅ > 250 μg m⁻³). Similar classification method was also adopted by Zheng et al. (2015). Based on the above classifications, the C, P, and H periods account for 24.8, 63.0 and 12.2% of this observational duration, respectively. This indicates that for most of the time within the observation period (more than 75%), Zibo was engulfed by particle pollution, and 12.2% of the time was heavily polluted.

3.2. Characteristics of chemical compositions

Table S1 lists the average value and standard deviation of species and gaseous precursors during the different conditions. The average concentration of PM₂.₅ in Zibo within this observation was 140.4 μg m⁻³, which was comparable to Beijing (158.4 μg m⁻³) in Jan 2013 (Liu et al., 2016), higher than Tianjin, Chengde and Shandianzi in 2010 (Zhao et al., 2013b). Based on the data in Table S1, we can conclude that the main constituents of PM₂.₅ were SIA and OM, which appeared to be the most compositions in PM₂.₅. Aside from these species, we can see that the average concentrations of various gaseous precursors are high, which represent the typical characteristics of emission conditions in winter, especially the concentration of SO₂, with an average of 138.5 ± 85.4 μg m⁻³. Along the order of C-P-H, concentrations of components and primary gases increased significantly. The concentrations of SO₂ and NO₂ during heavily polluted periods were 3.21 and 1.31 times higher than in clean periods, and their corresponding secondary species SO₄²⁻ and NO₃⁻ increased by 4.10 and 3.21 times, respectively. The low O₃ concentration and relatively high RH indicated a more important role of heterogeneous process than of the photochemical process in winter haze formation. Noting the
heterogeneous process in this study includes partitioning between phases and the chemical reaction happened in particle phase. In addition, the carbonaceous species showed a similar rising trend, with levels of EC and OM increased by 1.76 and 2.03 times, respectively. As shown in Fig. 3, the main constituents of PM$_{2.5}$ were SIA and OM, which accounted for 59.4% and 33.6% of the total PM$_{2.5}$, respectively. SIA, sulfate, nitrate, and ammonium contributed 22.7%, 20.9% and 15.8% of the total PM$_{2.5}$, respectively. Moreover, the chemical composition varied with increasing severity of pollution; proportions of SIA consistently increased. Nitrate increased from 15.9% to 19.1% from clean to heavily polluted; sulfate increased from 18.6% to 26.1%, and ammonium rose from 12.0% to 15.9%. This obvious enhancement of the SIA species can be ascribed to the high RH, which facilitated heterogeneous reactions and contributed to gas-particle partitioning (Hennigan et al., 2008). The detailed contribution of RH is discussed below. Both proportion of OM and EC, however, declined consistently with increasing PM$_{2.5}$ concentration. The proportion of OM declined from 45.1% to 32.1%. This decrease in carbonaceous matter from clean to polluted periods during winter in Beijing has also been reported in our previous work (Zheng et al., 2015) and in other studies (Quan et al., 2014), indicating the less contributing role of carbonaceous matter. Therefore, it can be concluded that the formation of heavy haze is mainly promoted by the secondary inorganic species.

We found that many factors influenced the process of haze evolution, including meteorological conditions, levels of gaseous pollutants, the conversion rate of secondary species, etc. We compared those factors with the mass concentration of PM$_{2.5}$, as shown in Fig. S4. It is obvious that as the PM$_{2.5}$ mass loading increased, those factors presented differently. For the meteorological parameters, the RH increased until the mass loading reached 325 $\mu$g m$^{-3}$, then it had a slight decrease. On average, the RH in heavily polluted periods was higher than in polluted and clean periods. Wind speed was another influential synoptic factor, showing a consistent declining trend with increasing PM$_{2.5}$. As reported previously, high relative humidity was usually favorable for aqueous reactions and the gas-particle partitioning process. Low wind speed lessened the diffusion of pollutants, increasing the accumulation process and resulting in secondary conversion (Gao et al., 2015; Zheng et al., 2016). As for the primary gaseous
pollutants, their concentrations showed an increasing trend until the mass loading reached 250 µg m⁻³; above this concentration, SO₂ and NO₃ maintained a relatively stable and high level, while the concentration of CO kept increasing. SOR (sulfate oxidation rate) and NOR (nitrate oxidation rate) are indicators of the secondary transition of SO₂ and NO₂ to form SO₄²⁻ and NO₃⁻. Their calculation followed:

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\text{NOR} = \frac{n(\text{NO}_3^-)}{n(\text{NO}_2) + n(\text{NO}_3^-)} \quad \text{SOR} = \frac{n(\text{SO}_4^{2-})}{n(\text{SO}_2) + n(\text{SO}_4^{2-})}
\]

In this study, both of these showed an increasing trend with PM₂.₅. SO₄²⁻ can be formed through either oxidation of SO₂ by a hydroxyl radical in the atmosphere or via oxidants (H₂O₂, O₃ etc.) dissolved in water (Zhao et al., 2013c); NO₃⁻ originated from reactions either between NO₂ with ozone in the gas phase or from the decomposition of N₂O₅ through a heterogeneous channel (Wang et al., 2013). As shown in Fig. S4 (a), as the mass loading increased, the concentration of O₃ declined significantly, while the RH increased, resulting in a decrease in the photochemical process and an increase in the heterogeneous process. Under this condition, the high oxidation rate of sulfate and nitrate can be mostly explained by the enhancement of heterogeneous reactions and gas-particle partitioning. Meanwhile, photochemistry was too weak to contribute to haze formation in cold season, which will be discussed further below. In addition to the increased rate of transitions, the high concentrations of gaseous precursors and low wind speed jointly resulted in the rapid increase in the concentrations of sulfate and nitrate. Fig. S4 (b) shows that although the mass concentration of species increased as a function of the mass loading of PM₂.₅, the fraction or contribution of species to the particulate mass did not necessarily correspond to these increases in the mass loading. This phenomenon indicates that the higher levels of particulate pollution in winter were caused by a synergistic effect of various pollutants, which is similar to the observation of Zhang et al. (2014). This synergistic effect means that the occurrence of haze was the integrate result of various pollutants, some of which may contribute more and others less.

As mentioned above, the main contributors by mass to the particulate pollution were SIA and OC (OM), relative to other known species. Hence, the existing forms of these species were important in further exploring the complexity of the atmospheric processes. To improve our understanding, we compared the mole concentration of NH₄⁺ versus the mole concentration of sulfate (NH₄⁺·2SO₄⁻), all those data were corrected by the off-line value. This plot is based on the assumption that NH₄⁺ tends to combine more readily with SO₄²⁻ because (NH₄)₂SO₄ is more thermostable than NH₄NO₃ (Duan et al., 2003; Zhang et al., 2013). As shown in Fig. S5 (a), in clean (C), polluted (P), and heavily polluted (H) periods, the slope was larger than 1, meaning that the relative content of NH₄⁺ is more than sufficient to neutralize sulfate. Thus, the main form of sulfate is likely to be (NH₄)₂SO₄. In addition, NH₄⁺/SO₄²⁻ increases from clean to polluted to heavily polluted periods, indicating that increased ammonium could be partially responsible for the worsening of the particulate pollution. The same increase can also be identified in Fig. S5b, as the slope between (NH₄⁻·2SO₄⁻) and NO₂ becomes larger in more polluted periods in comparison with clean periods. Note during the clean periods, the slope is less than 1, indicating a relatively poor ammonium environment for nitrate to form NH₄NO₃. In general, nitrate is mainly in the form of NH₄NO₃, and some other proportion of nitrate may exist as other forms such as NaNO₃, as reported in previous studies (Milford et al., 2013; Perrino et al., 2012). However, in the polluted and heavily polluted periods, the slopes were both greater than 1, which further provides evidence for the contribution of NH₄⁺ to the formation of haze. Based on these results, we can infer that sulfate was mainly in the form of (NH₄)₂SO₄ via the heterogeneous reaction of H₂SO₄ with NH₃. Further, nitrate was formed mainly via the heterogeneous reaction of nitric acid and NH₃. The loss of NO₂⁻ caused by the equilibrium of NH₄NO₃ between the gas and particle phase was minimized due to the low temperature and high RH in polluted periods (Wang et al., 2012a).

With respect to carbonaceous matter, OC can be divided into primary organic carbon (POC) and secondary organic carbon (SOC). The method we adopted was the EC-scaled method (Snyder et al., 2009). We used the smallest ratio of particle OC to EC as the value of (OC/EC)primary (Li et al., 2015; Strader et al., 1999; Sun et al., 2014), which is 1.18. The main OC exists as SOC, as indicated by a slope greater than 0.5 (C and P) or near 0.5 (H). It is possible that when haze pollution reached its highest level, the sharp reduction of photochemistry had a greater effect on the oxidation of SOC, and thus the ratio of SOC to OC was reduced. Based on the trend of SOC/OC, we infer that both photochemistry and heterogeneous reactions affected the formation of SOC, but their relative importance varied along the severity of pollution. Overall, SOC was the main fraction, accounting for more than 50% of OC, which agrees with previous reports (Duan et al., 2005; Wang et al., 2016b).

3.3. Secondary conversion: heterogeneous and photochemical processes

As mentioned above, the secondary conversion of gaseous precursors contributed a lot to the haze events, among which the heterogeneous process was more influential than photochemistry. Here we will further discuss and compare those two processes in winter haze formation in Zibo. RH was generally regarded as one of the main factors facilitating the formation of haze through heterogeneous reaction (Chen et al., 2016), while O₃ was commonly regarded as an indicator of the photochemical process (Zheng et al., 2015). Although the effects of RH on sulfate, nitrate, and SOC varied, the aqueous chemical reaction was important for all (Lim et al., 2010; Liu et al., 2015; Wang et al., 2012b). However, rarely has work been reported that systematically compares the relative importance of heterogeneous and photochemical processes for different secondary species in winter. Therefore, we tried to distinguish the effects of RH on the formation of sulfate, nitrate, and OM to clarify the main formation processes in Zibo in winter. Subsequently, a comparison of the impact caused by RH and O₃ on secondary transition in winter was performed to elucidate the relative importance of photochemical and heterogeneous reactions during haze pollution. The heterogeneous process (reaction) in the following discussion covers both aqueous chemical reactions and gas-particle partitioning.

As shown in Fig. 4, as the RH increased, each species demonstrated an increasing trend, while O₃ did the opposite, that is, decreased. With increasing RH, the pre-existing SO₄²⁻, NO₃⁻, and NH₄⁺ were able to absorb water, enlarging the size of the particles and surface area, and thus giving the particles more capacity to accommodate heterogeneous reactions (Cheng et al., 2015). Meanwhile, the high RH resulted in a decrease in the particles' viscosity, lifting the mass transfer limits for gaseous pollutants into the particle phase kinetically, resulting in more pollutants' transfer into the particle form, which also aids the heterogeneous reaction (George et al., 2015). Afterwards, newly formed SIA would increase the particles' hygroscopicity and continue the above process in turn. This positive feedback loop would keep running until an external interruption, such as high wind speed, occurs. The net effect created by this feedback was the enlargement of particle size, and an increase in the extinction effect of particles by scattering.
Fig. 4. Variations of species and species versus EC as a function of RH. The data are grouped in RH bins. The solid signal represents the average value while the semi-solid symbol refers to the corresponding species versus EC. The gray shaded areas indicate the standard deviation.

and absorbing, which led to the reduction of photochemistry, as well as O₃ (Tao et al., 2015; Wang et al., 2015). EC presented an overall increasing trend; however, EC is a nearly-hydrophobic species (Wang et al., 2014), such that this fluctuation was primarily the result of accumulation (or dilution) rather than secondary conversion. Therefore, we can use EC to exclude physical effects for other species. We also found that both the SIA concentration and the corresponding EC-scaled values increased significantly until the RH value reached 60.0%, indicating that the enhanced heterogeneous process was more influential than a reduction in photochemistry. However, this variation trend differed when the RH was greater than 60.0%; only sulfate kept rising, whereas the other species maintained relatively stable levels. This result demonstrates the different impacts caused by the RH on the chemical species. The relatively flat trend of EC-scaled NO₃ indicated the limited effects of the RH on its formation. Another interesting phenomenon shown in Fig. 4 is the relatively flat level of SOC with increasing RH, especially the EC-scaled SOC. This may be caused by the reduced conversion of VOC (volatile organic carbon) to SOC in winter or the weak hygroscopicity of low-oxidized SOC, which resulted in a lower sensitivity to the RH (Sun et al., 2013a).

The heterogeneous reaction was weak enough to neglect when the RH was less than 30.0%, because particle phase water was negligible when RH was less than 30%, thus the heterogeneous process was weak (Khoder, 2002; Sun et al., 2013a). Based on Fig. 4, O₃ approached nearly zero when the RH was greater than 60%, indicating weak photochemical reactivity. Accordingly, we plotted correlations between every pair of species and a linear regression within different RH (<30% or >60%) and O₃ (<10 and >40 µg m⁻³) ranges. Based on the results presented in Fig. 5(a), overall, good correlations existed between each pair of secondary species, and their correlations were strongly RH dependent. With the increase of RH from 30.0 to 60.0%, the R² increased correspondingly, except between NO₃ and SO₄²⁻, but this exception was acceptable considering their correlation coefficient (0.89) was high when the RH was less than 30.0%. The increase in correlation coefficients indicated that with the increase of RH (and with the worsening in the severity of pollution), the formation process of three secondary species exhibited greater similarity. During high pollution periods, both the significantly high RH and low O₃ facilitated the secondary transition to be more inclined to happen in the particle phase. In addition, with increasing RH, the slope between the species changed, and to some extent, this likely reflects the different impacts of RH on different secondary species. For SOC and SO₄²⁻, their slope decreased from 0.66 (RH<30%) to 0.34 (RH>60%), indicating that the effect of RH was more significant for SO₄²⁻ than for SOC. Similarly, the impact of the RH was more apparent on SO₄²⁻ than on NO₃, and more significant for NO₃ than SOC. Overall, the impact of RH on secondary species was in the order of SO₄²⁻ > NO₃ > SOC. However, the order was completely reversed with respect to the impact of O₃ on secondary species when the same analysis is conducted using Fig. 5(b). The influence of O₃ on the three species was in the order of SOC > NO₃ > SO₄²⁻. Those results also indicate the relative importance of heterogeneous and photochemical processes on these three species, respectively. Considering the contrasting effect of these two processes, the differences in species variation in Fig. 5 are easier to understand. The most RH-vulnerable and least O₃-influenced species, sulfate, kept a constant increase with RH. The most O₃-impacted and least RH-affected species, SOC, appeared to be more stable compared to other secondary species, considering that the significant decrease of O₃ exerted the most negative influence on its formation. Finally, the both medium RH and O₃-impacted NO₃ presented a rapid increase at first but approached a stable level when the RH was greater than 60.0%.

Based on the above discussion, we found that the relative importance of RH and O₃ (or heterogeneous and photochemical channels) varied between the three main secondary species and thus also varied for the formation of particles. The various relative importance of these factors can be illustrated in a conceptual model (Fig. 6). During clean periods, strong solar radiation and low RH produce an environment that favors photochemistry and suppresses heterogeneous reactions. In this condition, photochemical processes are the dominant formation method for the three secondary species. With an increase in RH, the positive feedback...
between particles and enhanced secondary formation of SIA reduces the photochemistry effect while heterogeneous processes increase. As these processes continue, pollution levels move from clean to polluted. Under the polluted condition, the atmosphere keeps a relative equivalent condition for both photochemistry and heterogeneous reactions. For sulfate, the formation from heterogeneous processes increases most significantly since it is most sensitive to the RH, while its decrease via photochemistry is minimal as it is not very sensitive to O3. Based on the relative importance sequence, the increase of SOC is smallest, while the decrease of photochemistry is most significant. Nitrate has moderate changes in both formation channels. As the pollution continues to worsen, the RH reaches its highest level and O3 reaches the lowest. The increasing effect of heterogeneous reactions is most significant for sulfate, followed by nitrate and then SOC. Conversely, the decreasing impact of photochemistry was most obvious for SOC, then nitrate, and finally sulfate. Consequently, sulfate increased most rapidly, then nitrate, and lastly SOC. Note that the descriptions of importance and contribution described here indicate the magnitude of influence on secondary species caused by photochemistry and heterogeneous reactions, and do not represent absolute production because the final production of each species does not rely solely on the transition processes but also on the concentrations of gaseous precursors. In addition, since the RH was the main cause of pollution in winter, this finding can only be applied to describe pollution characteristics in winter, whereas in summer or other seasons the conditions may change. The universality of this result needs to be further investigated in follow-up studies.

3.4. Regional transport

To better understand the impact of regional transport on Zibo in the different pollution levels, we plotted 24-h back trajectories for identified clusters from January 12 to 25 and started with a height 100 m above ground. The calculation of clusters was performed using the TrajStat model (Wang et al., 2009). During the observation period in this study, a total of six clusters were identified, indicating that the main air masses are coming from six directions (as shown in Fig. 7). We further compared the main chemical compositions of PM$_{2.5}$ in the six clusters to determine the regional impact on chemical species in particle pollution. For cluster 1, the air mass originated from the east (Huanghai direction), passed over the coastal cities Qingdao, and then moved west to Zibo with moderate speed. The air mass from this direction contributed 21.40% to the total air mass. During this period, PM$_{2.5}$
was 124.5 \mu g m^{-3}, and the most abundant species were carbonaceous (OC at 26.0% and EC at 10.0%). This may have been caused by the incomplete combustion of fossil fuel from the electrical power industry located in Qingdao. As for cluster 2, the most polluted trajectory, it originated from the north and passed over the Bohai economic zones, including the Hebei and Tianjin provinces, which are one of the most industrialized and densely populated areas in China and has the highest emissions of SO2 and NOx (Zhang et al., 2009). This cluster accounted for 14.29% of particulate pollution during this investigation. PM2.5 also reached a maximum level of 212.3 \mu g m^{-3} with extremely high concentrations of SIA species. Specifically, sulfate, nitrate, and ammonium were 42.4, 32.4, and 25.9 \mu g m^{-3}, respectively. The significant enriching of secondary species may be the result of the higher concentration of gaseous precursors plus the secondary formation of species along this trajectory. In addition, the RH was high in this air mass because it passed by Bohai, which may have further facilitated secondary conversion. The air mass in cluster 3 came from the arid inner Mongolia with a high wind speed and straight direction. This driving wind exerted a scavenging effect and cleared pollution, such that PM2.5 reached a relatively low value of 105.3 \mu g m^{-3} during this time. However, the occurrence of cleaning air occurred only at a frequency of 7.14%. The high concentration of Ca^{2+} in this cluster further demonstrates that the main source of particle pollution under this condition was dust from the northwest. The air mass in cluster 4 came from the arid Mongolia with a high wind speed and straight direction. This driving wind exerted a scavenging effect and cleared pollution, such that PM2.5 reached a relatively low value of 105.3 \mu g m^{-3} during this time. However, the occurrence of cleaning air occurred only at a frequency of 7.14%. The high concentration of Ca^{2+} in this cluster further demonstrates that the main source of particle pollution under this condition was dust from the northwest. The air mass in cluster 4 (accounting for 14.29%) appeared to be a very stable air motion reflected by its shortest trajectory length; this stable meteorological condition caused the second-most serious level of particulate pollution (164.7 \mu g m^{-3}) in Zibo. This trajectory passes through the northwest and center of Shandong, which is highly industrialized with abundant petroleum resources and large petrochemical industries. As a result, the levels of SIA were the second highest among the clusters. In addition, Zibo itself is a heavily industrialized city, particularly in the ceramic industry. The usage of fossil fuel during industrial processes contributed to the highest ratio of OC among various species. This enriched emission of primary pollutants and stable air motion in cluster 4 caused the high concentration of PM2.5 and its species during this period. The air mass in cluster 5 (28.6%) originated from the north of Jiangsu, a heavily polluted area (He et al., 2016), and moved at a moderate speed. However, the particulate concentration was unexpectedly low at 102.4 \mu g m^{-3}; this may be explained by the relatively frequent rain and snow events during these periods (January 20 and 23). Due to the cleaning effect of precipitation, the concentration of particulate pollution was the lowest of the observation period. The pollution condition caused by cluster 6 (accounting for 14.29%) was higher (120.8 \mu g m^{-3}) due to its whirling and low speed. In addition, it passed through the southwest of Shandong where large power plants are located, such as the ones in Jining and Zaozhuang city (Cheng et al., 2011). These high emissions of primary pollutants (e.g., SO2, NOx) resulted in relatively high concentrations of particulate pollution and species, especially SIA. Overall, regional transport exerted a significant influence on the pollution in Zibo considering the surroundings are almost all high-emission areas. As mentioned, the NCP region was a heavily polluted location and cities within here are both donors and receptors, so that pollutants are transferred from city to city. Hence, to effectively reduce pollution, regional joint prevention is necessary and inevitable. Up to now, many observation campaigns have been conducted especially in BTH, the Yangtze River Delta and the Pearl River Delta. However, the hot observational area were nearly all based on the partition of economic or administrative standard, which cannot represent the vulnerable pollution.
area accurately. Zibo in this study, located in Shandong province, is in the outside of BTH, can influence BTH and be influenced by the regional transportation of pollutants from BTH meanwhile. Thus, government may set a new way to divide the area into joint pollution prevention region from the perspective of regional transportation of pollutants. Based on the new set of pollution area, collaborations between provinces can be more effective and specific.

4. Conclusions

The investigation of the chemical characteristics and formation of PM$_{2.5}$ was conducted from 11 to 25 January 2015 in Zibo, an industrial city in northern China. Averagely, the main constituents of PM$_{2.5}$ by mass were SIA and OM, which accounted for 59.4% and 33.6%, respectively. For SIA, sulfate contributed the most with a proportion of 22.7%, then nitrate (20.9%), and ammonium (15.8%). Moving from clean to polluted state then to the heavily polluted states, nitrate increased from 15.9% to 19.1%, sulfate increased from 18.6% to 26.1%, and ammonium rose from 12% to 15.9%. Conversely, OM declined from 45.1% to 32.1% and EC from 8.5% to 6.8%. Those variations show the contribution of secondary formation of inorganic species to the worsening of pollution. In addition, we explored the main existing forms of sulfate, nitrate, and OC. Because Zibo is a relatively ammonia-rich area, the main sulfate and nitrate species exist as (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$, and about 50% of the organic carbon was from secondary transition.

Aside from chemical composition, meteorology is also important in PM pollution in Zibo, particularly RH. Initially we found a continuous increase in RH as a function of mass loading of PM$_{2.5}$. Then, by adopting a semi-quantitative method (correlation scatter and linear regression), we compared the relative importance of RH and O$_3$ on the three main secondary species: sulfate, nitrate, and SOC. The result indicates that the importance of or contribution to RH regarding these species is in the order of SO$_4^{2-}$ > NO$_3^-$ > SOC, while the impact of O$_3$ is reversed with the order of SOC > NO$_3^-$ > SO$_4^{2-}$. This finding helps us to understand the variation of these species related the changes in RH or pollution level. Based on this finding, we propose a conceptual model (Fig. 6), which illustrates the changes in the contribution of photochemical and heterogeneous processes with increasing severity of particle pollution. Decreasing wind speed can also be a factor contributing to the worsening of pollution.

Finally, a cluster of backward trajectories was conducted to analyze the regional transport effect in Zibo. Six clusters were identified; 7.14% of the air mass originated from the northwest with relative clean effect. The others were either from a coastal area or
highly industrialized economic zone and accounted for 14.29, 21.43, and 28.57% of the air mass, respectively, generally with slow and whirling air mass motion.

In general, heavy haze pollution occurred in Zibo in winter, which can be ascribed to locally high emissions and secondary conversion. Meanwhile, pollution in Zibo was also affected by regional transport reflecting the fact that Zibo is surrounded by heavy industrial sources in the BTH area. Cities within the BTH region or the area surrounding it are both sources and receptors, suggesting that regional collaboration for effectively controlling pollution emissions should be the primary focus for the government. Meanwhile, to further uncover the health problem associated with haze is a necessary work for government and researchers in the future.

Notes
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Appendix A. Supplementary data
Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.05.081.

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