Haze pollution in winter and summer in Zibo, a heavily industrialized city neighboring the Jin-Jin-Ji area of China: source, formation, and implications

Hui Li, Fengkui Duan*, Yongliang Ma, Kebin He*, Lidan Zhu, Tao Ma, Siqi Ye, Shuo Yang, Tao Huang, Takashi Kimoto

*Corresponding authors.
E-mail: duanfk@tsinghua.edu.cn, hekb@tsinghua.edu.cn.

State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing Key Laboratory of Indoor Air Quality Evaluation and Control, Tsinghua University, Beijing 100084, China
Kimoto Electric Co. Ltd, Funahashi-Cho, Tennouji-Ku Osaka 543-0024, Japan

Phone: +86-10-62797900
Fax: +86-10-62797900
Abstract

Continuous field observations of haze pollution were conducted in winter and summer during 2015 in Zibo, a highly industrialized city in the North China Plain that is adjacent to the Jing-Jin-Ji area. PM$_{2.5}$ concentration averaged 146.7 ± 85.8 and 82.2 ± 44.3 μg m$^{-3}$ in winter and summer, respectively. The chemical component contributions to PM$_{2.5}$ showed obvious seasonal variation. Organics were high in winter, but secondary inorganic aerosols (SIA) were high in summer. From non-haze to haze days, the concentration of SIA increased, implying an important role of secondary processes in the evolution process of the pollution. The diurnal behavior of several pollutants during haze days appeared to fluctuate more, but during non-haze days, it was much more stable, suggesting that complex mechanisms are involved. Specifically, gaseous precursors, mixed layer height (MLH), photochemical activity, and relative humidity (RH) also played important roles in the diurnal variation of the pollutants. Normally, larger gaseous precursor concentrations, photochemical activity, and RH, and lower MLH favored high concentrations. In winter, the formation of sulfate was mainly influenced by RH, indicating the importance of heterogeneous reactions in its formation. In contrast, in summer, photochemistry and SO$_2$ concentration had the largest impact on the sulfate level. We found that Zibo was an ammonia-rich city, especially in winter, meaning that the formation of nitrate was through homogeneous reactions between HNO$_3$ and NH$_3$ in the gas phase, followed by partitioning into the particle phase. The RH, NO$_2$, and “Excess NH$_4^+$” were the main influencing factors for nitrate in winter, whereas “Excess NH$_4^+$”, RH, and temperature were the key factors in summer. The secondary organic carbon (SOC) level depended on the MLH and photochemistry. In winter, the effect of the MLH was stronger than that of photochemistry, but a reversed situation occurred in summer because of the intensive photochemistry. Our work suggested that the inter-transport between Zibo, one of the most polluted cities in north China, and its adjacent areas should be taken into
account when formulating air pollution control policy.

Keywords: haze days; secondary inorganic aerosol; mixed layer height; regional air transport
1. Introduction

Airborne particles have adverse impacts on human health (Fang et al., 2016), lead to reductions of visibility (Zhao et al., 2011), and play a role in global climate (Woo et al., 2008), and this is especially so for PM$_{2.5}$, particles with an aerodynamic diameter smaller than 2.5 μm (Janssen et al., 2011). Particle pollution is caused by a wide variety of anthropogenic emissions, such as those from coal combustion, vehicles, and chemical (and other) industries, and it has become a major environmental issue in recent years. To address this problem better, more complete knowledge about the particle sources, chemical characteristics, and formation processes is necessary. To present, many scholars have carried out research on PM$_{2.5}$ pollution in China from various aspects. For example, Hu et al. (2012) investigated the features and sources of carbonaceous matter at Back Garden, a rural site 50 km northwest of Guangzhou, using a semi-continuous thermal-optical carbon analyzer. Andersson et al. (2015) characterized the combustion sources during the January 2013 haze events over eastern China using dual carbon isotope constrained source apportionment methods for the North China Plain (NCP), Yangtze River Delta (YRD) and Pearl River Delta (PRD). He et al. (2014) proposed that mineral dust and NO$_x$ contribute to the transformation of SO$_2$ to sulfate during polluted days based on smog chamber results. Han et al. (2014) adopted the Regional Atmospheric Modeling System–Community Multiscale Air Quality (RAMS-CMAQ) modeling system), coupled with an aerosol optical property scheme, to simulate the meteorological conditions, main particle composition, and visibility over the NCP in 2011. However, despite the large number of studies that have been done in China, particle pollution control in China and many other countries remains a huge challenge because of the complexity in sources (Sun et al., 2014), compositions (Zhang et al., 2012), processes (Tao et al., 2014) and influencing factors (Kadiyala and Kumar, 2012).

The NCP is one of the most developed and most polluted regions in the world (van Donkelaar et
al., 2010), and much research has already been done to investigate the air pollution there. Sun et al. (2016) characterized the evolution of haze formation on the NCP and investigated the associated stagnant meteorological conditions, including temperature inversions, low wind speed, and high relative humidity. Xu et al. (2011) carried out an observation on gaseous pollutants and meteorological parameters in Wuqing, located between Beijing and Tianjin in the NCP, from July 9, 2009, to January 21, 2010. Furthermore, according to modeling results, the summer high pressure systems make the East China Plain a “basin” of ozone pollution (Zhao et al., 2009). The Paris Agreement, which was signed on April 4, 2016, has drawn more attention to the problem of climate change worldwide. China faces a serious challenge of air pollution control, especially in the NCP, thus a wide range of research on haze pollution in the NCP area is needed.

In this work, we conducted a field investigation from January 15–25 and from July 14–31, 2015, in Zibo, a heavy industry city in Shandong Province near the Jing-Jin-Ji area, the most polluted area in China. A typical winter and summer month were studied together to obtain an improved understanding of the characteristics of the PM$_{2.5}$ pollution. First, time series of pollutants, meteorological parameters, and chemical compositions are presented to provide a primary summary of the pollution condition in the two seasons. Then, we examine the diurnal variation of various parameters, including particles, species, and meteorological factors to understand the possible links and causes of the diurnal patterns. Furthermore, an analysis of the main particle constituents is undertaken to provide a deeper knowledge of the formation mechanisms and main influencing factors, which should facilitate the implementation of appropriate actions to optimize the air quality effectively. Finally, we analyze the causes of the air pollution from a regional perspective. In summary, this paper aims to characterize (1) the chemical composition of PM$_{2.5}$ in Zibo in both winter and summer; (2) the diurnal behavior of different pollutants; (3) the formation processes of sulfate, nitrate, and organic matter (OM); and (4) the regional contribution
to the particle pollution in Zibo.

Figure 1. Location of Zibo (green area) within Shandong Province (red area), China.

2. Methodology

A comprehensive field observation of atmospheric PM$_{2.5}$ was carried out in Zibo during typical winter and summer periods, i.e., from 15 to 25 January 2015 and from 14 to 31 July 2015. The instruments were set up on the roof of a building on the campus of the Shandong University of Technology in Zibo, Shandong province. The inlets of the PM$_{2.5}$ devices were at about 20 m above ground level. The continuous monitoring of the hourly concentration of PM$_{2.5}$ of its main chemical species and of the meteorological parameters formed the foundation for this study. Specifically, a dichotomous monitor (PM-712; Kimoto Electric, Ltd., Japan) was employed to measure the concentration of PM$_{2.5}$ at a flow rate of 16.7 L min$^{-1}$; a more detailed description of this instrument has been given in previous work (Duan et al., 2016). Water-soluble inorganic ions (SO$_4^{2-}$, NO$_3^-$), were monitored simultaneously by deploying a dichotomous aerosol chemical
speciation analyzer (Model ACSA-08; Kimoto Electric, Ltd., Japan). The carbonaceous species OC (organic carbon) and EC (elemental carbon) were obtained by an ACP-710 instrument, which makes use of optical measurements at different wavelengths to derive hourly OC and EC, as introduced in a patent of Kimoto Electric, Ltd, Japan (application number: 2015-039568, Japan Patent Office, https://www.j-platpat.inpit.go.jp/web/all/top/BTmTopPage). In this study, OM was estimated as 1.6 times OC whereby the choice of the multiplication factor is based on a previous study in China (Cao et al., 2007). Note that the original hourly ammonium concentration was derived from assuming that ammonium is essentially present as (NH₄)₂SO₄ and NH₄NO₃ (Yang et al., 2007); however, the final hourly ammonium was corrected with the off-line data which made it more reliable. Hourly averaged concentrations of gaseous pollutants, such as NOₓ, SO₂, CO and O₃, were obtained using a MCSAM-13 system (Kimoto Electric, Ltd., Japan). Hourly average values of meteorological parameters, including WS (wind speed), WD (wind direction), pressure, temperature and relative humidity, were also obtained.

In addition to the above monitoring work, we carried out off-line analyses for different anionic and cationic species in samples collected daily with quartz fiber filters from 1/15 to 1/25 and from 7/14 to 7/31 in 2015. The ionic species included SO₄²⁻, NO₃⁻, NH₄⁺ (with their sum representing SIA), Cl⁻, Na⁺, K⁺, Mg²⁺, and Ca²⁺. The analyses for these ions were made by ion chromatography (IC); more details on these analyses were given in our previous work (Duan et al., 2016).

3. Results and discussion

3.1 General characteristics

Figure 2 shows a comparison of the time series of PM₂.₅, chemical species, gaseous pollutants, and the main meteorological parameters in winter (1/15 0:00 to 1/24 23:00, 2015) and summer.
(7/14 0:00 to 7/31 23:00, 2015). On average, the pollution in winter was substantially worse than that in summer, as reflected by the higher concentration of PM$_{2.5}$ and its species. In winter, the hourly PM$_{2.5}$ concentration varied from 34.5 to 358.0 μg m$^{-3}$, with an average of 146.7 μg m$^{-3}$. In contrast, in summer, PM$_{2.5}$ ranged from 9.6 to 222.6 μg m$^{-3}$, with an average of 82.2 μg m$^{-3}$. Additionally, the concentrations of the primary gas pollutants, including SO$_2$, NO$_2$, and CO, were characterized by higher values in winter. As listed in Table 1, the mean concentrations of SO$_2$, NO$_2$, and CO were 137.0 ± 78.6 μg m$^{-3}$, 74.9 ± 33.1 μg m$^{-3}$, and 1.9 ± 1.1 mg m$^{-3}$ in winter and 93.4 ± 67.9 μg m$^{-3}$, 60.9 ± 32.4 μg m$^{-3}$, and 1.3 ± 0.7 mg m$^{-3}$ in summer, respectively. The increase of SO$_2$, NO$_2$, and CO from summer to winter was by a factor of 1.47, 1.23, and 1.51, respectively, and was caused mainly by the enhancement of primary emissions (e.g., urban heating) and the more stable atmospheric conditions in winter (Quan et al., 2015). The different enhancement of these gases, characterized by higher increase for SO$_2$ and CO than for NO$_2$, suggests a prevalence of coal combustion compared with vehicle emissions; note that SO$_2$ and NO$_2$ are typically emitted by both combustion sources but that CO originates mainly from coal combustion. Ozone (O$_3$), which is a product of photochemistry, exhibited a much higher concentration in summer (90.0 ± 74.8 μg m$^{-3}$) than in winter (18.1 ± 20.3 μg m$^{-3}$), indicating the much more active photochemistry in the hot season. Similar results were obtained by Huang et al. (2016). With regard to the summer/winter difference of the main meteorological parameters, relative humidity (RH) was higher in summer (61.8 ± 15.9%) than in winter (45.3 ± 20.1%), atmospheric pressure was higher in winter (1018.1 ± 4.2 hPa) than in summer (997.2 ± 2.0 hPa), and temperature in winter (3.8 ± 3.3 °C) was obviously lower than temperature in summer (29.1 ± 3.8 °C). The lower temperature and higher pressure in winter together create a stable atmosphere, which favors particle formation in the cold season (Liu et al., 2016). In winter, RH was not as high as in summer, but the increase of RH in winter from non-haze days (28.3 ± 7.1%) to haze days (55.7 ± 17.2%) was by nearly a
factor of two, indicating the important role of RH in the evolution of haze pollution in winter (Sun et al., 2013a). Furthermore, the wind speed (WS) was quite low in both summer and winter, with an average value of $1.3 \pm 0.7$ and $1.3 \pm 0.7$ m s$^{-1}$, respectively. This does not favor the dilution of pollutants but instead worsens the pollution (Xu et al., 2011). To elucidate the characteristics of the chemical species and the relevant formation mechanisms better, we identified the following series of events: H1 (1/15 3:00–1/16 17:00), H2 (1/22 21:00–1/24 23:00), N1 (1/16 19:00–1/19 3:00), and N2 (1/19 13:00–1/20 19:00) in winter, and H3 (7/20 13:00–7/27 12:00), N3 (7/14 2:00–7/15 18:00), and N4 (7/27 14:00–7/31 23:00) in summer, in which H means haze episodes and N means non-haze episodes, respectively.

**Figure 2.** Time series of PM$_{2.5}$, chemical species, gaseous pollutants, temperature and RH, and WS (color indicates wind direction: 0 means north and 90 means east) in Zibo from 1/15 0:00 to 1/24 23:00 (winter) and from 7/14 0:00 to 7/31 23:00 (summer), 2015. The solid long vertical
line locates the break between winter and summer. H1 means Haze 1, N1 means Non-Haze 1, and so forth.

Aside from the main species shown in Figure 2, additional details about different pollution levels are listed in Table 1. The main constituents of the PM$_{2.5}$ are secondary inorganic aerosols (SIA) and OM, which account for 44.5% and 24.9% of the PM$_{2.5}$ in winter and 43.2% and 15.0% in summer, respectively. These values are comparable with the findings in Jinan (Yang et al., 2012). From non-haze to haze, the concentrations of sulfate, nitrate, ammonia, and OM are enriched by factors of 3.5, 3.1, 3.8, and 2.2 in winter and 2.1, 7.3, 2.7, and 1.2 in summer. The significant increase of SIA species demonstrates its non-negligible role in the evolution of the air pollution.

A large enrichment of SIA on haze days was also found in Beijing by Sun et al. (2013c). The enhanced formation of the secondary species is further illustrated by the increasing values of sulfate oxidation rate (SOR) and nitrate oxidation rate (NOR) from non-haze to haze, because these values represent the secondary transition rates from the gaseous precursors to their corresponding particle-phase products (Huang et al., 2016). The calculation for these follows:

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

In addition, the meteorology contributed to the worsening of the pollution. Lower WS and higher RH can be identified in haze events in both seasons (Deng et al., 2016; Zhou et al., 2014). Generally, wind exerts a scavenging effect on pollutants when it has high speed, but low-speed wind does not have a cleaning effect and so favors the accumulation of pollutants, thus facilitating secondary transitions (Wu et al., 2016). RH influences the generation and growth of particles in various ways. First, higher RH benefits the hygroscopic behaviors of SIA, especially for sulfate, thus it can encourage cloud condensation nuclei in the air, which then evolve into particles (Qu et al., 2015). Second, high RH can favor the entering of some semi-volatile or volatile species, such as thermal-instable nitrate and various secondary organic carbon (SOC), into the particle
phase (Liu et al., 2015). Third, SIA species on pre-existing particles can absorb more water content under high RH in the atmosphere, enlarging the volume and surface of the particles, which provides more sites for heterogeneous reactions (Orozco et al., 2016). Overall, the effect of high RH can be very important, which necessitates its further discussion below.

Table 1. Mean value ± standard deviation for various parameters under corresponding conditions (the unit of pollutant concentration is μg m$^{-3}$).

<table>
<thead>
<tr>
<th></th>
<th>Winter</th>
<th></th>
<th>Summer</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Haze</td>
<td>N-Haze</td>
<td>Ave</td>
<td>Haze</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>223.2±75.1</td>
<td>83.2±28.2</td>
<td>146.7±85.8</td>
<td>107.6±36.0</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>33.7±10.8</td>
<td>10.7±6.2</td>
<td>23.2±14.3</td>
<td>11.7±11.6</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>38.6±20.9</td>
<td>11.0±5.5</td>
<td>24.7±19.6</td>
<td>30.2±11.4</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>27.2±10.3</td>
<td>7.3±3.5</td>
<td>17.4±11.9</td>
<td>10.7±5.0</td>
</tr>
<tr>
<td>OM$^1$</td>
<td>52.6±24.7</td>
<td>23.7±8.7</td>
<td>36.6±22.4</td>
<td>12.6±3.0</td>
</tr>
<tr>
<td>EC$^1$</td>
<td>10.3±7.0</td>
<td>5.3±3.5</td>
<td>7.6±6.0</td>
<td>4.4±3.1</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>89.4±36.7</td>
<td>62.6±22.2</td>
<td>74.9±33.1</td>
<td>70.6±34.7</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>169.3±80.3</td>
<td>115.8±55.5</td>
<td>137.0±78.6</td>
<td>129.0±82.0</td>
</tr>
<tr>
<td>O$_3$</td>
<td>14.7±21.2</td>
<td>24.6±21.7</td>
<td>18.1±20.3</td>
<td>97.6±88.8</td>
</tr>
<tr>
<td>CO$^1$</td>
<td>2.6±1.0</td>
<td>1.3±0.6</td>
<td>1.9±1.1</td>
<td>1.5±0.6</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>2.1±0.6</td>
<td>2.1±0.6</td>
<td>1.9±0.6</td>
<td>1.3±0.2</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.3±0.2</td>
<td>0.2±0.2</td>
<td>0.2±0.2</td>
<td>0.6±0.1</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.8±0.2</td>
<td>0.9±0.2</td>
<td>0.8±0.2</td>
<td>1.2±0.19</td>
</tr>
<tr>
<td>K$^+$</td>
<td>3.1±0.8</td>
<td>1.9±0.5</td>
<td>2.4±0.9</td>
<td>1.8±0.2</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>9.6±2.5</td>
<td>6.2±1.6</td>
<td>7.6±2.7</td>
<td>2.2±1.1</td>
</tr>
<tr>
<td>SOR</td>
<td>0.15±0.10</td>
<td>0.06±0.03</td>
<td>0.11±0.08</td>
<td>0.17±0.09</td>
</tr>
<tr>
<td>NOR</td>
<td>0.22±0.08</td>
<td>0.11±0.06</td>
<td>0.17±0.09</td>
<td>0.11±0.08</td>
</tr>
<tr>
<td>RH (%)</td>
<td>55.7±17.2</td>
<td>28.3±7.1</td>
<td>45.3±20.1</td>
<td>63.5±13.2</td>
</tr>
<tr>
<td>WS (m s$^{-1}$)</td>
<td>1.2±0.7</td>
<td>1.6±0.8</td>
<td>1.3±0.7</td>
<td>1.0±0.5</td>
</tr>
<tr>
<td>P (hpa)</td>
<td>1016.8±3.3</td>
<td>1018.7±5.5</td>
<td>1018.1±4.2</td>
<td>996.9±1.8</td>
</tr>
</tbody>
</table>

Note 1. The unit for carbonaceous matter (i.e., OM and EC) is μg C m$^{-3}$ and the unit for CO is mg m$^{-3}$. 


The compositions of PM$_{2.5}$ in winter and summer are shown in Figure 3. Chemical species ratios varied from season to season and from non-haze to haze. Seasonally, OM accounted for most of the PM$_{2.5}$ in winter, whereas sulfate dominated the PM$_{2.5}$ in summer. This difference was also found by Sun et al. (2015). The lower contribution of OM to particles during warm days may be caused by the volatility of some semi-volatile organic constituents (Cousins et al., 1999), such as polycyclic aromatic hydrocarbons (PAH) (Bocchi et al., 2016). The higher ratio of sulfate in summer is attributable to the intense photochemistry, high temperature, and RH in this season. Different from nitrate, sulfate is a thermal-stable species, thus high temperature favors its photochemical reactions (Zhang et al., 2008). In addition, sulfate can more easily serve as cloud condensation nuclei (CCN) under high RH, which contributes to the increased sulfate in particles (Andreae and Rosenfeld, 2008). Under the cumulative effect of the favorable conditions, the larger enrichment of sulfate in summer can be understood.

Differences from non-haze to haze were also noticeable within each season. In summer (Figure 3 (b)), nitrate increased significantly from non-haze days (4.4%) to haze days (15.3%), indicating the important role of nitrate in the evolution of pollution. The approximately three-times increase may be caused by the higher concentration of ammonium, higher RH, more intensive photochemical reactivity (high O$_3$), and higher concentration of NO$_2$ (Chang et al., 2009; Lin and Cheng, 2007). A detailed discussion of its formation mechanisms is provided later. Furthermore, other SIA species (sulfate and ammonium) also increased, while OM decreased correspondingly, from non-haze to haze in both summer and winter, suggesting that enhanced secondary inorganic species play a vital role in haze events (Huang et al., 2014). These results are similar to those of Gao et al. (2015). On average, SIA species dominated particles with a 60.6% portion in summer and a 53.4% portion in winter; OM accounted for 22.7% and 29.9% correspondingly. A similar higher percentage of sulfate–nitrate–ammonium (SNA) in summer and higher portion of OM in
winter was also found by Sun et al. (2015).

**Figure 3.** Chemical composition of PM$_{2.5}$ in (a) winter and (b) summer. The text above each pie indicates the specific period. For example, W Non-Haze means the selected non-haze period in winter, W Haze means the haze period in winter, and W-ave denotes the average in winter. The analogous practice is used in the summer (b) column. MI is the abbreviation for metal ions, including K$^+$, Ca$^{2+}$, Na$^+$, and Mg$^{2+}$. The white-boxed value in the center of each pie denotes the concentration of PM$_{2.5}$ in the corresponding period.

### 3.2 Diurnal variation

The discussion above described the general pollution characteristics in the hot and cold seasons. In this section, we focus on the diurnal behaviors of various parameters to understand the characteristics of the pollution better.

Figure 4 shows the diurnal patterns of various factors in winter and summer. Generally, PM$_{2.5}$
peaked in the late night (about 23:00) and the early morning (about 9:00) and reached its lowest value around 16:00. This variation trend is similar to the trend of atmospheric pressure, which also showed higher value and lower level at the corresponding moments, indicating that the atmospheric dilution condition may have vital role in the formation of particles. A similar diurnal trend was investigated in Nanjing (Wang et al., 2016b).

Generally, the diurnal changes of SIA species were very similar, especially in winter, and were characterized by higher values at night and lower values during the daytime. In winter, SNA in haze events underwent frequent fluctuations, indicating the more complicated mechanisms involved in their formation. The high average levels of sulfate and nitrate in winter were related to the higher concentrations of their precursors (SO$_2$ and NO$_2$), higher RH, lower WS, and lower mixed layer height (MLH) at night. In contrast, the lower level of SIA during the daytime may be attributed to the higher MLH, which favored the dilution of pollutants, as indicated by the decrease of CO from 10:00 to 17:00. CO is an inactive primary gas pollutant in the atmosphere. Thus, assuming that the sources of the main pollutants were relatively unchanged within one month, the variation of CO can be used to signify physical processes such as dilution and precipitation (Zhang et al., 2015). Specifically, some unique peaks of sulfate and nitrate emerged at around 11:00 and 16:00 in haze events, respectively. These peaks were caused by a higher transition rate, as supported by the corresponding peaks of SOR and NOR. The faster secondary process at 11:00 was a synergetic effect of photochemistry and heterogeneous reactions, because both the values of O$_3$ and RH exhibited high levels. The peak that occurred at around 16:00 was mainly contributed by photochemistry, as indicated by the highest level of O$_3$, and the higher temperature in the afternoon further assisted the gaseous reactions (Han et al., 2016). In summer, SNA also showed higher concentration at night, but lower concentration on average during the daytime. In summer haze event, SIA shared a peak value at around 8:00, corresponding to the
simultaneous higher concentrations of SO$_2$ and NO$_2$. Meanwhile, the value of CO decreased only slightly, meaning that the increased concentration of gaseous precursors was not caused by a physical process but rather by enhanced emission. Considering that 8:00 is the start time for most industries and also a morning rush hour, the quick increase of SO$_2$ and NO$_2$ is understandable. Different from sulfate which peaked at 14:00, nitrate decreased continuously from 8:00 to 18:00. In summer, the photochemistry was quite intensive, as indicated by the extremely high level of O$_3$ during the daytime, which favored the formation of sulfate from SO$_2$ through the gaseous reaction. This positive effect overwhelmed the dilution effect of higher MLH. However, for nitrate, the dilution effect and the higher temperature in the afternoon together exerted a decisive influence. Compared with sulfate, nitrate is more vulnerable to MLH (Quan et al., 2014). In addition, nitrate (mainly NH$_4$NO$_3$), is a thermal-instable species that more easily enters the gas phase under high temperature (Bai et al., 1995). This negative effect caused by temperature was different from the case in winter. A common feature shared by SIA in both winter and summer was a relatively stable and low value in non-haze period, which was especially apparent in summer. The totally different diurnal behaviors of SIA under different pollution conditions further demonstrates their roles in haze events.

Carbonaceous species including OM and EC had distinct diurnal patterns. In winter, they were high at night but low during the daytime, which was similar in general to SIA. The same variations of species were also investigated by Sun et al. (2013b). The high values of OM and EC were caused mainly by the stable meteorological condition at night. Compared with OM, EC presented a more significant diurnal variation characterized by quick increase or decrease. EC is a main primary pollutant (Hou et al., 2011); hence, its variation is more sensitive to physical changes within a day. The portion of OM formed by secondary reaction is called secondary organic aerosol (SOA), and the primary constituents of OM are known as primary organic aerosol
Figure 4. Diurnal pattern of PM$_{2.5}$, chemical species, gaseous pollutants, and meteorological parameters in (a) winter and (b) summer. In each figure, the solid square means the average level of each parameter in the corresponding season, the hollow upper triangle refers to the variation of the corresponding value in haze event, and the lower triangle denotes the fluctuations in non-
haze event. Note that the abridged initial values of the Y-axis are 0; otherwise, the specific initial
value is given.

(POA) (Hu et al., 2012). SOA can form through photochemistry in the gas phase and also by a
heterogeneous process in the particle phase (Chapleski et al., 2016). Thus, during the daytime,
the positive effect of photochemistry can compensate the negative effect of dilution. This
possibility can be further proved by the small peak at around 13:00, when the photochemistry
was the most active.

Based on these results, we found typical meteorological conditions that favored increase of
pollutants, which are lower WS, higher RH, and lower MLH. This result is consistent with
previous studies (Tan et al., 2009). Moreover, similarities and differences in diurnal behaviors
among various species were also investigated, which demonstrated the different formation
processes of species. The distinct formation mechanisms of sulfate, nitrate, and OC (OM) in
different seasons are discussed further below.

3.3 Sulfate

Sulfate can form from SO$_2$ through either a homogeneous process (i.e., oxidized by hydroxyl
radical) or a heterogeneous reaction (i.e., oxidized by dissolved oxidants such as H$_2$O$_2$, O$_3$,
usually accompanied by metal catalysts) (Harris et al., 2013; Khoder, 2002). As mentioned above,
the concentration of sulfate is influenced by many factors, including RH, photochemical activity,
and others, which demonstrates its complex formation mechanisms. Understanding these
complex processes is necessary to take appropriate actions to reduce sulfate, and thus PM$_{2.5}$,
because sulfate accounts for the main part of particles, especially in haze event.

Figure 5 shows the correlation between sulfate and EC. EC is adopted here to exclude the effect
of dilution (Lin et al., 2009). The correlation variations between these can present the contribution
of secondary processes on sulfate formation despite any physical impact. The lines in each figure are linear regressions under the corresponding condition, denoted by the legend, in which $S$ means the slope for the corresponding line, that is the ratio of $SO_4^{2-}/EC$. In winter (Figure 5 (a)), with the increasing of the RH and $O_3$, the ratio of $SO_4^{2-}/EC$ increased, indicating that the heterogeneous process and photochemical reaction both favored the secondary formation of the sulfate in the cold season. Meanwhile, the irregular size variation (i.e., SO$_2$ concentration) indicated that the sources of SO$_2$ were more complicated than those of EC. The complex sources of SO$_2$ may be attributed to a combination of various local industrial activities, stable meteorological conditions, and regional transport. Additionally, we found that when the pollution condition became worse, as reflected by higher EC and sulfate (areas marked with (1), (2), and (3)), RH increased and $O_3$ decreased compared with clean period (as shown in area marked by (4)). Especially, the sulfate in area (2) peaked while EC, $O_3$, and SO$_2$ concentration did not attain a particular high level, meaning that RH has the most decisive effect on the formation of sulfate compared with photochemistry and the emission of precursors in winter.
Figure 5. Correlations between sulfate and EC in (a) winter and (b) summer. Note that the first list in (a) and (b) is colored by RH, but the second list in each is colored by O$_3$. In addition, the size of each symbol is scaled by the concentration of SO$_2$, i.e., the large the size, the higher the SO$_2$ concentration. The slope (S) and correlation coefficient ($R^2$) are given in the legend. The dashed lines divide the points distribution into four sections, as marked in the first figure by (1), (2), (3), and (4); the other three obey the same area ordering convention.

In summer, different results occurred. As shown in Figure 5(b), an unexpected phenomenon emerged: the sulfate-to-EC ratio decreased with increase of RH. This trend is a reverse trend compared with the result in winter. Zibo is within the zone of continental monsoon climate, which means that it is rainy in summer. Thus, with the scavenging effect of rainfall, the concentration of sulfate decreased more significantly than the primary pollutants EC. This may be the reason for the negative relationship between SO$_4^{2-}$/EC and RH. In addition, RH was always at a high level in summer, averaging 61.8 ± 15.9% (Figure 2; Table 1), thus the atmosphere was always humid enough for the heterogeneous process, which may not be the key cause for the haze pollution in summer. By contrast, with the increasing of O$_3$, sulfate rose more rapidly. In the second panel in row (b), the highest level of sulfate is located in areas (1) and (2). Area (1) is characterized by the highest level of O$_3$ and lower SO$_2$, whereas area (2) is characterized by lower concentration of O$_3$ but higher SO$_2$. They had nearly an opposite condition but shared a similar sulfate level. These features indicate that both the emission of gas precursors and photochemistry had vital impacts on the formation of sulfate in summer. Moreover, the general variation of SO$_2$ concentration fits the increase of EC better than it does in winter, indicating a lower number of various sources of SO$_2$ in summer. In summary, the formation of the sulfate in summer was highly vulnerable to the concentration of gaseous precursors and photochemistry.
3.4 Nitrate

Nitrate comes mainly from homogeneous reactions between NH$_3$ and HNO$_3$ in the gas phase, followed by gas-particle partitioning, or heterogeneous channels through the hydrolysis of N$_2$O$_5$ (Bertram et al., 2009; Russell et al., 1986). In an ammonia-rich area, the favorable formation mechanism of nitrate is homogeneous reactions, but in an ammonia-poor area, nitrate tends to be formed via the hydrolysis of N$_2$O$_5$ (Huang et al., 2011). Hence, whether Zibo is an ammonia-rich or an ammonia-poor zone needs to be discussed firstly. Figure 6 shows a plot of the NO$_3^-$ concentration as function of Excess NH$_4^+$. The “Excess NH$_4^+$” here is defined as the amount of ammonium beyond that needed for $[\text{NH}_4^+]/[\text{SO}_4^{2-}] = 1.5$ (i.e., $[\text{Excess NH}_4^+] = [\text{NH}_4^+] - 1.5[\text{SO}_4^{2-}]$; note that the calculation is under the unit of nmol m$^{-3}$). If “Excess NH$_4^+$” is a positive number, the area can be regarded as ammonium-rich; otherwise, it is ammonium-poor (Pathak et al., 2009). Based on this standard, Zibo is an ammonium-rich city in winter. With increasing “Excess NH$_4^+$”, nitrate rose significantly. Some negative values of “Excess NH$_4^+$” occurred in summer, which may have been caused by the high temperature, as indicated by the larger size of the symbols in the ammonium-poor area in Figure 6 (b). This correlation is similar to a previous finding in Guangzhou (Huang et al., 2011). In the ammonium-poor zone (Figure 6(b)), the concentration of nitrate is extremely low, nearly approaching zero. However, in the ammonium-rich ozone, similar to the trend in winter, nitrate increased significantly with increasing “Excess NH$_4^+$”. These results demonstrate that the formation of nitrate was mainly through the homogeneous reaction between NH$_3$ and HNO$_3$ in the gas phase, with subsequent partitioning into the particle phase. In addition, an opposite trend between nitrate and ozone was observed, especially in summer, as indicated by the colored symbols. Hydrolysis of N$_2$O$_5$ (the production of O$_3$ and NO$_2$) occurs mainly at night, thus the lower concentration of O$_3$ may be a result of its contribution to N$_2$O$_5$, that is, HNO$_3$ at night (Pathak et al., 2011b). In winter, a temperature
dependence of nitrate was not obvious. However, in summer, low nitrate appeared to cluster more frequently at high temperature, meaning that temperature was more influential on particle-phase nitrate in summer than in winter. This result is reasonable considering the thermal instability of NH$_4$NO$_3$. A similar temperature dependency of nitrate was also investigated by Hu et al. (2011).

![Figure 6](image_url)

**Figure 6.** Concentration of nitrate versus “Excess NH$_4^+$” in (a) winter and (b) summer. Each plot is colored by the concentration of O$_3$, and scaled by the temperature. The dashed line divides the “A Rich” and “A Poor” areas. A refers to ammonium in (b).

Based on above discussion, we realized that the primary formation mechanism of nitrate was the homogeneous reactions in gas phase between NH$_3$ and HNO$_3$, followed by gas-particle partitioning. Many factors can influence this process, including temperature, RH, and precursor emissions (Lyu et al., 2016). Probing the interrelationships between the influencing factors and nitrate further can facilitate the taking of actions to reduce its formation.

Figure 7 presents the correlations between nitrate and NO$_2$ in the two seasons. Generally, nitrate increased with the increase of gas precursors. In winter (Figure 7 (a)), we divided the variation of nitrate into three periods (1–3). In zone 1, NO$_2$ concentration is low, and nitrate formation is
correspondingly at a low level. During this period, the formation of nitrate was less related to RH or temperature, but limited to its gas precursors. In zone 2, the increase of nitrate along with NO$_2$ is most significant, which may be facilitated by the high RH (a1), but it is less related with temperature (a2). With the continuous increase of NO$_2$, points fell into zone 3, which is characterized by an extremely high concentration of gas precursors but a moderate concentration of nitrate. This may be caused by the synergistic effect of relatively low RH (less than 60%) and low “Excess NH$_4^+$” (a2). The results above indicate that the main factors controlling nitrate formation in winter were gas precursor concentration, RH, and level of “Excess NH$_4^+$”. These influence of these factors on nitrate varied under different ranges of gas precursors. When NO$_2$ was low (<50 μg m$^{-3}$ in this study), both the RH and “Excess NH$_4^+$” had no obvious influence on the nitrate; when NO$_2$ was within the range 50–130 μg m$^{-3}$, nitrate was significantly impacted by RH. Although the formation of nitrate occurs mainly through homogeneous reactions in gas phase, RH favors nitrate partitioning into particles (Shi et al., 2014). Once the NO$_2$ surpassed a certain value, the increasing rate of nitrate versus NO$_2$ slow and was impacted by RH and “Excess NH$_4^+$”. Based on the investigations described above, control strategies for nitrate in winter should focus on reduction of gaseous precursor NO$_2$ (less than 50 μg m$^{-3}$ in this study) and emission of NH$_3$, because RH is far more difficult to reduce artificially.

In summer (Figure 7 (b)), the variation periods were divided into four parts, as shown. Basically, zones 1, 3, and 4 are characterized by lower concentration of nitrate no matter whether NO$_2$ was high or low, which may a result of the lower level of “Excess NH$_4^+$” and higher temperature. NH$_4$NO$_3$ is a thermal-unstable specie that can decompose easily and enter the gas phase under high temperature (Zhang et al., 2016), thus temperature has a more obvious influence on nitrate in summer than in winter (Heald et al., 2012). More specifically, nitrate in zones 1 and 4 has low concentration, which was caused by the unfavorable conditions, including the low gas precursors...
level, low “Excess NH$_4^+$”, high temperature, and low RH. In zone 3, gas precursors are higher, and

Figure 7. Correlation between NO$_3^-$ and NO$_2$ in (a) winter and (b) summer. In row (a), (a1) is colored by RH and scaled by the concentration of CO; (a2) is colored by temperature and scaled by “Excess NH$_4^+$”. In row (b), (b1) is colored by RH and scaled by the concentration of CO; (b2) is colored by temperature and scaled by “Excess NH$_4^+$”. Note that larger symbols denote higher value of its corresponding parameter.

RH slightly higher compared to zones 1 and 4. Still, nitrate is low, which may be explained by the low level of “Excess NH$_4^+$”, indicating that in summer, the effect of “Excess NH$_4^+$” on nitrate is more significant than the effect of RH. In contrast, zone 2 has the characteristic of the higher concentration of nitrate, and the points within this zone are generally accompanied by higher “Excess NH$_4^+$”, which offers sufficient reactants to form nitrate (Wen et al., 2015). Moreover, the
higher RH and lower temperature in this zone favor gas-particle partitioning after the homogeneous reactions (Trebs et al., 2004). The results described above demonstrate that the effects of “Excess NH₄⁺”, RH, and temperature on nitrate were significant in summer. Their relative importance was roughly in the order of “Excess NH₄⁺” > RH > temperature. Thus, for control of nitrate in summer, close attention should be paid to sources of NH₃. Generally, the gaseous NH₃ concentration was higher in summer, which was caused by the volatility of ammonia and the more active agriculture activity (Ianniello et al., 2010).

In addition, the sources of NO₂ were less complicated in winter than in summer. (a1) and (b1) are both scaled by CO concentration. In (a1), the fit between symbol size and X-axis is better than in (b1), which may be a result of the complicated photochemistry in summer, considering that NO₂ is more activated than CO in the photochemical circle (Jacob, 2000).

### 3.5 Carbonaceous species

Carbonaceous matter consists of EC and OC (OM), which have important roles in human health, climate change, and radiative forcing (Mauderly and Chow, 2008; Novakov and Penner, 1993). In Zibo, OC and EC concentrations were 22.8 and 7.6 μgC m⁻³ in winter and 7.7 and 3.6 μgC m⁻³ in summer, respectively. This result is comparable with finding of Zhao et al. (2013) in Beijing. Moreover, OM and EC accounted for 22.7 and 6.2% of the particles in summer and 29.9 and 6.2% in winter, demonstrating that these are main constituents, especially OM, thus a clearer understanding about its formation was necessary.

OC can be subdivided into two categories, POC from primary sources and SOC from the oxidation of volatile organic compounds (VOCs) (Pathak et al., 2011α). In this study, SOC was calculated using the EC-scaled method (i.e., [SOC] = [OC] – [EC] × [OC/EC]primary and [POC] = [OC] – [SOC]); the [OC/EC]primary in this study was the minimum value of the OC/EC in winter and summer, respectively (Strader et al., 1999; Wang et al., 2016a). We found that SOC accounted...
for 62% of the OC in winter and 68% in summer, indicating the dominant role of SOC in organic matter. This proportion was higher than that in Jinan (47.5%) (Yang et al., 2012) but lower than that at Mount Tai (73.4%) (Wang et al., 2012). The high SOC percentage in summer could be the result of the high photochemistry and high concentration of VOCs (Lin et al., 2009), whereas the similarly high value of SOC in winter may be a result of the synergistic effect of coal combustion, stable metrological condition, and low temperature (Cheng et al., 2014).

Figure 8 show us the diurnal variations of POC, SOC, and some relevant parameters. In winter (Figure 8(a)), the concentrations of SOC and POC appeared to be higher during the nighttime, but lower in the daytime, which is similar to the CO trend. These results demonstrate that the atmospheric dilution condition had the decisive influence on organic matter from both primary and secondary sources. In the daytime, the decrease of SOC was slower than that of POC, which might be attributable to a certain compensation effect from photochemistry, as indicated by the rising O$_3$. The main causes of the high concentration of organic matter in winter were enhanced emission and stable meteorological condition, thus the high MLH in the daytime can effectively lower the concentration of OC. In summer, the variation of POC was also similar to that of CO, but SOC appeared to have a nearly opposite trend with CO and was more likely to follow O$_3$. From 0:00 to 9:00, SOC and POC were comparable, but POC had increased more than SOC at 6:00. By combining with the increasing concentration of CO, we can further attribute the variation of POC to the atmospheric dilution condition, which is similar to the trend found in winter. After 9:00, with the increasing O$_3$ and decreasing CO, SOC rose significantly, while POC started to fall, and the differences between these became more and more obvious. We can infer that in summer, the positive effect on SOC from the photochemistry overwhelmed the negative impact caused by higher MLH. Another interesting phenomenon shown in Figure 8 is the weaker relation between RH and SOC. Generally, higher RH favor the condensation of semi-volatile
organic compounds (SVOCs), thus a positive correlation between RH and SOC should have been more obvious, especially in summer, but this did not emerge according to Figure 8. This may be attributed to the reversed trend between O\textsubscript{3} and RH, thus an indirect effect made RH less important for SOC. A similar increasing of SOC with O\textsubscript{3} was also found by Hu et al. (2012), and the seemingly opposite trend between RH and SOC was similar to the result of an investigation in Yucheng, another city in Shandong (Yao et al., 2016).

Overall, the concentration of organic matter was 1.97 times higher in winter for multiple reasons. From the sources perspective, coal combustion for heating contributes abundant pollutants (Wang et al., 2015a) and the time required for motor vehicle to cold start is prolonged because of the low temperature in winter, which favors the transfer of SVOCs to the particle phase (Chow et al., 1993). From the meteorological perspective, stable air motion and frequent thermal inversion facilitate the accumulation of contaminants and favor the condensation and absorption of VOCs (Wang et al., 2015a). SOC/OC was slightly higher in summer, the result of a nearly 4.11 times higher photochemical reactivity (if using O\textsubscript{3} concentration to estimate). However, the enhancement of SOC/OC in the hot season (68% in summer and 62% in winter) did not emerge as appreciably as the enhancement of photochemistry. This was caused by the accompanying higher temperature with high O\textsubscript{3} (as shown in Figure 3). High temperature favors the evaporation of VOCs and SVOCs, which exerts a negative impact on the formation of SOC in the particle phase (Lamorena and Lee, 2008). Nevertheless, the increasing of SOC in daytime during summer further emphasizes that photochemistry weighed heavily on its formation.
Figure 8. Diurnal variation of POC, SOC, CO (colored by RH), and O3 (gray area) in (a) winter and (b) summer.

3.6 Regional contributions

As mentioned above, Zibo is located in the NCP and is surrounded by highly industrialized cities, thus the regional transport of pollutants to Zibo cannot be overlooked. Figure 9(a) presents fire maps coupled with back trajectories in winter (1/15–1/25) and summer (1/14–1/31). The fire data were downloaded from https://firms.modaps.eosdis.nasa.gov/download/request.php, and the 24-hour trajectories and clusters were calculated using the TrajStat model (Wang et al., 2009). In winter, the directions of air mass motion differed significantly. Cluster 1 first passed through Jinan, where many coal industries are located (Baldasano et al., 2003), then the air mass turned back to Zibo. This motion of air brought a high concentration of PM$_{2.5}$ of 129.92 μg m$^{-3}$ to Zibo. OM and sulfate were the most abundant species during this period due to the enhanced pollutants emission, especially from coal combustion, which can be proved further by the high SO$_2$
concentration level of 152.54 μg m⁻³ under this condition. Cluster 2 came from Inner Mongolia and then passed over Hebei, Beijing, and Tianjin (abbreviated as BTH in the following discussion) successively. As demonstrated previously, BTH is a highly industrialized and heavily polluted region (Jiang et al., 2015; Wang et al., 2015b). Thus, the PM₂.₅ concentrations during this time were the second highest concentrations, with an average of 236.02 μg m⁻³, and were characterized by the most abundant SIA constituents. Along the transport of the air mass, particles aged progressively (Guo et al., 2014). In addition, this trajectory passed by Bohai, resulting in high RH (58.10%), which favored the formation of SIA species in winter, as discussed above. Cluster 3 brought Zibo the cleanest air, which came from acrid Mongolia and moved with the highest speed. The RH during this duration was the lowest because the air moved within inland areas. The high speed and direct motion of the air exerted a scavenging effect, cleaning the pollutants in Zibo. Cluster 4 came from northern Jiangsu, then passed over Linyi (a city in southeast Shandong Province) with moderate speed. Southern Shandong is a heavily industrialized region, where large power plants and some chemical industries are located (Cheng et al., 2011). Because of the complex sources, the species were both at high but relatively balanced levels. Cluster 5 appeared to be the most polluted one and had the highest particle concentration (265.70 μg m⁻³). It started from Bohai, then moved southwesterly. Southwest Shandong is a densely industrialized region and also a coastal area. Thus, the air mass of this cluster was very moist with plenty of pollutants; the enhanced primary emission can also be proved by the high concentration of EC. Cluster 6 had the characteristic of the highest RH but lower concentration of pollutants compared with cluster 5. The lower pollutants level may be caused by the wet precipitation when the air mass passed through Bohai. Nitrate was the most abundant species among SIA, a result of the petroleum industry in northern Shandong. According to the distribution of fire spots, open biomass burning was not significant in winter around Zibo.
Figure 9. (a) Back trajectories for each identified cluster in winter (left row) and summer (right row) (originated at 100 m agl height). The red circle with black border denotes the location of Zibo, and the red dots are fire spots (data were downloaded from NASA). (b) Concentration of PM$_{2.5}$, chemical species, and RH (gray area) under different clusters. In the labels of the abscissa, WN means Cluster N in winter (e.g., W1 denotes cluster 1 in winter), and SN means Cluster N in summer (e.g., S1 means cluster 1 in summer).

In summer, biomass burning was much more severe, demonstrating it as a main source. Cluster 1 came from Qingdao, a coastal city. During this period, OM was the most abundant species on particles, and it may have been contributed by the biomass burning along the trajectory. Similarly, cluster 5 started from the Yellow Sea and moved alongside cluster 1, thus these clusters shared...
similar concentrations of pollutants. In particular, the increasing nitrate in cluster 5 may be attributable to the reaction between HNO$_3$ and NaCl, a typical sea salt, through which NaNO$_3$ is generated and HCl is released (Ianniello et al., 2011). The apparently higher concentration of Cl$^-$ supports the contribution of a sea salt source. Cluster 2 originated from Linyi, as mentioned above, a highly industrialized city with a rich source of coal. Many airborne pollutants could be delivered to Zibo in this cluster, and high concentration of SIA could be the result of this regional transport. Especially, the high concentration of ammonia favored nitrate formation, hence the combination of regional transport and interrelation between secondary species may be the key reason for the high concentration of SIA. Clusters 3 and 4 moved forward with significantly higher speed, especially cluster 4. The faster-moving air mass, such as cluster 3 in winter, had a cleaning effect that brought Zibo the cleanest air. In addition, K$^+$ was the most abundant metal ion (35.3% for cluster 3 and 39.8% for cluster 4), which may be a contribution of biomass burning along the trajectory. Similarly, K$^+$ also accounted for the largest portion of metal ions in cluster 2 (37.4%). Clusters 6 and 3 came from a similar direction but with different speed. The air mass with slower speed (cluster 6) brought Zibo more pollutants. The most increased species in cluster 6 compared with cluster 3 was nitrate, which may have been a result of loss of nitrate with the moving air. Regional transport does not favor the accumulation of nitrate because of its volatility, thus local transport contributes more nitrate (Huffman et al., 2009; Yang et al., 2011). Generally, a longer trajectory was accompanied by a lower ratio of nitrate. A similar trend also occurred for clusters 3 and 4. Zibo is a city that both influences the condition of the air in the NCP and is influenced by the air in the NCP. Thus, joint prevention between cities is necessary and inevitable.
Author Information

Corresponding Authors

*Phone: +86-10-62797900; fax: +86-10-62797900;

E-mail: duanfk@tsinghua.edu.cn, hekb@tsinghua.edu.cn

Notes

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