



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

Continuous field observations of haze pollution were conducted in winter and summer during 15 2015 in Zibo, a highly industrialized city in the North China Plain that is adjacent to the Jing-Jin-16 Ji area. PM_{2.5} concentration averaged 146.7 \pm 85.8 and 82.2 \pm 44.3 µg m⁻³ in winter and summer, 17 respectively. The chemical component contributions to PM_{2.5} showed obvious seasonal variation. 18 Organics were high in winter, but secondary inorganic aerosols (SIA) were high in summer. From 19 20 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 21 22 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, 23 mixed layer height (MLH), photochemical activity, and relative humidity (RH) also played 24 important roles in the diurnal variation of the pollutants. Normally, larger gaseous precursor 25 concentrations, photochemical activity, and RH, and lower MLH favored high concentrations. In 26 27 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 SO₂ 28 29 concentration had the largest impact on the sulfate level. We found that Zibo was an ammoniarich city, especially in winter, meaning that the formation of nitrate was through homogeneous 30 reactions between HNO₃ and NH₃ in the gas phase, followed by partitioning into the particle 31 phase. The RH, NO₂, and "Excess NH₄⁺" were the main influencing factors for nitrate in winter, 32 33 whereas "Excess NH4⁺", RH, and temperature were the key factors in summer. The secondary 34 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 35 36 because of the intensive photochemistry. Our work suggested that the inter-transport between 37 Zibo, one of the most polluted cities in north China, and its adjacent areas should be taken into





- 38 account when formulating air pollution control policy.
- 39 Keywords: haze days; secondary inorganic aerosol; mixed layer height; regional air transport





40 1. Introduction

Airborne particles have adverse impacts on human health (Fang et al., 2016), lead to reductions 41 of visibility (Zhao et al., 2011), and play a role in global climate (Woo et al., 2008), and this is 42 43 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 44 45 from coal combustion, vehicles, and chemical (and other) industries, and it has become a major 46 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 47 present, many scholars have carried out research on PM2.5 pollution in China from various aspects. 48 For example, Hu et al. (2012) investigated the features and sources of carbonaceous matter at 49 Back Garden, a rural site 50 km northwest of Guangzhou, using a semi-continuous thermal-50 optical carbon analyzer. Andersson et al. (2015) characterized the combustion sources during the 51 52 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 53 River Delta (PRD). He et al. (2014) proposed that mineral dust and NO_x contribute to the 54 55 transformation of SO₂ to sulfate during polluted days based on smog chamber results. Han et al. (2014) adopted the Regional Atmospheric Modeling System-Community Multiscale Air Quality 56 (RAMS-CMAQ) modeling system), coupled with an aerosol optical property scheme, to 57 58 simulate the meteorological conditions, main particle composition, and visibility over the NCP 59 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 60 complexity in sources (Sun et al., 2014), compositions (Zhang et al., 2012), processes (Tao et al., 61 62 2014) and influencing factors (Kadiyala and Kumar, 2012).

63 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 64 al. (2016) characterized the evolution of haze formation on the NCP and investigated the 65 66 associated stagnant meteorological conditions, including temperature inversions, low wind speed, 67 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 68 69 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 70 71 Paris Agreement, which was signed on April 4, 2016, has drawn more attention to the problem of 72 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. 73

In this work, we conducted a field investigation from January 15–25 and from July 14–31, 2015, 74 in Zibo, a heavy industry city in Shandong Province near the Jing-Jin-Ji area, the most polluted 75 area in China. A typical winter and summer month were studied together to obtain an improved 76 77 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 78 79 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 80 possible links and causes of the diurnal patterns. Furthermore, an analysis of the main particle 81 82 constituents is undertaken to provide a deeper knowledge of the formation mechanisms and main 83 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 84 perspective. In summary, this paper aims to characterize (1) the chemical composition of PM_{2.5} 85 86 in Zibo in both winter and summer; (2) the diurnal behavior of different pollutants; (3) the 87 formation processes of sulfate, nitrate, and organic matter (OM); and (4) the regional contribution





to the particle pollution in Zibo.

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

92 2. Methodology

93 A comprehensive field observation of atmospheric PM_{2.5} was carried out in Zibo during typical 94 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 95 Technology in Zibo, Shandong province. The inlets of the PM_{2.5} devices were at about 20 m 96 97 above ground level. The continuous monitoring of the hourly concentration of PM2.5 of its main chemical species and of the meteorological parameters formed the foundation for this study. 98 99 Specifically, a dichotomous monitor (PM-712; Kimoto Electric, Ltd., Japan) was employed to 100 measure the concentration of PM_{2.5} at a flow rate of 16.7 L min⁻¹; a more detailed description of 101 this instrument has been given in previous work (Duan et al., 2016). Water-soluble inorganic ions (SO₄²⁻, NO₃⁻), were monitored simultaneously by deploying a dichotomous aerosol chemical 102





103 speciation analyzer (Model ACSA-08; Kimoto Electric, Ltd., Japan). The carbonaceous species 104 OC (organic carbon) and EC (elemental carbon) were obtained by an ACP-710 instrument, which 105 makes use of optical measurements at different wavelengths to derive hourly OC and EC, as 106 introduced in a patent of Kimoto Electric, Ltd, Japan (application number: 2015-039568, Japan 107 Patent Office, https://www.j-platpat.inpit.go.jp/web/all/top/BTmTopPage). In this study, OM was 108 estimated as 1.6 times OC whereby the choice of the multiplication factor is based on a previous 109 study in China (Cao et al., 2007). Note that the original hourly ammonium concentration was 110 derived from assuming that ammonium is essentially present as (NH₄)₂SO₄ and NH₄NO₃ (Yang 111 et al., 2007); however, the final hourly ammonium was corrected with the off-line data which 112 made it more reliable. Hourly averaged concentrations of gaseous pollutants, such as NO_x, SO₂, CO and O₃, were obtained using a MCSAM-13 system (Kimoto Electric, Ltd., Japan). Hourly 113 114 average values of meteorological parameters, including WS (wind speed), WD (wind direction), 115 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 SO_4^{2-} , NO_3^{-} , NH_4^+ (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).

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123 **3. Results and discussion**

124 **3.1 General characteristics**

Figure 2 shows a comparison of the time series of $PM_{2.5}$, chemical species, gaseous pollutants, and the main meteorological parameters in winter (1/15 0:00 to 1/24 23:00, 2015) and summer





127 (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 128 hourly PM_{2.5} concentration varied from 34.5 to 358.0 μ g m⁻³, with an average of 146.7 μ g m⁻³. In 129 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. 130 131 Additionally, the concentrations of the primary gas pollutants, including SO₂, NO₂, and CO, were characterized by higher values in winter. As listed in Table 1, the mean concentrations of SO_2 , 132 NO₂, and CO were 137.0 \pm 78.6 µg m⁻³, 74.9 \pm 33.1 µg m⁻³, and 1.9 \pm 1.1 mg m⁻³ in winter and 133 134 $93.4 \pm 67.9 \ \mu g \ m^{-3}$, $60.9 \pm 32.4 \ \mu g \ m^{-3}$, and $1.3 \pm 0.7 \ m g \ m^{-3}$ in summer, respectively. The increase 135 of SO₂, NO₂, 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 136 more stable atmospheric conditions in winter (Quan et al., 2015). The different enhancement of 137 these gases, characterized by higher increase for SO₂ and CO than for NO₂, suggests a prevalence 138 139 of coal combustion compared with vehicle emissions; note that SO₂ and NO₂ are typically emitted 140 by both combustion sources but that CO originates mainly from coal combustion. Ozone (O₃), 141 which is a product of photochemistry, exhibited a much higher concentration in summer (90.0 \pm 74.8 μ g m⁻³) than in winter (18.1 \pm 20.3 μ g m⁻³), indicating the much more active photochemistry 142 143 in the hot season. Similar results were obtained by Huang et al. (2016). With regard to the 144 summer/winter difference of the main meteorological parameters, relative humidity (RH) was higher in summer ($61.8 \pm 15.9\%$) than in winter ($45.3 \pm 20.1\%$), atmospheric pressure was higher 145 146 in winter (1018.1 \pm 4.2 hPa) than in summer (997.2 \pm 2.0 hPa), and temperature in winter (3.8 \pm 147 3.3 °C) was obviously lower than temperature in summer (29.1 \pm 3.8 °C). The lower temperature and higher pressure in winter together create a stable atmosphere, which favors particle formation 148 149 in the cold season (Liu et al., 2016). In winter, RH was not as high as in summer, but the increase 150 of RH in winter from non-haze days $(28.3 \pm 7.1\%)$ to haze days $(55.7 \pm 17.2\%)$ was by nearly a





151 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, 152 with an average value of 1.3 ± 0.7 and 1.3 ± 0.7 m s⁻¹, respectively. This does not favor the 153 154 dilution of pollutants but instead worsens the pollution (Xu et al., 2011). To elucidate the 155 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 $(1/22\ 21:00-1/24\ 23:00)$, 156 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 13:00–7/27 157 158 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 159 means haze episodes and N means non-haze episodes, respectively.



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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





- 164 line locates the break between winter and summer. H1 means Haze 1, N1 means Non-Haze 1,
- 165 and so forth.
- 166 Aside from the main species shown in Figure 2, additional details about different pollution levels 167 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 168 169 summer, respectively. These values are comparable with the findings in Jinan (Yang et al., 2012). 170 From non-haze to haze, the concentrations of sulfate, nitrate, ammonia, and OM are enriched by 171 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 172 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 173 enhanced formation of the secondary species is further illustrated by the increasing values of 174 175 sulfate oxidation rate (SOR) and nitrate oxidation rate (NOR) from non-haze to haze, because 176 these values represent the secondary transition rates from the gaseous precursors to their 177 corresponding particle-phase products (Huang et al., 2016). The calculation for these follows:

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$$NOR = \frac{n(NO_3^-)}{n(NO_2) + n(NO_3^-)} \qquad SOR = \frac{n(SO_4^{2-})}{n(SO_2) + n(SO_4^{2-})}$$

179 In addition, the meteorology contributed to the worsening of the pollution. Lower WS and higher 180 RH can be identified in haze events in both seasons (Deng et al., 2016; Zhou et al., 2014). 181 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 182 183 secondary transitions (Wu et al., 2016). RH influences the generation and growth of particles in 184 various ways. First, higher RH benefits the hygroscopic behaviors of SIA, especially for sulfate, 185 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, 186 187 such as thermal-instable nitrate and various secondary organic carbon (SOC), into the particle





- 188 phase (Liu et al., 2015). Third, SIA species on pre-existing particles can absorb more water
- 189 content under high RH in the atmosphere, enlarging the volume and surface of the particles,
- 190 which provides more sites for heterogeneous reactions (Orozco et al., 2016). Overall, the effect
- 191 of high RH can be very important, which necessitates its further discussion below.
- 192 Table 1. Mean value ± standard deviation for various parameters under corresponding conditions
- 193 (the unit of pollutant concentration is $\mu g m^{-3}$).

		Winter			Summer	
	Haze	N-Haze	Ave	Haze	N-Haze	Ave
PM _{2.5}	223.2±75.1	83.2±28.2	146.7±85.8	107.6±36.	46.4±17.0	82.2±44.3
NO ₃ -	33.7±10.8	10.7±6.2	23.2±14.3	11.7±11.6	1.6±1.8	7.1±9.3
SO4 ²⁻	38.6±20.9	11.0±5.5	24.7±19.6	30.2±11.4	14.2±6.2	21.2±12.0
$\mathrm{NH_4}^+$	27.2±10.3	7.3±3.5	17.4±11.9	10.7 ± 5.0	3.9±1.8	7.2±4.9
OM^1	52.6±24.7	23.7±8.7	36.6±22.4	12.6±3.0	10.6±6.2	12.3±5.4
EC^1	10.3±7.0	5.3±3.5	$7.6{\pm}6.0$	4.4±3.1	2.3±1.4	3.6±2.6
NO_2	89.4±36.7	62.6±22.2	74.9±33.1	70.6±34.7	39.5±19.9	60.9±32.4
SO_2	169.3±80.3	115.8±55.5	137.0±78.6	129.0±82.	74.5±41.0	93.4±67.9
O3	14.7±21.2	24.6±21.7	18.1±20.3	97.6±88.8	102.7±64.8	90.0±74.8
CO^1	2.6±1.0	1.3±0.6	1.9±1.1	1.5±0.6	$0.9{\pm}0.5$	1.3 ± 0.7
Na^+	2.1±0.6	2.1±0.6	1.9±0.6	1.3±0.2	$1.0{\pm}0.4$	1.2 ± 0.4
Mg^{2+}	0.3±0.2	0.2±0.2	0.2±0.2	0.6±0.1	0.5±0.2	0.6 ± 0.2
Ca^{2+}	0.8±0.2	0.9±0.2	0.8±0.2	1.2±0.19	1.0±0.3	$1.1{\pm}0.3$
\mathbf{K}^+	3.1±0.8	1.9±0.5	2.4±0.9	1.8±0.2	1.1±0.2	$1.4{\pm}0.4$
Cl ⁻	9.6±2.5	6.2±1.6	7.6±2.7	2.2±1.1	$0.7{\pm}0.5$	1.9±1.5
SOR	0.15±0.10	0.06 ± 0.03	0.11 ± 0.08	0.17 ± 0.09	0.13 ± 0.08	0.16±0.11
NOR	0.22 ± 0.08	0.11±0.06	0.17±0.09	0.11 ± 0.08	0.03 ± 0.04	0.07 ± 0.07
RH (%)	55.7±17.2	28.3±7.1	45.3±20.1	63.5±13.2	54.2±17.0	61.8±15.9
WS (m s ⁻¹)	1.2±0.7	1.6±0.8	1.3±0.7	1.0±0.5	1.5±0.7	1.3±0.7
P (hpa)	1016.8±3.3	1018.7±5.5	1018.1±4.2	996.9±1.8	996.3±1.6	997.2±2.0

194 Note 1. The unit for carbonaceous matter (i.e., OM and EC) is µgC m⁻³ and the unit for CO is mg

195 m⁻³.





196 The compositions of PM_{2.5} in winter and summer are shown in Figure 3. Chemical species ratios 197 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 198 199 found by Sun et al. (2015). The lower contribution of OM to particles during warm days may be 200 caused by the volatility of some semi-volatile organic constituents (Cousins et al., 1999), such as 201 polycyclic aromatic hydrocarbons (PAH) (Bocchi et al., 2016). The higher ratio of sulfate in 202 summer is attributable to the intense photochemistry, high temperature, and RH in this season. 203 Different from nitrate, sulfate is a thermal-stable species, thus high temperature favors its 204 photochemical reactions (Zhang et al., 2008). In addition, sulfate can more easily serve as cloud 205 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 206 207 larger enrichment of sulfate in summer can be understood.

208 Differences from non-haze to haze were also noticeable within each season. In summer (Figure 209 3 (b)), nitrate increased significantly from non-haze days (4.4%) to haze days (15.3%), indicating 210 the important role of nitrate in the evolution of pollution. The approximately three-times increase 211 may be caused by the higher concentration of ammonium, higher RH, more intensive 212 photochemical reactivity (high O₃), and higher concentration of NO₂ (Chang et al., 2009; Lin and 213 Cheng, 2007). A detailed discussion of its formation mechanisms is provided later. Furthermore, 214 other SIA species (sulfate and ammonium) also increased, while OM decreased correspondingly, 215 from non-haze to haze in both summer and winter, suggesting that enhanced secondary inorganic 216 species play a vital role in haze events (Huang et al., 2014). These results are similar to those of 217 Gao et al. (2015). On average, SIA species dominated particles with a 60.6% portion in summer 218 and a 53.4% portion in winter; OM accounted for 22.7% and 29.9% correspondingly. A similar 219 higher percentage of sulfate-nitrate-ammonium (SNA) in summer and higher portion of OM in





220 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⁺, Ca²⁺, Na⁺, and Mg²⁺. The white-boxed value in the center of each pie denotes the concentration of PM_{2.5} in the corresponding period.

229 **3.2 Diurnal variation**

230 The discussion above described the general pollution characteristics in the hot and cold seasons.

- 231 In this section, we focus on the diurnal behaviors of various parameters to understand the
- characteristics of the pollution better.
- 233 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).

239 Generally, the diurnal changes of SIA species were very similar, especially in winter, and were 240 characterized by higher values at night and lower values during the daytime. In winter, SNA in 241 haze events underwent frequent fluctuations, indicating the more complicated mechanisms 242 involved in their formation. The high average levels of sulfate and nitrate in winter were related to the higher concentrations of their precursors (SO₂ and NO₂), higher RH, lower WS, and lower 243 mixed layer height (MLH) at night. In contrast, the lower level of SIA during the daytime may 244 245 be attributed to the higher MLH, which favored the dilution of pollutants, as indicated by the 246 decrease of CO from 10:00 to 17:00. CO is an inactive primary gas pollutant in the atmosphere. 247 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 248 249 precipitation (Zhang et al., 2015). Specifically, some unique peaks of sulfate and nitrate emerged 250 at around 11:00 and 16:00 in haze events, respectively. These peaks were caused by a higher 251 transition rate, as supported by the corresponding peaks of SOR and NOR. The faster secondary 252 process at 11:00 was a synergetic effect of photochemistry and heterogeneous reactions, because 253 both the values of O_3 and RH exhibited high levels. The peak that occurred at around 16:00 was 254 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, 255 256 SNA also showed higher concentration at night, but lower concentration on average during the 257 daytime. In summer haze event, SIA shared a peak value at around 8:00, corresponding to the





258 simultaneous higher concentrations of SO₂ and NO₂. Meanwhile, the value of CO decreased only 259 slightly, meaning that the increased concentration of gaseous precursors was not caused by a 260 physical process but rather by enhanced emission. Considering that 8:00 is the start time for most 261 industries and also a morning rush hour, the quick increase of SO₂ and NO₂ is understandable. 262 Different from sulfate which peaked at 14:00, nitrate decreased continuously from 8:00 to 18:00. 263 In summer, the photochemistry was quite intensive, as indicated by the extremely high level of 264 O_3 during the daytime, which favored the formation of sulfate from SO_2 through the gaseous 265 reaction. This positive effect overwhelmed the dilution effect of higher MLH. However, for 266 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 267 268 addition, nitrate (mainly NH_4NO_3), is a thermal-instable species that more easily enters the gas 269 phase under high temperature (Bai et al., 1995). This negative effect caused by temperature was 270 different from the case in winter. A common feature shared by SIA in both winter and summer 271 was a relatively stable and low value in non-haze period, which was especially apparent in 272 summer. The totally different diurnal behaviors of SIA under different pollution conditions 273 further demonstrates their roles in haze events.

274 Carbonaceous species including OM and EC had distinct diurnal patterns. In winter, they were 275 high at night but low during the daytime, which was similar in general to SIA. The same 276 variations of species were also investigated by Sun et al. (2013b). The high values of OM and EC 277 were caused mainly by the stable meteorological condition at night. Compared with OM, EC 278 presented a more significant diurnal variation characterized by quick increase or decrease. EC is 279 a main primary pollutant (Hou et al., 2011); hence, its variation is more sensitive to physical 280 changes within a day. The portion of OM formed by secondary reaction is called secondary 281 organic aerosol (SOA), and the primary constituents of OM are known as primary organic aerosol







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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

289 value is given.

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(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.

302 3.3 Sulfate

303 Sulfate can form from SO_2 through either a homogeneous process (i.e., oxidized by hydroxyl 304 radical) or a heterogeneous reaction (i.e., oxidized by dissolved oxidants such as H_2O_2 , O_3 , 305 usually accompanied by metal catalysts) (Harris et al., 2013; Khoder, 2002). As mentioned above, 306 the concentration of sulfate is influenced by many factors, including RH, photochemical activity, 307 and others, which demonstrates its complex formation mechanisms. Understanding these 308 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. 309 310 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





312 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 313 means the slope for the corresponding line, that is the ratio of SO_4^{2-}/EC . In winter (Figure 5 (a)), 314 with the increasing of the RH and O_3 , the ratio of SO_4^{2-}/EC increased, indicating that the 315 316 heterogeneous process and photochemical reaction both favored the secondary formation of the sulfate in the cold season. Meanwhile, the irregular size variation (i.e., SO₂ concentration) 317 indicated that the sources of SO₂ were more complicated than those of EC. The complex sources 318 319 of SO₂ may be attributed to a combination of various local industrial activities, stable 320 meteorological conditions, and regional transport. Additionally, we found that when the pollution 321 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 322 (4)). Especially, the sulfate in area (2) peaked while EC, O_3 , and SO_2 concentration did not attain 323 324 a particular high level, meaning that RH has the most decisive effect on the formation of sulfate 325 compared with photochemistry and the emission of precursors in winter.



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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 SO₂ 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.

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In summer, different results occurred. As shown in Figure 5(b), an unexpected phenomenon 334 335 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 336 means that it is rainy in summer. Thus, with the scavenging effect of rainfall, the concentration 337 of sulfate decreased more significantly than the primary pollutants EC. This may be the reason 338 339 for the negative relationship between SO_4^{2-}/EC and RH. In addition, RH was always at a high 340 level in summer, averaging $61.8 \pm 15.9\%$ (Figure 2; Table 1), thus the atmosphere was always 341 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 342 343 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 344 345 concentration of O_3 but higher SO₂. They had nearly an opposite condition but shared a similar 346 sulfate level. These features indicate that both the emission of gas precursors and photochemistry 347 had vital impacts on the formation of sulfate in summer. Moreover, the general variation of SO₂ concentration fits the increase of EC better than it does in winter, indicating a lower number of 348 349 various sources of SO₂ in summer. In summary, the formation of the sulfate in summer was highly 350 vulnerable to the concentration of gaseous precursors and photochemistry.





351 3.4 Nitrate

Nitrate comes mainly from homogeneous reactions between NH₃ and HNO₃ in the gas phase, 352 followed by gas-particle partitioning, or heterogeneous channels through the hydrolysis of N_2O_5 353 354 (Bertram et al., 2009; Russell et al., 1986). In an ammonia-rich area, the favorable formation 355 mechanism of nitrate is homogeneous reactions, but in an ammonia-poor area, nitrate tends to be 356 formed via the hydrolysis of N_2O_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 NO₃⁻ 357 358 concentration as function of Excess NH4⁺. The "Excess NH4⁺" here is defined as the amount of ammonium beyond that needed for $[NH_4^+]/[SO_4^{2-}] = 1.5$ (i.e., [Excess $NH_4^+] = [NH_4^+] -$ 359 1.5[SO₄²⁻]; note that the calculation is under the unit of nmol m^{-3}). If "Excess NH₄⁺" is a positive 360 number, the area can be regarded as ammonium-rich; otherwise, it is ammonium-poor (Pathak et 361 al., 2009). Based on this standard, Zibo is an ammonium-rich city in winter. With increasing 362 "Excess NH4⁺", nitrate rose significantly. Some negative values of "Excess NH4⁺" occurred in 363 summer, which may have been caused by the high temperature, as indicated by the larger size of 364 the symbols in the ammonium-poor area in Figure 6 (b). This correlation is similar to a previous 365 366 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-367 rich ozone, similar to the trend in winter, nitrate increased significantly with increasing "Excess 368 NH4⁺". These results demonstrate that the formation of nitrate was mainly through the 369 370 homogeneous reaction between NH₃ and HNO₃ in the gas phase, with subsequent partitioning 371 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 N₂O₅ (the production 372 373 of O_3 and NO_2) occurs mainly at night, thus the lower concentration of O_3 may be a result of its 374 contribution to N_2O_5 , that is, HNO₃ 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
NH4NO3. A similar temperature dependency of nitrate was also investigated by Hu et al. (2011).



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).

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Based on above discussion, we realized that the primary formation mechanism of nitrate was the homogeneous reactions in gas phase between NH₃ and HNO₃, 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





393 correspondingly at a low level. During this period, the formation of nitrate was less related to RH 394 or temperature, but limited to its gas precursors. In zone 2, the increase of nitrate along with NO₂ 395 is most significant, which may be facilitated by the high RH (a1), but it is less related with 396 temperature (a2). With the continuous increase of NO_2 , points fell into zone 3, which is 397 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 398 low "Excess NH_4^{+} " (a2). The results above indicate that the main factors controlling nitrate 399 400 formation in winter were gas precursor concentration, RH, and level of "Excess NH4⁺". These 401 influence of these factors on nitrate varied under different ranges of gas precursors. When NO₂ was low (<50 µg m⁻³ in this study), both the RH and "Excess NH4⁺" had no obvious influence on 402 the nitrate; when NO₂ was within the range $50-130 \ \mu g \ m^{-3}$, nitrate was significantly impacted by 403 RH. Although the formation of nitrate occurs mainly through homogeneous reactions in gas phase, 404 405 RH favors nitrate partitioning into particles (Shi et al., 2014). Once the NO₂ surpassed a certain 406 value, the increasing rate of nitrate versus NO₂ slow and was impacted by RH and "Excess NH₄+". 407 Based on the investigations described above, control strategies for nitrate in winter should focus on reduction of gaseous precursor NO₂ (less than 50 μ g m⁻³ in this study) and emission of NH₃, 408 because RH is far more difficult to reduce artificially. 409

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 NO₂ was high or low, which may a result of the lower level of "Excess NH_4^+ " and higher temperature. NH₄NO₃ 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





- 417 level, low "Excess NH4⁺", high temperature, and low RH. In zone 3, gas precursors are higher,
- 418 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.

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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





- 431 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 432 effects of "Excess NH₄⁺", RH, and temperature on nitrate were significant in summer. Their 433 relative importance was roughly in the order of "Excess NH_4^+ " > RH > temperature. Thus, for 434 435 control of nitrate in summer, close attention should be paid to sources of NH₃. Generally, the 436 gaseous NH₃ concentration was higher in summer, which was caused by the volatility of ammonia 437 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 438 both scaled by CO concentration. In (a1), the fit between symbol size and X-axis is better than in 439
- 440 (b1), which may be a result of the complicated photochemistry in summer, considering that NO₂
- 441 is more activated than CO in the photochemical circle (Jacob, 2000).
- 442 **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 μ gC m⁻³ in winter and 7.7 and 3.6 μ gC 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., 2011a) In this study, SOC was calculated using the EC-scaled method (i.e., $[SOC] = [OC] - [EC] \times [OC/EC]_{primary}$ 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





455 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 456 457 that at Mount Tai (73.4%) (Wang et al., 2012). The high SOC percentage in summer could be the 458 result of the high photochemistry and high concentration of VOCs (Lin et al., 2009), whereas the 459 similarly high value of SOC in winter may be a result of the synergistic effect of coal combustion, 460 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 461 462 (Figure 8(a)), the concentrations of SOC and POC appeared to be higher during the nighttime, 463 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 464 and secondary sources. In the daytime, the decrease of SOC was slower than that of POC, which 465 might be attributable to a certain compensation effect from photochemistry, as indicated by the 466 467 rising O₃. 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 468 lower the concentration of OC. In summer, the variation of POC was also similar to that of CO, 469 470 but SOC appeared to have a nearly opposite trend with CO and was more likely to follow O_3 . 471 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 472 473 variation of POC to the atmospheric dilution condition, which is similar to the trend found in 474 winter. After 9:00, with the increasing O_3 and decreasing CO, SOC rose significantly, while POC 475 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 476 477 impact caused by higher MLH. Another interesting phenomenon shown in Figure 8 is the weaker 478 relation between RH and SOC. Generally, higher RH favor the condensation of semi-volatile





479	organic compounds (SVOCs), thus a positive correlation between RH and SOC should have been
480	more obvious, especially in summer, but this did not emerge according to Figure 8. This may be
481	attributed to the reversed trend between O3 and RH, thus an indirect effect made RH less
482	important for SOC. A similar increasing of SOC with O3 was also found by Hu et al. (2012), and
483	the seemingly opposite trend between RH and SOC was similar to the result of an investigation
484	in Yucheng, another city in Shandong (Yao et al., 2016).
485	Overall, the concentration of organic matter was 1.97 times higher in winter for multiple reasons.
486	From the sources perspective, coal combustion for heating contributes abundant pollutants (Wang
487	et al., 2015a) and the time required for motor vehicle to cold start is prolonged because of the
488	low temperature in winter, which favors the transfer of SVOCs to the particle phase (Chow et al.,
489	1993). From the meteorological perspective, stable air motion and frequent thermal inversion
490	facilitate the accumulation of contaminants and favor the condensation and absorption of VOCs
491	(Wang et al., 2015a). SOC/OC was slightly higher in summer, the result of a nearly 4.11 times
492	higher photochemical reactivity (if using O3 concentration to estimate). However, the
493	enhancement of SOC/OC in the hot season (68% in summer and 62% in winter) did not emerge
494	as appreciably as the enhancement of photochemistry. This was caused by the accompanying
495	higher temperature with high O ₃ (as shown in Figure 3). High temperature favors the evaporation
496	of VOCs and SVOCs, which exerts a negative impact on the formation of SOC in the particle
497	phase (Lamorena and Lee, 2008). Nevertheless, the increasing of SOC in daytime during summer
498	further emphasizes that photochemistry weighed heavily on its formation.
499	







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Figure 8. Diurnal variation of POC, SOC, CO (colored by RH), and O₃ (gray area) in (a) winter
and (b) summer.

503 **3.6 Regional contributions**

As mentioned above, Zibo is located in the NCP and is surrounded by highly industrialized cities, 504 505 thus the regional transport of pollutants to Zibo cannot be overlooked. Figure 9(a) presents fire 506 maps coupled with back trajectories in winter (1/15-1/25) and summer (1/14-1/31). The fire data 507 were downloaded from https://firms.modaps.eosdis.nasa.gov/download/request.php, and the 24-508 hour trajectories and clusters were calculated using the TrajStat model (Wang et al., 2009). In 509 winter, the directions of air mass motion differed significantly. Cluster 1 first passed through 510 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. 511 512 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_2 513





concentration level of 152.54 µg m⁻³ under this condition. Cluster 2 came from Inner Mongolia 514 515 and then passed over Hebei, Beijing, and Tianjin (abbreviated as BTH in the following discussion) 516 successively. As demonstrated previously, BTH is a highly industrialized and heavily polluted 517 region (Jiang et al., 2015; Wang et al., 2015b). Thus, the $PM_{2.5}$ concentrations during this time were the second highest concentrations, with an average of $236.02 \,\mu g \, m^{-3}$, and were characterized 518 519 by the most abundant SIA constituents. Along the transport of the air mass, particles aged 520 progressively (Guo et al., 2014). In addition, this trajectory passed by Bohai, resulting in high 521 RH (58.10%), which favored the formation of SIA species in winter, as discussed above. Cluster 522 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. 523 The high speed and direct motion of the air exerted a scavenging effect, cleaning the pollutants 524 in Zibo. Cluster 4 came from northern Jiangsu, then passed over Linyi (a city in southeast 525 526 Shandong Province) with moderate speed. Southern Shandong is a heavily industrialized region, 527 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 5 528 appeared to be the most polluted one and had the highest particle concentration ($265.70 \ \mu g \ m^{-3}$). 529 530 It started from Bohai, then moved southwesterly. Southwest Shandong is a densely industrialized 531 region and also a coastal area. Thus, the air mass of this cluster was very moist with plenty of 532 pollutants; the enhanced primary emission can also be proved by the high concentration of EC. 533 Cluster 6 had the characteristic of the highest RH but lower concentration of pollutants compared 534 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 535 536 petroleum industry in northern Shandong. According to the distribution of fire spots, open 537 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





551 similar concentrations of pollutants. In particular, the increasing nitrate in cluster 5 may be 552 attributable to the reaction between HNO₃ and NaCl, a typical sea salt, through which NaNO₃ is 553 generated and HCl is released (Ianniello et al., 2011). The apparently higher concentration of Cl⁻ 554 supports the contribution of a sea salt source. Cluster 2 originated from Linvi, as mentioned above, 555 a highly industrialized city with a rich source of coal. Many airborne pollutants could be delivered 556 to Zibo in this cluster, and high concentration of SIA could be the result of this regional transport. 557 Especially, the high concentration of ammonia favored nitrate formation, hence the combination 558 of regional transport and interrelation between secondary species may be the key reason for the 559 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 560 that brought Zibo the cleanest air. In addition, K^+ was the most abundant metal ion (35.3% for 561 cluster 3 and 39.8% for cluster 4), which may be a contribution of biomass burning along the 562 563 trajectory. Similarly, K⁺ also accounted for the largest portion of metal ions in cluster 2 (37.4%). 564 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 565 566 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 567 transport contributes more nitrate (Huffman et al., 2009; Yang et al., 2011). Generally, a longer 568 trajectory was accompanied by a lower ratio of nitrate. A similar trend also occurred for clusters 569 570 3 and 4. Zibo is a city that both influences the condition of the air in the NCP and is influenced 571 by the air in the NCP. Thus, joint prevention between cities is necessary and inevitable.

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