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Dr. Willy Maenhaut

Dear Dr. Maenhaut,

We appreciate your detailed corrections on our manuscript. Following your suggestions, the manuscript was revised accordingly. Please find in next pages the marked-up manuscript with the relevant changes.

Thank you very much for your time, and we look forward to hearing back from you.

Sincerely,

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1 Long-term real-time measurements of aerosol particle composition in  
2 Beijing, China: seasonal variations, meteorological effects, and source  
3 analysis

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20 **Abstract**

21 High concentrations of fine particles ( $PM_{2.5}$ ) are frequently observed during all seasons in  
22 Beijing, China, leading to severe air pollution and human health problems in this  
23 megacity. In this study, we conducted real-time measurements of non-refractory  
24 submicron aerosol (NR- $PM_1$ ) species (sulfate, nitrate, ammonium, chloride, and organics)  
25 in Beijing using an Aerodyne Aerosol Chemical Speciation Monitor for 1 year, from July  
26 2011 to June 2012. This is the first long-term, highly time-resolved ( $\sim 15$  min)  
27 measurement of fine particle composition in China. The seasonal average ( $\pm 1\sigma$ ) mass  
28 concentration of NR- $PM_1$  ranged from  $52 (\pm 49) \mu\text{g m}^{-3}$  in the spring season to  $62 (\pm 49)$   
29  $\mu\text{g m}^{-3}$  in the summer season, with organics being the major fraction (40–51%), followed  
30 by nitrate (17–25%) and sulfate (12–17%). Organics and chloride showed pronounced  
31 seasonal variations, with much higher concentrations in winter than in the other seasons,  
32 due to enhanced coal combustion emissions. Although the seasonal variations of  
33 secondary inorganic aerosol (SIA = sulfate + nitrate + ammonium) concentrations were  
34 not significant, higher contributions of SIA were observed in summer (57–61%) than in  
35 winter (43–46%), indicating that secondary aerosol production is a more important  
36 process than primary emissions in summer. Organics presented pronounced diurnal  
37 cycles that were similar among all seasons, whereas the diurnal variations of nitrate were  
38 mainly due to the competition between photochemical production and gas–particle  
39 partitioning. Our data also indicate that high concentrations of NR- $PM_1$  ( $> 60 \mu\text{g m}^{-3}$ ) are  
40 usually associated with high ambient relative humidity (RH) ( $> 50\%$ ) and that severe  
41 particulate pollution is characterized by different aerosol composition in different  
42 seasons. All NR- $PM_1$  species showed evident concentration gradients as a function of  
43 wind direction, generally with higher values associated with wind from the south,  
44 southeast or east. This was consistent with their higher potential as source areas, as  
45 determined by potential source contribution function analysis. A common high potential  
46 source area, located to the southwest of Beijing along the Taihang Mountains, was  
47 observed during all seasons except winter, when smaller source areas were found. These  
48 results demonstrate a high potential impact of regional transport from surrounding  
49 regions on the formation of severe haze pollution in Beijing.

## 50 **1 Introduction**

51 Severe haze pollution episodes, characterized by high concentrations of fine particles  
52 ( $\text{PM}_{2.5}$ ), occur frequently during all seasons in China (Sun et al., 2013b; Guo et al., 2014;  
53 Zheng et al., 2015), not only reducing visibility significantly, but also exerting harmful  
54 effects on public health (Cao et al., 2012). The mass concentrations of  $\text{PM}_{2.5}$  often far  
55 exceed the China National Ambient Air Quality Standard (NAAQS;  $75 \mu\text{g m}^{-3}$  as a 24-  
56 hour average), particularly in the economically developed regions of Beijing–Tianjin–  
57 Hebei and Yangtze River Delta (YRD). According to Beijing Environmental Statements,  
58 the annual average mass concentration of  $\text{PM}_{2.5}$  was 89.5 and  $85.9 \mu\text{g m}^{-3}$  in 2013 and  
59 2014, respectively, 2.5 times the NAAQS ( $35 \mu\text{g m}^{-3}$  as an annual average), indicating  
60 that Beijing is still facing severe fine particle pollution. While extensive studies have  
61 been conducted in recent years to characterize severe haze pollution (e.g., Guo et al.,  
62 2014; Huang et al., 2014; Sun et al., 2014; Zheng et al., 2015), most were carried out in a  
63 particular season. In reality, the very different compositions, sources, and evolution  
64 processes of severe haze pollution among the different seasons mean that a longer-term  
65 approach is needed to meet the challenge of mitigating fine particle pollution in Beijing.

66 A number of long-term measurements and source analyses have been conducted in  
67 Beijing during the last decade. Zhao et al. (2009) reported pronounced seasonal variations  
68 of  $\text{PM}_{2.5}$ , with higher concentrations in winter than summer. Similarly, Yang et al. (2011)  
69 conducted a long-term study of carbonaceous aerosol from 2005 to 2008 in urban  
70 Beijing. Both organic carbon (OC) and elemental carbon (EC) showed pronounced  
71 seasonal variations, with the highest concentrations occurring in winter and the lowest  
72 values in summer. A more detailed investigation of the chemical composition and sources  
73 of  $\text{PM}_{2.5}$  in urban Beijing can be found in Zhang et al. (2013a). Sources of fine particles  
74 also vary greatly among the different seasons; for instance, coal combustion during  
75 periods requiring more domestic heating, biomass burning in harvest seasons, and dust  
76 storms in spring (Zheng et al., 2005; Zhang et al., 2013a). Despite this, most previous  
77 long-term studies either focused on limited aerosol species, relied upon weekly filter  
78 samples, or used one month's worth of data to represent an entire season (Zhang et al.,  
79 2013a; Zhang et al., 2013b). Therefore, our understanding of the full spectrum of  
80 seasonal variations of aerosol species and sources remains quite poor.

81 The Aerodyne Aerosol Mass Spectrometer (AMS) is unique in its ability to provide  
82 real-time, online measurements of size-resolved submicron aerosol composition (Jayne et  
83 al., 2000; Canagaratna et al., 2007). While the AMS has been widely used in China in  
84 recent years (Xu et al., 2014a and references therein), real-time, long-term measurements  
85 of aerosol particle composition are still rare. Zhang et al. (2013b) conducted a four-month  
86 measurement campaign of submicron aerosol composition and size distributions using a  
87 quadrupole AMS in urban Beijing. Their results showed higher concentration of organics  
88 during wintertime and secondary inorganic species in summer. Furthermore, positive  
89 matrix factorization (PMF) analysis of organic aerosol (OA) showed higher primary OA  
90 (POA) in winter and secondary OA (SOA) in summer. However, measurements over  
91 only one month or even less were conducted for each season, due to the high cost and  
92 maintenance of the AMS. The recently developed Aerosol Chemical Speciation Monitor  
93 (ACSM) is specially designed for long-term routine measurements of submicron aerosol  
94 composition (Ng et al., 2011). The ACSM has been proven reliable by several recent  
95 long-term field measurements, e.g., in Paris (Petit et al., 2015), north-central Oklahoma  
96 (Parworth et al., 2015), and Santiago de Chile (Carbone et al., 2013). Although the  
97 ACSM has been deployed at various sites in China (Sun et al., 2012; Sun et al., 2013b;  
98 Zhang et al., 2015), long-term measurements have yet to be reported.

99 In this study, the first of its kind, we conducted long-term, real-time measurements of  
100 non-refractory submicron aerosol (NR-PM<sub>1</sub>) composition with an ACSM in Beijing,  
101 China, from July 2011 to June 2012. The seasonal variations of mass concentration and  
102 composition of submicron aerosol were characterized, and the diurnal cycles of aerosol  
103 species during the four seasons elucidated. The effects of meteorological parameters,  
104 particularly relative humidity and temperature, on aerosol composition and formation  
105 mechanisms were investigated. Finally, the potential source areas leading to high  
106 concentrations of aerosol species during the four seasons were investigated via potential  
107 source contribution function (PSCF) analysis.

## 108 **2 Experimental methods**

### 109 **2.1 Sampling site**

110 The ACSM was deployed on the roof of a two-story building (~8 m) at the Institute of

111 Atmospheric Physics (IAP), Chinese Academy of Sciences (39°58'28''N, 116°22'16''E,  
112 Fig. 1a) from July 2011 to June 2012. The sampling site is located between the north  
113 third and fourth ring road in Beijing, which is a typical urban site with influences from  
114 local traffic and cooking sources (Sun et al., 2012). The wind rose plots (Fig. 1b) show  
115 that southwesterly winds dominate all seasons except winter, when northwesterly and  
116 northerly winds prevail. The spring and fall seasons are also characterized by high  
117 frequencies of northwesterly and northerly winds. Also note that the prevailing winds  
118 with high wind speeds are more frequent during winter and spring than summer.

119 The meteorological parameters, including wind speed (WS), wind direction, relative  
120 humidity (RH), and temperature ( $T$ ) were obtained from a 325 m meteorological tower at  
121 the same location. The parameters of pressure ( $P$ ), solar radiation (SR), and precipitation  
122 were obtained from a ground meteorological station located nearby. The monthly  
123 variations of these meteorological parameters are presented in Fig. 2. Pronounced  
124 seasonal variations were observed for all meteorological parameters except WS. RH  
125 averaged at  $\sim 60\%$  in summer and presented its minimum value ( $< 30\%$ ) in February.  
126 Temperature and solar radiation showed similar seasonal cycles, with high values in  
127 summer and low values in winter. The monthly variations of WS were relatively flat, yet  
128 slightly higher values in spring were observed. In addition, a considerable amount of  
129 precipitation was observed from June to August, yet it was negligible during wintertime.

## 130 **2.2 Aerosol and gas measurements**

131 The submicron aerosol particle composition including organics, sulfate, nitrate,  
132 ammonium, and chloride was measured *in-situ* by the ACSM at a time resolution of  $\sim 15$   
133 min. The ACSM, built upon previous AMSs (Jayne et al., 2000; Drewnick et al., 2005;  
134 DeCarlo et al., 2006), is specially designed for long-term routine measurements of fine  
135 particle composition (Ng et al., 2011). The ACSM has been successfully deployed at  
136 various sites for chemical characterization of submicron aerosol (Ng et al., 2011;  
137 Budisulistiorini et al., 2013; Carbone et al., 2013; Sun et al., 2013b; Parworth et al.,  
138 2015). In this study, ambient aerosol particles were delivered to the sampling room  
139 through a stainless steel tubing (outer diameter: 1.27 cm) with a flow rate of  $\sim 3 \text{ L min}^{-1}$ ,  
140 out of which  $\sim 84 \text{ cc min}^{-1}$  was sampled into the ACSM. A  $\text{PM}_{2.5}$  URG cyclone (URG-

141 2000-30ED) was installed in front of the sampling line to remove coarse particles ( $> 2.5$   
142  $\mu\text{m}$ ). To reduce the uncertainties of collection efficiency (CE), a silica gel diffusion dryer  
143 was set up in the front of the ACSM to ensure that the aerosol particles sampled were dry  
144 ( $<40\%$ ). The ACSM was calibrated routinely with pure ammonium nitrate particles for  
145 the response factor following the procedures detailed in Ng et al. (2011). A more detailed  
146 description of the ACSM calibration is ~~also~~ given in Sun et al. (2012). It should be noted  
147 that we did ~~not~~ not calibrate the ACSM with  $(\text{NH}_4)_2\text{SO}_4$  to determine the relative  
148 ionization efficiency (RIE) of sulfate since such an approach was only proposed recently.  
149 Using the method suggested by Budisulistiorini et al. (2014), the RIE of sulfate was  
150 estimated to be 1.1 – 1.6 during four seasons, leading to a highest uncertainty of 35% in  
151 sulfate quantification. Considering that aerosol particle acidity may vary largely between  
152 different seasons, the method of Budisulistiorini et al. (2014) may introduce additional  
153 uncertainties in sulfate quantification. Therefore, we kept the default RIE of sulfate for  
154 the data analysis in this study.

### 155 **2.3 ACSM data analysis**

156 The ACSM data were analyzed for the mass concentrations of NR- $\text{PM}_{10}$  species  
157 including organics, sulfate, nitrate, ammonium, and chloride using ACSM standard data  
158 analysis software. The RH in the sampling line, aerosol particle acidity and the fraction of  
159 ammonium nitrate ( $f_{\text{AN}}$ ) in NR- $\text{PM}_{10}$  are three major factors affecting the uncertainties of  
160 CE (Huffman et al., 2005; Matthew et al., 2008; Middlebrook et al., 2012). Because  
161 aerosol particles were dry and overall neutralized for most of the time, except some  
162 periods when the ratio of measured  $\text{NH}_4^+$  to predicted  $\text{NH}_4^+$  ( $= 2 \times \text{SO}_4^{2-} / 96 \times 18 +$   
163  $\text{NO}_3^- / 62 \times 18 + \text{Cl}^- / 35.5 \times 18$ ) (Zhang et al., 2007) was less than 0.8, the composition  
164 dependent CE recommended by Middlebrook et al. (2012), which is  $\text{CE} = \max(0.45,$   
165  $0.0833 + 0.9167 \times f_{\text{AN}})$ , was used in this study. The validity of the ACSM data using  
166 variable CE in summer and winter was reported previously in Sun et al. (2012) and Sun  
167 et al. (2013b) by comparing the NR- $\text{PM}_{10}$  with  $\text{PM}_{2.5}$  mass concentration measured by a  
168 TEOM system. The correlation between NR- $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  for the entire year is shown  
169 in Fig. S1. The measured NR- $\text{PM}_{10}$  overall tracked well with that of  $\text{PM}_{2.5}$ , and yet  
170 showed different slopes in different seasons. The average ratio of NR- $\text{PM}_{10}/\text{PM}_{2.5}$  for the  
171 entire year was 0.77 ( $r^2 = 0.66$ ). It should be noted that the  $\text{PM}_{2.5}$  was measured by a

172 heated TEOM (50°C), which might have caused significant losses of semi-volatile  
173 species, e.g., ammonium nitrate and semi-volatile organics. For example, Docherty et al.  
174 (2011) found an average loss of ~44% PM<sub>2.5</sub> mass through use of the heated TEOM  
175 compared to that measured with a filter dynamics measurement system. Assuming that  
176 the average loss of PM<sub>2.5</sub> mass by the heated TEOM is 30–50%, the NR-PM<sub>1</sub>/PM<sub>2.5</sub> ratio  
177 for the entire study would be ~0.5–0.6, which is close to that reported in Zhang et al.  
178 (2013b). Figure S1 also shows large variations of NR-PM<sub>1</sub>/PM<sub>2.5</sub> ratios in the different  
179 seasons. The reasons for the variations include: 1) the ACSM cannot detect refractory  
180 black carbon, mineral dust, and metals. For example, low ratios of NR-PM<sub>1</sub>/PM<sub>2.5</sub> (< 0.3)  
181 were observed during dust storm periods, when mineral dust is the dominant component  
182 of fine particles; 2) the contribution of semi-volatile species to PM<sub>2.5</sub> varied greatly  
183 among the different seasons; and 3) the contribution of particles in the range of 1–2.5 μm  
184 to the total PM<sub>2.5</sub> might also be different among different pollution episodes.

#### 185 **2.4 PSCF analysis**

186 The 72 hr back trajectories arriving at the IAP study site at a height of 300 m were  
187 calculated every 3 hr for the entire study period using the National Oceanic and  
188 Atmospheric Administration Hybrid Single-Particle Lagrangian Integrated Trajectory  
189 model, version 4.8 (Draxler and Rolph, 2003). Each trajectory contained a series of  
190 latitude-longitude coordinates every 1 h backward in time for 72 hr. If a trajectory end  
191 point falls into a grid cell (i, j), the trajectory is assumed to collect material emitted in the  
192 cell (Polissar *et al.*, 1999). The number of end points falling into a single grid cell is  $n_{ij}$ .  
193 Some of these trajectory end points are associated with the data with the concentration of  
194 aerosol species higher than a threshold value. The number of these points is  $m_{ij}$ . The  
195 potential source contribution function (PSCF) is then calculated as the ratio of the  
196 number of points with concentration higher than a threshold value ( $m_{ij}$ ) to the total  
197 number of points ( $n_{ij}$ ) in the  $ij$ -th grid cell. Higher PSCF values indicate higher potential  
198 source contributions to the receptor site. In this study, the domain for the PSCF was set in  
199 the range of (34–44°N, 110–124°E). The 75<sup>th</sup> percentile for each aerosol species during  
200 the four seasons (Table S1) was used as the threshold value to calculate  $m_{ij}$ . To reduce the  
201 uncertainties of  $m_{ij}/n_{ij}$  for those grid cells with a limited number of points, a weighting



202 function ( $w_{ij}$ ) recommended by Polissar et al. (1999) was applied to the PSCF in each  
203 season.

$$w_{ij} = \begin{cases} 1.00 & 80 < n_{ij} \\ 0.70 & 20 < n_{ij} \leq 80 \\ 0.42 & 10 < n_{ij} \leq 20 \\ 0.05 & n_{ij} \leq 10 \end{cases}$$

### 204 3 Results and discussion

#### 205 3.1 Mass concentration and chemical composition

206 The average mass concentration of NR-PM<sub>1</sub> was 62  $\mu\text{g m}^{-3}$  in summer (Fig. 3),  
207 which is higher than the 50  $\mu\text{g m}^{-3}$  for July–August 2011 reported in Sun et al. (2012)  
208 due to the biomass burning impacts in June 2012 (Fig. S2). The summer NR-PM<sub>1</sub> level is  
209 close to that measured by a High Resolution Aerosol Mass Spectrometer during the  
210 Beijing 2008 Olympic Games (Huang et al., 2010), but ~20% lower than that determined  
211 in summer 2006 (Sun et al., 2010). The average NR-PM<sub>1</sub> mass concentrations were  
212 relatively similar during the other three seasons, varying from 52 to 59  $\mu\text{g m}^{-3}$  and with  
213 slightly higher concentration during wintertime (Fig. 3). The NR-PM<sub>1</sub> measured in urban  
214 Beijing is overall higher than those previously reported in the Yangtze River Delta  
215 (YRD) region (27–43  $\mu\text{g m}^{-3}$ ) (Huang et al., 2012; Huang et al., 2013; Zhang et al., 2015)  
216 and Pearl River Delta (PRD) region (31–48  $\mu\text{g m}^{-3}$ ) (He et al., 2011; Huang et al., 2011;  
217 Gong et al., 2012), indicating more severe submicron aerosol pollution in Beijing  
218 compared to other places in China. Indeed, the annual average NR-PM<sub>1</sub> concentration (57  
219  $\mu\text{g m}^{-3}$ ) was much higher than the China NAAQS of PM<sub>2.5</sub> (35  $\mu\text{g m}^{-3}$  as an annual  
220 average). Assuming a similar PM<sub>2.5</sub> level as that (89.5  $\mu\text{g m}^{-3}$ ) in Beijing in 2013, NR-  
221 PM<sub>1</sub> on average accounted for 64% of PM<sub>2.5</sub>, which is overall consistent with the results  
222 reported in previous studies (Sun et al., 2012; Sun et al., 2013b; Zhang et al., 2013b).

223 As indicated in Fig. 4, the summer season showed the highest frequency with NR-  
224 PM<sub>1</sub> loading in the range of 30–60  $\mu\text{g m}^{-3}$  (36% of the time), while the winter season  
225 presented the highest frequency of low mass loadings (< 20  $\mu\text{g m}^{-3}$ , 34% of the time) due  
226 to the prevailing northwesterly winds (Fig. 1b). However, high NR-PM<sub>1</sub> loading (> 90  $\mu\text{g}$   
227  $\text{m}^{-3}$ ) occurred 31% of the time during the winter season, substantially more than during

228 any of the other seasons (25%, 25% and 21% during summer, fall and spring,  
229 respectively), indicating that heavy pollution occurred more frequently during winter than  
230 the other seasons. The fall and spring seasons showed similar variations of frequencies,  
231 which overall decreased monotonically as a function of NR-PM<sub>1</sub> loadings. Note that  
232 heavily polluted events, with NR-PM<sub>1</sub> mass concentrations larger than 150 μg m<sup>-3</sup>,  
233 occurred during all seasons, on average accounting for 3–7% of the total time. Such  
234 heavily polluted events were mainly caused by agricultural burning in summer and fall,  
235 and coal combustion in winter, particularly under stagnant meteorological conditions  
236 (Sun et al., 2013b; Cheng et al., 2014).

237 The NR-PM<sub>1</sub> species varied dramatically and differently during the four seasons (Fig.  
238 3). Overall, organics dominated NR-PM<sub>1</sub> during all seasons, accounting for 40–51% on  
239 average. The dominance of organics in NR-PM<sub>1</sub> has been widely observed at various  
240 sites in China, e.g., 31–52% in the YRD region (Huang et al., 2012; Huang et al., 2013;  
241 Zhang et al., 2015), 36–46% in the PRD region (He et al., 2011; Huang et al., 2011; Gong  
242 et al., 2012), and 47% in northwest China (Xu et al., 2014a). Organics showed the largest  
243 contribution to NR-PM<sub>1</sub> in winter due to a large amount of carbonaceous aerosol emitted  
244 from coal combustion (Chen et al., 2005; Zhang et al., 2008). This is also consistent with  
245 the highest contribution of chloride, with coal combustion being a major source in winter  
246 (Zhang et al., 2012). High concentrations of organics were also observed during late June  
247 and early October, due to the impacts of agricultural burning in these two months.  
248 Secondary inorganic aerosol (SIA = sulfate + nitrate + ammonium) contributed the  
249 largest fraction of NR-PM<sub>1</sub> during the summer season (59%) and the lowest fraction  
250 during the winter season (44%). Such seasonal differences in PM composition reflect the  
251 different roles played by primary emissions and secondary formation. While  
252 photochemical production of secondary aerosol associated with higher O<sub>3</sub> and stronger  
253 solar radiation (Fig. 2) plays a dominant role in affecting aerosol composition in summer,  
254 primary emissions play enhanced roles in winter when photochemical processing is  
255 weaker (Sun et al., 2013b). It is interesting to note that nitrate, on average, showed a  
256 higher contribution than sulfate during the four seasons. Compared to previous AMS  
257 measurements in Beijing (Huang et al., 2010; Sun et al., 2010), the nitrate contribution to  
258 NR-PM<sub>1</sub> appears to show an increasing trend. The ratio of NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> varied from 1.3–

259 1.8 in this study, which is overall higher than those (0.8–1.5) observed during the four  
260 seasons in 2008 (Zhang et al., 2013b). This result likely indicates a response of secondary  
261 inorganic aerosol composition to the variations of precursors of NO<sub>x</sub> and SO<sub>2</sub> in recent  
262 years. For instance, a continuous effort to reduce SO<sub>2</sub> emissions is accompanied with a  
263 gradual increase in NO<sub>x</sub> emissions (Wang et al., 2014b), which results in an increasingly  
264 more important role played by nitrate in PM pollution in Beijing. Indeed, a recent model  
265 analysis of the response of SIA to their precursors from 2000–2015 showed that the  
266 increase of nitrate would exceed the reduction of sulfate in northern China, assuming no  
267 change to NH<sub>3</sub> emissions (Wang et al., 2013). A higher concentration of nitrate than  
268 sulfate has also been frequently observed at urban and rural sites in China in recent years,  
269 e.g., Nanjing, in the YRD region (Zhang et al., 2015), and Changdao Island (Hu et al.,  
270 2013).

### 271 | 3.2 Seasonal variations

272 The monthly average NR-PM<sub>1</sub> mass concentration stayed relatively constant  
273 throughout the year, with the average value ranging from 46 to 60 μg m<sup>-3</sup>, except in June  
274 2012 (Fig. 5). The month of June presented the highest NR-PM<sub>1</sub> (89 μg m<sup>-3</sup>) due to the  
275 impact of agricultural burning. Consistently, a higher concentration of NR-PM<sub>1</sub> was  
276 observed in the summer of 2008 (5 June – 3 July) than the other seasons in Beijing  
277 (Zhang et al., 2013b). Zhao et al. (2009) also observed the highest concentration of PM<sub>2.5</sub>  
278 in June 2007, due to the influences of agricultural burning. These results indicate that  
279 agricultural burning is a large source of PM pollution in Beijing in summer. The lowest  
280 concentration of NR-PM<sub>1</sub> in this study summer occurred in July, mainly due to the  
281 abundant precipitation and high temperatures, which facilitated wet scavenging and  
282 convection of PM, respectively (Fig. 2). Similarly lower concentrations of PM<sub>2.5</sub> in  
283 summer than in the other seasons were also observed previously at an urban site in  
284 Beijing (Zhao et al., 2009).

285 Among the NR aerosol species, organics and chloride presented pronounced seasonal  
286 variations, showing higher concentrations in winter than in the other seasons (Fig. 5). The  
287 concentration of organics increased from 17 μg m<sup>-3</sup> in July to ~30 μg m<sup>-3</sup> in October, and  
288 then remained relatively stable across the whole of wintertime. The concentration of

289 organics reached a minimum in April ( $17 \mu\text{g m}^{-3}$ ), and then rapidly increased to  $37 \mu\text{g}$   
290  $\text{m}^{-3}$  in June. Correspondingly, the contribution of organics to NR-PM<sub>1</sub> increased from  
291  $\sim 40\%$  in summer to above  $50\%$  during wintertime (Fig. 6). A higher concentration of  
292 carbonaceous aerosol in winter, compared to the other three seasons, was also observed  
293 in Beijing (Zhang et al., 2013a; Zhao et al., 2013). The seasonal variation of organics is  
294 primarily driven by emissions from various sources and secondary production. While the  
295 POA, particularly from coal combustion emissions, is significantly elevated during  
296 wintertime, the photochemically processed SOA dominates OA in summer (Sun et al.,  
297 2012; Sun et al., 2013b). In the present study, chloride showed a similar seasonal  
298 variation to that of organics. The chloride concentration during wintertime ( $2.8\text{--}3.3 \mu\text{g}$   
299  $\text{m}^{-3}$ ) was approximately six times that ( $0.5 \mu\text{g m}^{-3}$ ) in summer. The contribution of  
300 chloride to NR-PM<sub>1</sub> showed a similar seasonal trend, with the lowest contribution in  
301 summer ( $\sim 1\%$ ) and the highest in winter ( $\sim 5\text{--}6\%$ ) (Fig. 6). High concentrations of  
302 chloride in winter are associated with enhanced coal combustion emissions (Sun et al.,  
303 2013b), but also with low ambient temperature, which facilitates the formation of  
304 particle-phase ammonium chloride. Also note that chloride showed a twice as high  
305 concentration and contribution in June than the other two months in summer because  
306 agricultural burning is also a large source of chloride (Viana et al., 2008; Cheng et al.,  
307 2014).

308 The seasonal variation of sulfate is different from organics and chloride. The sulfate  
309 concentration gradually decreased from  $10.1 \mu\text{g m}^{-3}$  in August to  $4.9 \mu\text{g m}^{-3}$  in  
310 November, which was associated with a synchronous decrease in solar radiation and O<sub>3</sub>  
311 (Fig. 2). The contribution of sulfate to NR-PM<sub>1</sub> showed a corresponding decrease from  
312  $19\%$  to  $10\%$ . The sulfate concentration then increased to  $8.3\text{--}8.8 \mu\text{g m}^{-3}$  in December  
313 and January, likely due to a significant increase of precursor SO<sub>2</sub> associated with an  
314 increased demand for domestic heating during the winter season, which can be oxidized  
315 to form sulfate via either gas-phase oxidation or aqueous-phase processing (Xu et al.,  
316 2014b). Sulfate showed the highest concentration in June ( $13.5 \mu\text{g m}^{-3}$ ) due to secondary  
317 production, but possibly the impact of biomass burning as well. Indeed, a recent study in  
318 the YRD region also found a large enhancement of sulfate in biomass burning plumes in  
319 summer (Zhang et al., 2015). Nitrate showed minor seasonal variation, with the monthly

320 average concentration ranging from 8 to 15  $\mu\text{g m}^{-3}$ , except in June (23  $\mu\text{g m}^{-3}$ ). It is  
321 interesting that a higher concentration of nitrate was observed in summer and spring than  
322 in winter. On average, nitrate accounted for ~25% of NR-PM<sub>1</sub> during summertime, but  
323 decreased to ~15% during wintertime (Fig. 6). Although high temperatures in summer  
324 favor the dissociation of ammonium nitrate particles to gas-phase ammonia and nitric  
325 acid, the correspondingly high RH and excess gaseous ammonia facilitate the  
326 transformation of nitric acid to aqueous NH<sub>4</sub>NO<sub>3</sub> particles (Meng et al., 2011; Sun et al.,  
327 2012). The lowest concentration of nitrate during wintertime might be primarily caused  
328 by the weak photochemical production associated with low solar radiation and oxidants  
329 (e.g., O<sub>3</sub>). In addition, the higher particle acidity in winter (Liu, 2012) and lower mixing  
330 ratio of gaseous ammonia may also suppress the formation of ammonium nitrate particles  
331 (Zhang et al., 2007). The seasonal variation of ammonium is similar to that of sulfate and  
332 nitrate because ammonium primarily exists in the form of NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

### 333 3.3 Diurnal variations

334 As demonstrated in Fig. 7, the diurnal cycles of organics during the four seasons were  
335 overall similar, characterized by two pronounced peaks occurring at noon and during the  
336 evening time. PMF analysis of OA suggested that the noon peak was primarily caused by  
337 cooking emissions, while the evening peak was driven by different primary emissions  
338 (e.g., cooking, traffic, and coal combustion emissions) among the different seasons (Sun  
339 et al., 2012; Sun et al., 2013b). It should be noted that the noon peaks in summer ~~were~~  
340 ~~was~~ more significant than ~~those~~ in fall and winter. Indeed, the cooking emissions,  
341 determined by subtracting the background (10:00–11:00) from the noon peak (12:00–  
342 13:00), were ~1.5–2  $\mu\text{g m}^{-3}$  from September to the following March, which were lower  
343 than the ~3.5  $\mu\text{g m}^{-3}$  calculated for June and July. This seasonal trend agreed with that of  
344 temperature, indicating that cooking emissions are temperature dependent, probably  
345 because of increased cooking activity in hot summers than cold winters.

346 Relatively flat diurnal cycles were observed for sulfate during most months,  
347 indicating the regional characteristics of sulfate. In fact, multi-day build-up of sulfate was  
348 frequently observed during all seasons (Fig. 3), supporting the notion of regional  
349 influences on sulfate in Beijing. It should be noted that the daytime photochemical

350 production of sulfate from gas-phase oxidation of SO<sub>2</sub> might be masked by an elevated  
351 planetary boundary layer (PBL). Considering the dilution effect of the PBL, Sun et al.  
352 (2012) found that sulfate increased gradually from morning to late afternoon,  
353 demonstrating the daytime photochemical production of sulfate. In this study, sulfate in  
354 May, June and October showed an evident daytime increase until late afternoon,  
355 indicating an important role played by gas-phase photochemical processing in driving the  
356 sulfate diurnal cycle.

357 Nitrate showed substantially different diurnal cycles among different months. A clear  
358 daytime increase starting from about 8:00 to 19:00 was found in the five months of  
359 January, February, March, November and December, indicating that such a diurnal  
360 pattern is more significant during wintertime compared to the fall and spring seasons.  
361 Figure 2 shows that the temperature during these five months was generally low (<  
362 10°C), under which the partitioning of NH<sub>4</sub>NO<sub>3</sub> into gaseous NH<sub>3</sub> and HNO<sub>3</sub> would not  
363 be significant. As a result, photochemical production would be the primary factor driving  
364 the diurnal variations. The photochemical production rate calculated from the daytime  
365 increase was 0.6–0.8 μg m<sup>-3</sup> hr<sup>-1</sup> during winter and ~0.2–0.3 μg m<sup>-3</sup> hr<sup>-1</sup> in November  
366 and March. Nitrate presented pronounced diurnal cycles in summer (June, July and  
367 August), with the concentrations gradually decreasing during daytime and reaching a  
368 minimum at ~16:00. Similar diurnal cycles have been observed on many occasions in  
369 summer in Beijing (Huang et al., 2010; Sun et al., 2012; Zhang et al., 2015). The  
370 evaporative loss of NH<sub>4</sub>NO<sub>3</sub> associated with high temperatures, which overcomes the  
371 amount of photochemical production, plays the major role in driving such diurnal cycles.  
372 The rising PBL plays an additional role in the low concentrations of nitrate during  
373 daytime (Sun et al., 2012). The diurnal cycle of nitrate in May and September was also  
374 significant, characterized by a pronounced morning peak occurring at ~10:00, when  
375 photochemical production dominated over the gas–particle partitioning of NH<sub>4</sub>NO<sub>3</sub>.  
376 Nitrate showed a relatively flat diurnal cycle in April, indicating a combined effect of  
377 various nitrate formation mechanisms.

378 Chloride in this study was primarily detected as ammonium chloride because ACSM  
379 is insensitive to refractory NaCl and/or KCl at its vaporizer temperature of 600°C. As  
380 shown in Fig. 7, two different diurnal cycles were observed throughout different months.

381 For the months of July, August, September, April and May, chloride presented a morning  
382 peak when both temperatures and the PBL were at their lowest, and then rapidly  
383 decreased to a low ambient level at ~18:00. Such a diurnal cycle was likely primarily  
384 driven by temperature dependent gas–particle partitioning (Hu et al., 2008). The diurnal  
385 cycles of chloride during the remaining months were also significant, all of which were  
386 characterized by high concentrations at night. Coincidentally, these months fell during  
387 the season of high domestic-heating demand, which usually starts on 15 November and  
388 ends on 15 March. Coal combustion has been found to be a large source of chloride  
389 (Zhang et al., 2012; Sun et al., 2013b). Therefore, the diurnal cycle of chloride is likely  
390 dominantly driven by coal combustion emissions that are intensified at night for domestic  
391 heating.

### 392 **3.4 Weekend effects**

393 Because the switch between clean periods and pollution episodes arising from  
394 different source areas happens frequently in Beijing (Sun et al., 2013b; Guo et al., 2014),  
395 the diurnal cycles of aerosol species can vary greatly due to the influences of different  
396 occurrences of clean periods between weekdays and weekends (Sun et al., 2013b).  
397 Therefore, periods with low aerosol loadings ( $\text{NR-PM}_{10} < 20 \mu\text{g m}^{-3}$ ) were excluded from  
398 the results (Fig. 8) for a better investigation of the weekend effects (for the average  
399 diurnal cycles with clean periods included, see Fig. S3). As shown in Fig. 8, there were  
400 no clear weekend effects in the summer, except for slightly lower concentrations of  
401 organics, sulfate and nitrate in the late afternoon ~~at-on~~ weekends. This suggests that ~~there~~  
402 ~~are~~ no significant differences in anthropogenic activity between weekdays and weekends  
403 in summer. Although some enhanced traffic emissions between 00:00 and 06:00 ~~at-on~~  
404 weekends might have occurred, as indicated by the higher concentration of NO (Fig. S4),  
405 they appeared to have negligible impacts on secondary sulfate and nitrate. While the  
406 diurnal variations of organics and chloride were similar between weekdays and weekends  
407 during the fall season, sulfate and nitrate showed pronounced weekend effects, with  
408 persistently higher concentrations at weekends throughout the day. An explanation for  
409 this is the stronger photochemical production of secondary species associated with higher  
410 O<sub>3</sub> and solar radiation ~~at-on~~ weekends (Fig. S4). Consistently, SOA showed similar  
411 weekend effects as those of secondary inorganic species, while POA did not (Sun et al.,

412 in preparation). Because of the regional characteristics of secondary aerosols, further  
413 analysis is needed to address the impacts of regional transport on the weekend effects of  
414 secondary species. Winter showed the most pronounced weekend effects for all aerosol  
415 species. All aerosol species showed much lower concentrations ~~at~~ on weekends than on  
416 weekdays across the entire day, which was consistent with those of NO, SO<sub>2</sub>, and CO  
417 (Fig. S4). These results clearly indicate much reduced anthropogenic activity ~~at~~ on  
418 weekends during wintertime because of low ambient temperature (−4°C to −3°C).  
419 Further evidence is provided by the diurnal cycles of organics, which presented  
420 pronounced noon peaks ~~at~~ on weekends during all seasons except winter. This  
421 observation was consistent with much reduced cooking activity ~~at~~ on weekends during  
422 wintertime. Similar to summer, no evident weekend effects were observed in spring. The  
423 weekend effects of aerosol species in this study are overall consistent with those observed  
424 by Han et al. (2009), in which similar diurnal cycles of primary elemental carbon, CO,  
425 and CO<sub>2</sub> between weekdays and weekends under weak wind conditions were observed  
426 during the three seasons other than winter.

### 427 3.5 Meteorological effects

428 Figure 9 shows the RH and *T* dependent distributions of NR-PM<sub>1</sub> and WS for the  
429 entire year. The distribution of NR-PM<sub>1</sub> showed an obvious concentration gradient as a  
430 function of RH. NR-PM<sub>1</sub> showed the lowest mass loading, generally less than 20 μg m<sup>−3</sup>  
431 at RH < 20%, and had no clear dependence on *T*. This can be explained by the high WS  
432 (often larger than 5 m s<sup>−1</sup>; Fig. 9b) at low RH levels associated with clean air masses  
433 from the north and/or northwest. Previous studies have also found a strong association  
434 between low aerosol loading and high WS in Beijing (Han et al., 2009; Sun et al., 2013b).  
435 NR-PM<sub>1</sub> showed moderately high concentrations (~20–40 μg m<sup>−3</sup>) at low RH (20–40%),  
436 which rapidly increased to a high concentration level (> 60 μg m<sup>−3</sup>) at RH > 50%. These  
437 results indicate that severe haze episodes in Beijing mostly occur under high humidity  
438 conditions, when WS is low as well. Two different regions with high concentrations of  
439 NR-PM<sub>1</sub> are apparent in Fig. 9a: one in the top-right region with high temperature  
440 (>~15°C), and another in the bottom-right region with low ambient temperature (<~6°C).  
441 Such a difference in distribution illustrates the severity of PM pollution in different



442 seasons. Note that low concentrations of NR-PM<sub>1</sub> sometimes occurred at RH > 90%,  
443 likely due to the scavenging of particles by rain or winter snow.

444 The RH- and *T*-dependent distributions of major aerosol species (Fig. 10) allow us to  
445 further investigate the RH/*T* impacts on the formation of aerosol species. While all  
446 aerosol species showed similar concentration gradients as a function of RH to that of NR-  
447 PM<sub>1</sub>, the *T*-dependent patterns varied greatly. Organics generally showed the highest  
448 concentrations under low *T* (< 6°C) and high humidity conditions – very similar to the  
449 behavior of chloride, which is mainly derived from combustion sources, e.g., coal  
450 combustion or biomass burning (Zhang et al., 2012; Cheng et al., 2014). The results  
451 suggest that high concentrations of organics during wintertime are primarily caused by  
452 coal combustion emissions during the domestic-heating season, particularly from  
453 residential coal combustion (Zhang et al., 2008). In fact, a previous study by our group  
454 found that nearly one-third of OA during wintertime is primary coal combustion OA  
455 (CCOA) (Sun et al., 2013b). In contrast, organics showed much lower concentrations  
456 under the conditions of higher RH and higher *T*, for which one of the reasons was  
457 probably far fewer coal combustion emissions during summertime (Zheng et al., 2005;  
458 Zhang et al., 2013a). Consistently, CCOA has not yet been resolved from PMF analyses  
459 of AMS OA in summer in Beijing (Huang et al., 2010; Sun et al., 2010). Note that the  
460 region with a high concentration of organics corresponded to a high concentration of NR-  
461 PM<sub>1</sub>. In this region, organics accounted for the largest fraction of NR-PM<sub>1</sub>  
462 (approximately 40–50%), indicating that severe PM pollution under low temperature and  
463 high humidity conditions is dominantly contributed to by organics. The mass fraction of  
464 organics, however, showed an opposite distribution to that of mass loading. As shown in  
465 Fig. 10, organics presents the highest contribution to NR-PM<sub>1</sub> (~ > 50%) in the left-hand  
466 region with low RH, indicating the dominance of organics during periods with low NR-  
467 PM<sub>1</sub> mass loadings. Such a distribution is independent of temperature, suggesting a  
468 ubiquitously organics-dominant composition during clean days in all seasons.

469 The RH/*T* dependence of secondary inorganic species showed somewhat different  
470 behaviors from that of organics. Sulfate presented two high concentration regions, with  
471 the highest values occurring during wintertime when *T* was below 0°C and RH was  
472 above 70%. Aqueous-phase oxidation, mostly fog processing, has been found to play a

473 dominant role in sulfate formation under such meteorological conditions (Sun et al.,  
474 2013a). Surprisingly, the semi-volatile nitrate showed a relatively homogeneous  
475 distribution across different temperatures at RH > 40%. Despite high temperature in  
476 summer, high humidity facilitates the transformation of gaseous species into aqueous-  
477 phase nitrate particles (Sun et al., 2012), particularly in the presence of high abundance of  
478 gaseous ammonia (Ianniello et al., 2010). In fact, nitrate showed the highest contribution  
479 (>~25%) to NR-PM<sub>1</sub> mass under high *T* and high RH conditions, which were also the  
480 conditions under which high concentrations of NR-PM<sub>1</sub> were observed. The fact that  
481 nitrate contributed more than sulfate (~15–20%) to NR-PM<sub>1</sub> mass during these conditions  
482 suggests an important role played by nitrate in summer haze formation. While the  
483 concentration of nitrate at various temperatures was ~~el~~sesimilar, its contribution to NR-  
484 PM<sub>1</sub> was generally lower at low temperatures due to the greater enhancement of organics  
485 during wintertime. Also note that the two semi-volatile species, i.e., nitrate and chloride,  
486 show the lowest contributions to NR-PM<sub>1</sub> in the top-left region with the highest *T* and  
487 lowest RH. This illustrates the evaporative loss process of ammonium nitrate and  
488 ammonium chloride under high temperatures in summertime. However, sulfate shows a  
489 relatively higher contribution in this region since ammonium sulfate is less volatile than  
490 ammonium nitrate and chloride (Huffman et al., 2009).

### 491 3.6 Source analysis

492 In summer, all NR-PM<sub>1</sub> species showed evident wind sector gradients, with higher  
493 concentrations in association with winds from the east (E) and southeast (SE), and lower  
494 concentrations with northwest (NW) wind (Fig. 11). The average NR-PM<sub>1</sub> concentration  
495 from the SE was 89.5 μg m<sup>-3</sup>, which was more than twice that (39.4 μg m<sup>-3</sup>) from the  
496 NW. All aerosol species increased as wind sectors changed along the N–NE–E–SE  
497 gradient, and then decreased along the SE–S–SW–W gradient. Such wind sector  
498 dependence of aerosol composition is remarkably consistent with the spatial distribution  
499 of fine particles in Beijing in 2013 (Beijing Environmental Statement 2013). These  
500 results suggest an inhomogeneous distribution of air pollution around the IAP sampling  
501 site in summer. Organics dominated NR-PM<sub>1</sub> across different sectors (37–43%), followed  
502 by nitrate (21–28%), sulfate (15–20%), and ammonium (15–17%). While chloride  
503 contributed a small fraction of NR-PM<sub>1</sub> (0.7–1.8%), the mass concentration showed the

504 largest difference between SE and NW. The fall season showed a similar aerosol  
505 composition dependence as that in summer, with higher concentrations from the E, SE,  
506 and S. However, the gradients of wind sectors appeared to be smaller. For example, the  
507 average NR-PM<sub>1</sub> concentration ranged from 46.3 to 72.7 μg m<sup>-3</sup> in all eight sectors  
508 except NW. Organics showed a similar dominance in NR-PM<sub>1</sub>, accounting for 47–55%,  
509 and the contribution was ubiquitously higher than in summer for all wind sectors. It  
510 should be noted that the NW sector showed the largest difference between mean and  
511 median values for all species. The much lower median values suggest a dominance of  
512 clean days for most of the time in this sector. In contrast, the summer season showed  
513 higher median concentrations from the NW, indicating a higher regional background  
514 during this season. The winter season showed consistently high concentrations of PM  
515 across the different wind sectors, except for NW, where the mass concentrations were  
516 approximately half of those in the other sectors. The average NR-PM<sub>1</sub> ranged from 55.0  
517 to 84.4 μg m<sup>-3</sup>, with organics being the major fraction, accounting for 46–54%. The  
518 spring season showed a similar wind sector dependence on aerosol composition as the  
519 fall season. The average NR-PM<sub>1</sub> ranged from 49.0 to 74.4 μg m<sup>-3</sup> for all of the wind  
520 sectors except the N (38.5 μg m<sup>-3</sup>) and NW (24.7 μg m<sup>-3</sup>), which had much lower mass  
521 concentrations. Similar to other seasons, organics dominated NR-PM<sub>1</sub> throughout the  
522 different sectors (36–53%), followed by nitrate (19–27%) and sulfate (11–16%).

523 As Fig. 12 shows, the potential source areas for aerosol species varied among the four  
524 seasons. In summer, high potential source areas were mainly located to the south,  
525 southwest and southeast of Beijing. Organics had a relatively small high potential source  
526 region in the south of Beijing (< 100 km) and a small source region located around  
527 Baoding – one of the most polluted cities in Hebei Province. A narrow and visible source  
528 area to the southeast of Beijing, including Tianjin and the Bohai Sea, was also observed.  
529 Nitrate and chloride showed similar source areas to organics. The high potential source  
530 area to the southeast of Beijing was mainly caused by open agricultural burning in June  
531 in northern China. Sulfate showed a distinct source region characterized by a narrow high  
532 PSCF band along Hengshui–Baoding–Langfang–Beijing. Such a pollution band agrees  
533 well with the topography of the North China Plain, with the Taihang Mountains to the  
534 west and Yan Mountains to the north. The wide area of high PSCF for sulfate also

535 indicates a regional characteristic of sulfate that is formed from gas-phase oxidation or  
536 cloud processing of precursor SO<sub>2</sub>, which is particularly high in Hebei Province (Ji et al.,  
537 2014). Secondary nitrate showed a similar, yet much smaller, PSCF region compared to  
538 sulfate. One reason for this might be ~~due to~~ the evaporative loss of ammonium nitrate  
539 during the long-range transport in summer.

540 All aerosol species showed similar PSCF spatial distributions during the fall season,  
541 with high potential source regions located in a narrow area from Hengshui, Baoding to  
542 Beijing. These results suggest that regional transport from the southwest plays a  
543 dominant role in formation of severe haze pollution in fall. The wintertime results  
544 showed largely different PSCF distributions from the other seasons. High PSCF values  
545 were mainly located in a small region (< 50 km) in the south and southeast of Beijing.  
546 Although Hebei Province often has worse air pollution than Beijing during wintertime (Ji  
547 et al., 2014), the cities far away from Beijing appear not to be a very important source of  
548 wintertime air pollution in Beijing. One explanation for this is that stagnant  
549 meteorological conditions occur more frequently in winter due to low WS and *T*  
550 inversions. Thus, local emissions and transport from nearby regions would play a more  
551 significant role in affecting the pollution level in Beijing. While the spring season showed  
552 similarly small high potential source regions to those during wintertime, an obvious high  
553 potential source area in Hebei Province was also observed. The transport of air pollution  
554 from the SW to the NE along the Taihang Mountains in northern China has been  
555 observed many times in previous studies (Wang et al., 2014a; Wang et al., 2014c). Given  
556 that many cities located on this pathway are often highly polluted, such as  
557 Shijiazhuang, Baoding, and Hengshui, regional transport from these areas would have  
558 a potentially high impact on the formation of severe haze pollution in Beijing.

#### 559 **4 Conclusion**

560 This paper presents the results from a year-long, real-time measurement study of  
561 submicron aerosol particle composition using an ACSM, conducted at an urban site in  
562 Beijing from July 2011 to June 2012. The mass concentration of NR-PM<sub>1</sub> varied  
563 dramatically, with the seasonal average concentration ranging from 52 to 62 μg m<sup>-3</sup>.  
564 Organics comprised a major fraction of NR-PM<sub>1</sub> during all seasons, accounting for 40–

565 51% on average. The average contribution of nitrate to NR-PM<sub>1</sub> (17–25%) exceeded that  
566 of sulfate (12–17%) during all seasons, suggesting an enhanced role of nitrate in PM  
567 pollution in recent years. Organics and chloride were two species showing pronounced  
568 seasonal variations in both mass concentrations and mass fractions. The higher  
569 concentrations of organics and chloride in winter than summer were largely due to  
570 enhanced coal combustion emissions. We also observed high concentrations of organics  
571 and chloride in June and October – two months with strong agricultural burning impacts.  
572 The seasonal variations of secondary sulfate and nitrate were not significant because of  
573 the large variations of precursor concentrations, photochemical production, and also  
574 meteorological effects in different seasons. However, higher contributions of SIA in  
575 summer (57–61%) than in winter (43–46%) were still observed, indicating a more  
576 significant role of secondary production in summer. The diurnal cycles of organics were  
577 similar during all seasons, all characterized by two pronounced peaks. While the diurnal  
578 cycles of secondary sulfate were overall relatively flat during most months of the year,  
579 those of nitrate varied greatly in different seasons. It was evident that the diurnal cycles  
580 of nitrate are driven by gas-particle partitioning and daytime photochemical production in  
581 summer and winter, respectively. The winter season showed substantially different  
582 concentrations of aerosol species between weekdays and weekends, with much lower  
583 concentrations on weekends. However, no significant weekend effects were observed  
584 during the other seasons.

585 Meteorological conditions play important roles in the formation of severe PM  
586 pollution in Beijing. In this study, we illustrate the influences of RH and *T* on aerosol  
587 loading and chemistry in different seasons. All aerosol species increased significantly  
588 under stagnant meteorological conditions associated with high RH and low WS. NR-  
589 PM<sub>1</sub> showed two high concentration regions (> 60 μg m<sup>-3</sup>) at RH > 60%. While organics  
590 comprised a major fraction of NR-PM<sub>1</sub> in these two regions, the abundances of sulfate  
591 and nitrate and air temperature were largely different, suggesting they play different roles  
592 in causing PM pollution during different seasons. Under drier conditions (RH < 30%), the  
593 NR-PM<sub>1</sub> concentration was generally low and organics contributed more than 50% of its  
594 mass, indicating the importance of organics during clean periods. The semi-volatile  
595 nitrate presented the largest contribution under high RH and high *T*, highlighting the

596 importance of nitrate formation via aqueous-phase processing in summer. All NR-PM<sub>1</sub>  
597 species showed obvious dependence on wind direction, with higher concentrations  
598 commonly associated with winds from the S, E and SE. This was consistent with the  
599 results from PSCF analysis, which showed that the high potential source areas were  
600 mainly located to the S and SW of Beijing. The high potential source areas varied  
601 differently during the four seasons. A common high potential source area to the SW of  
602 Beijing, along the Taihang Mountains, was observed during all seasons except winter,  
603 demonstrating the potentially high impact of regional transport on severe PM pollution in  
604 Beijing. The winter season showed a much smaller source region compared to the other  
605 seasons, indicating that local and regional transport over a smaller regional scale are more  
606 important. High potential source areas to the SE of Beijing were also observed for  
607 organics, nitrate and chloride in summer, likely due to agricultural burning.

608

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852 **Tables**

853 **Table 1.** Summary of mass concentrations of NR-PM<sub>1</sub> species, gaseous pollutants and  
 854 meteorological parameters during the four seasons and entire study period.

	Entire study		Summer		Fall		Winter		Spring	
	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.
Org ( $\mu\text{g m}^{-3}$ )	25.7	22.1	24.5	20.7	26.8	24.7	29.6	24.8	21.7	16.0
SO <sub>4</sub> <sup>2-</sup> ( $\mu\text{g m}^{-3}$ )	8.1	8.3	10.6	8.2	6.5	7.5	7.7	9.2	7.3	7.6
NO <sub>3</sub> <sup>-</sup> ( $\mu\text{g m}^{-3}$ )	12.6	12.8	15.6	14.4	11.4	12.7	10.3	9.5	13.1	13.4
NH <sub>4</sub> <sup>+</sup> ( $\mu\text{g m}^{-3}$ )	8.5	7.9	10.2	8.2	6.9	7.3	8.1	7.4	8.8	8.1
Cl <sup>-</sup> ( $\mu\text{g m}^{-3}$ )	1.8	2.5	0.8	1.5	1.7	2.7	3.0	3.0	1.5	1.9
NR-PM <sub>1</sub> ( $\mu\text{g m}^{-3}$ )	56.6	48.2	61.6	48.8	53.3	49.7	58.7	50.5	52.3	42.7
SO <sub>2</sub> (ppb)	16.2	14.0	5.4	0.8			25.3	16.0	11.5	8.3
CO (ppm)	1.5	1.3	1.8	1.3			1.7	1.6	1.2	1.0
NO (ppb)	30.0	43.0	7.8	10.8	41.9	51.2	50.9	50.9	19.8	30.0
NO <sub>y</sub> (ppb)	64.0	55.5	35.6	17.9	77.8	63.1	89.1	66.6	54.0	43.3
O <sub>3</sub> (ppb)	21.2	23.8	33.3	29.1	20.3	24.4	7.9	8.5	20.8	19.3
RH (%)	47.0	23.4	62.7	18.9	52.7	20.0	35.6	20.3	36.5	22.5
T (°C)	13.3	11.6	26.3	3.6	14.1	7.0	-1.3	3.4	14.6	8.4
WS, 8 m ( $\text{m s}^{-1}$ )	1.2	0.8	1.0	0.5	0.9	0.7	1.4	1.0	1.4	0.9
WS, 240 m ( $\text{m s}^{-1}$ )	4.4	3.0	3.5	2.3	4.1	2.7	4.6	3.4	5.3	3.3

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855

856 **Figure captions:**

857 Fig. 1. (a) Map of the sampling site (IAP). (b) Wind rose plots, color coded by wind  
858 speed for each season. The frequencies are set to the same scales for all seasons.

859 Fig. 2. Monthly variation of (a) gaseous O<sub>3</sub> and NO<sub>y</sub>, (b) precipitation (Precip.) and solar  
860 radiation (SR), (c) wind speed (WS) and pressure (*P*), and (d) relative humidity (RH) and  
861 temperature (*T*). The WS at the heights of 8 m (solid gray circles) and 240 m (solid black  
862 circles) are shown in (c).

863 Fig. 3. Time series of NR-PM<sub>1</sub> species for the entire year. The pie charts show the  
864 average chemical composition of NR-PM<sub>1</sub> during the four seasons (summer, fall, winter  
865 and spring).

866 Fig. 4. Frequency of NR-PM<sub>1</sub> mass loadings during the four seasons: (a) summer; (b) fall;  
867 (c) winter; (d) spring. Note that the frequency was calculated with 15 min average data.

868 Fig. 5. Seasonal variation of non-refractory submicron aerosol species. The bars represent  
869 the 25<sup>th</sup> and 75<sup>th</sup> percentiles, and the solid circles are mean values.

870 Fig. 6. Monthly variation of (a) mass concentrations and (b) mass fractions of NR-PM<sub>1</sub>  
871 species.

872 Fig. 7. Monthly average diurnal cycle of (a) organics, (b) sulfate, (c) nitrate, and (d)  
873 chloride during the four seasons.

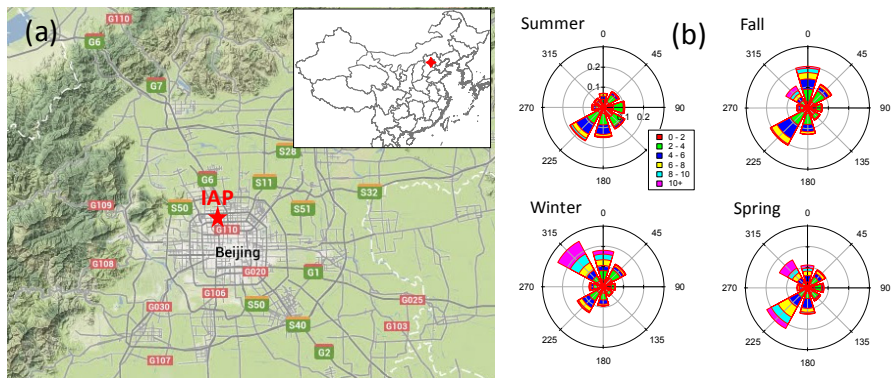
874 Fig. 8. Comparison of the average diurnal cycles of (a) organics, (b) SO<sub>4</sub><sup>2-</sup>, (c) NO<sub>3</sub><sup>-</sup>, and  
875 (d) Cl<sup>-</sup> between weekdays and weekends during the four seasons. Note that the periods  
876 with NR-PM<sub>1</sub> < 20 μg m<sup>-3</sup> are excluded.

877 Fig. 9. RH/*T* dependence of (a) NR-PM<sub>1</sub> mass concentration and (b) WS for a whole  
878 year. The data are grouped into grids with increments of RH and *T* being 5% and 3°C,  
879 respectively. Grids cells with the number of data points fewer than 10 are excluded.

880 Fig. 10. RH/*T* dependence of mass concentrations and mass fractions of aerosol species  
881 for a whole year: (a) organics; (b) sulfate; (c) nitrate; (d) chloride. The data are grouped  
882 into grids with increments of RH and *T* being 5% and 3°C, respectively. Grids cells with  
883 the number of data points fewer than 10 are excluded.

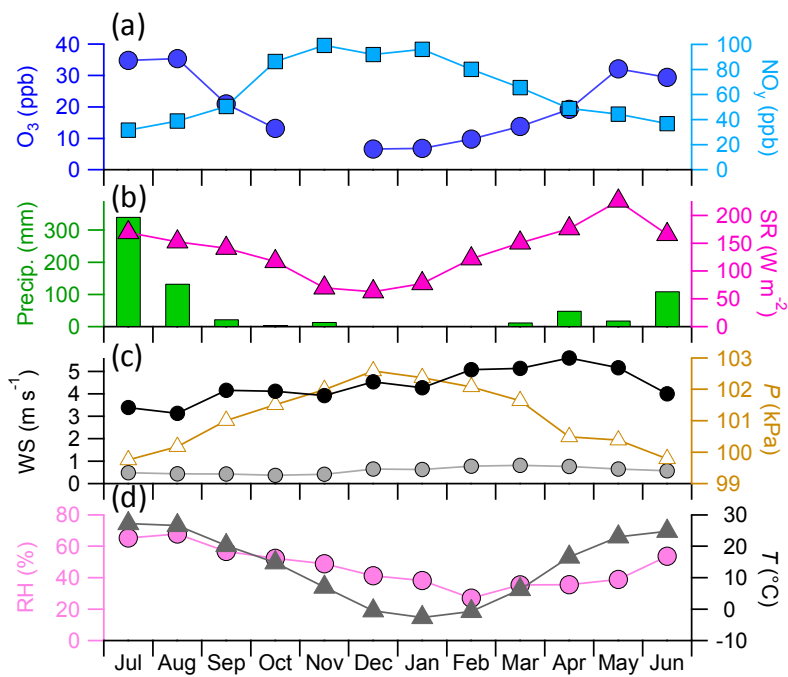
884 Fig. 11. Box plots of mass concentrations of (a) organics, (b) SO<sub>4</sub><sup>2-</sup>, (c) NO<sub>3</sub><sup>-</sup>, and (d) Cl<sup>-</sup>  
885 as a function of wind directions sectors. All the data were segregated into eight wind  
886 sectors representing north (N), northeast (NE), east (E), southeast (SE), south (S),  
887 southwest (SW), west (W), and northwest (NW). The mean (cross), median (horizontal  
888 line), 25th and 75th percentiles (lower and upper box), and 10th and 90th percentiles  
889 (lower and upper whiskers) are shown.

890 Fig. 12. PSCF of NR-PM<sub>1</sub> species during four seasons: (a) organics; (b) sulfate; (c)  
891 nitrate; (d) chloride. The cities marked in each panel are Beijing (BJ), Tianjing (TJ),  
892 Langfang (LF), Baoding (BD), Shijiazhuang (SJZ), and Hengshui (HS). The color scales  
893 indicate the values of PSCF.



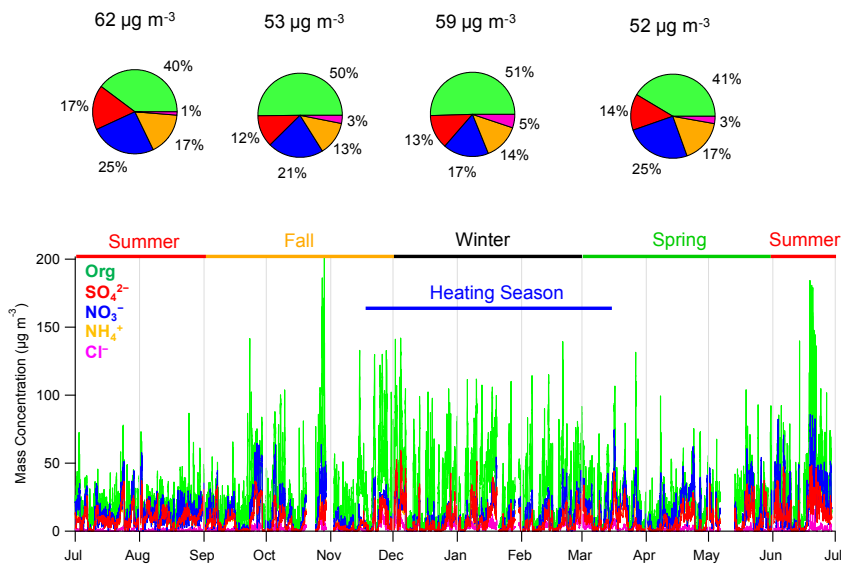
894

895 Fig. 1. (a) Map of the sampling site (IAP). (b) Wind rose plots, color coded by wind  
 896 speed for each season. The frequencies are set to the same scales for all seasons.

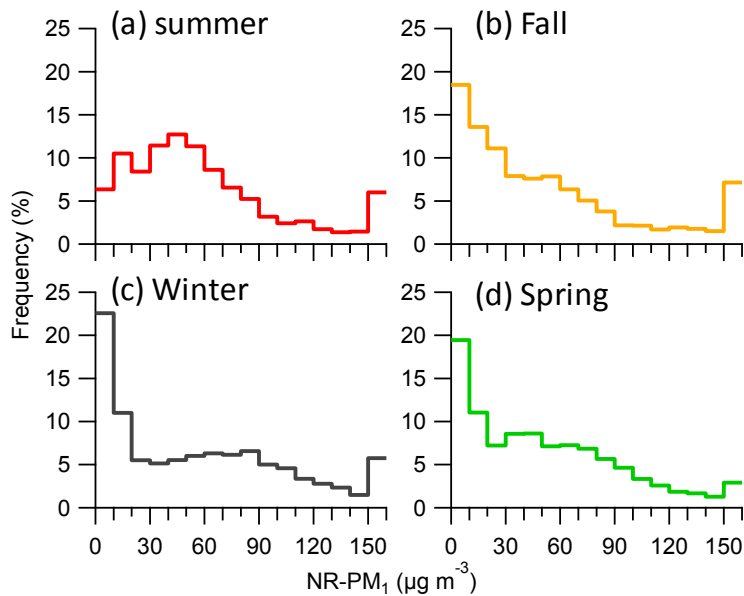


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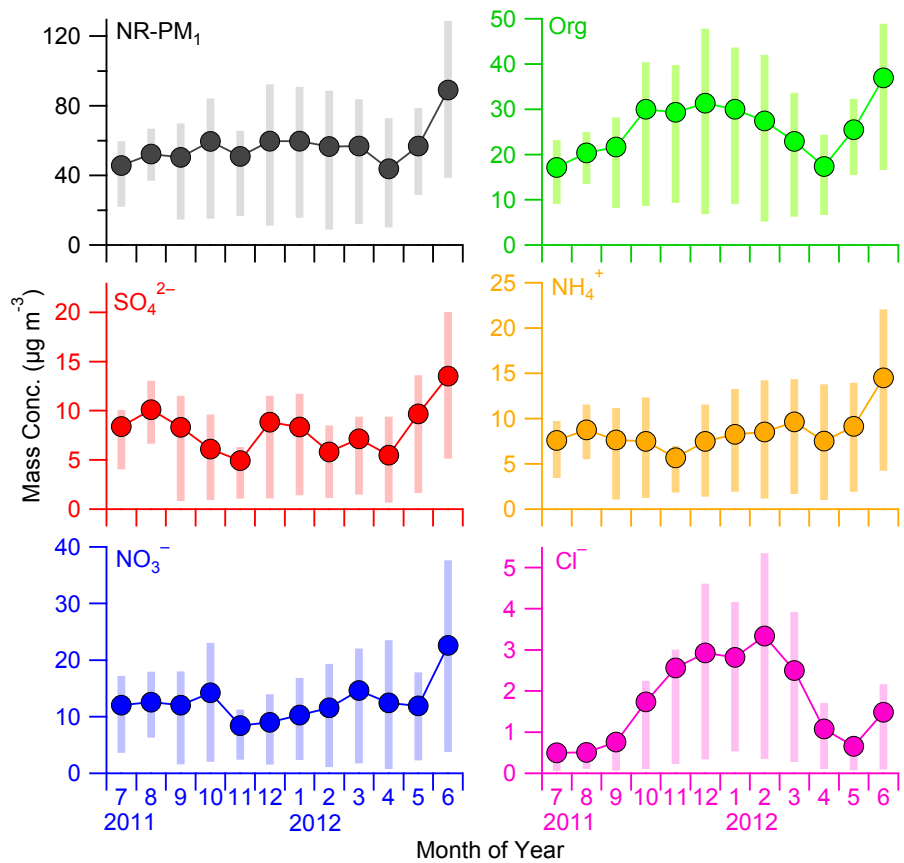
898 Fig. 2. Monthly variation of (a) gaseous O<sub>3</sub> and NO<sub>y</sub>, (b) precipitation (Precip.) and solar  
 899 radiation (SR), (c) wind speed (WS) and pressure (P), and (d) relative humidity (RH) and  
 900 temperature (T). The WS at the heights of 8 m (solid gray circles) and 240 m (solid black  
 901 circles) are shown in (c).



902 Fig. 3. Time series of NR-PM<sub>1</sub> species for the entire year. The pie charts show the  
 903 average chemical composition of NR-PM<sub>1</sub> during the four seasons (summer, fall, winter  
 904 and spring).  
 905



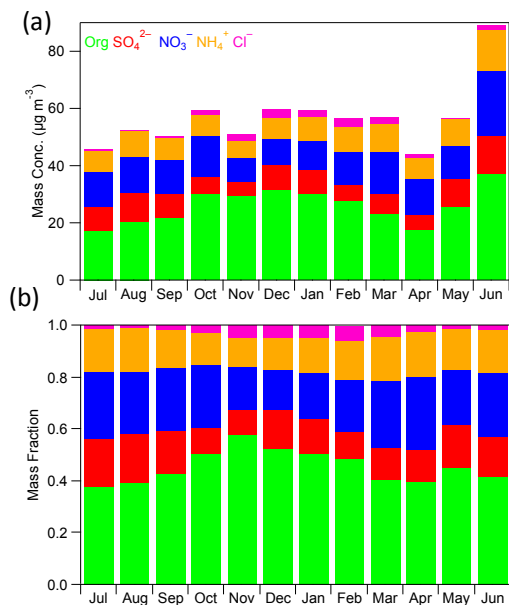
906 Fig. 4. Frequency of NR-PM<sub>1</sub> mass loadings during the four seasons: (a) summer; (b) fall;  
 907 (c) winter; (d) spring. Note that the frequency was calculated with 15 min average data.  
 908



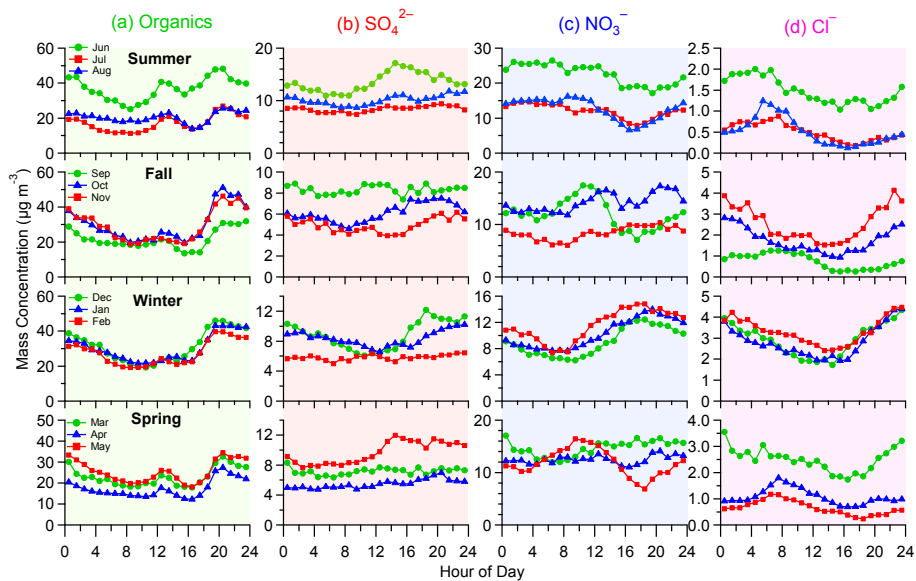
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911 Fig. 5. Seasonal variation of non-refractory submicron aerosol species. The bars represent  
912 the 25<sup>th</sup> and 75<sup>th</sup> percentiles, and the solid circles are mean values.

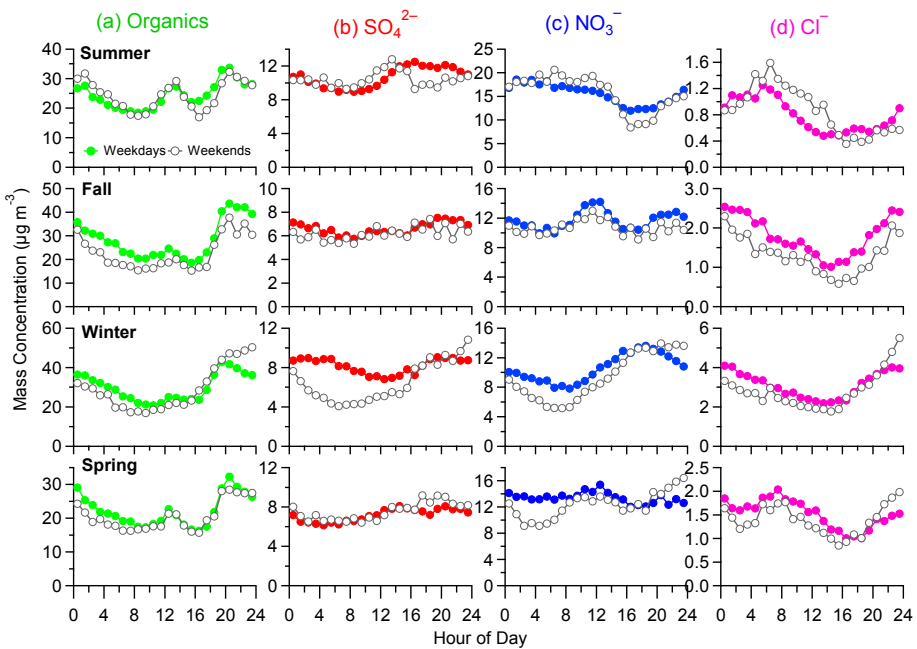




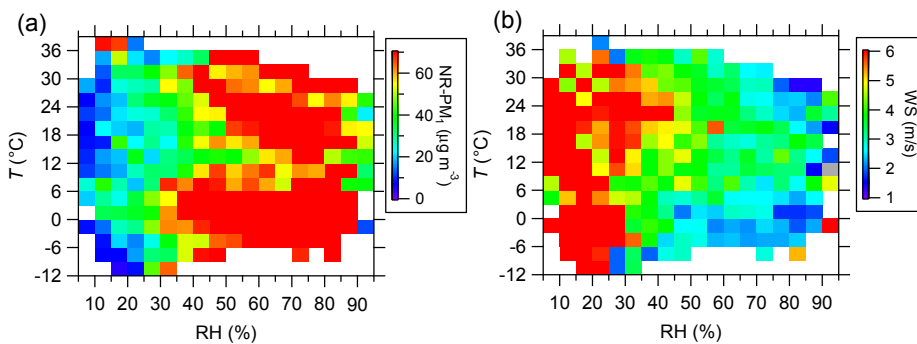
913  
 914 Fig. 6. Monthly variation of (a) mass concentrations and (b) mass fractions of NR-PM<sub>1</sub>  
 915 species.



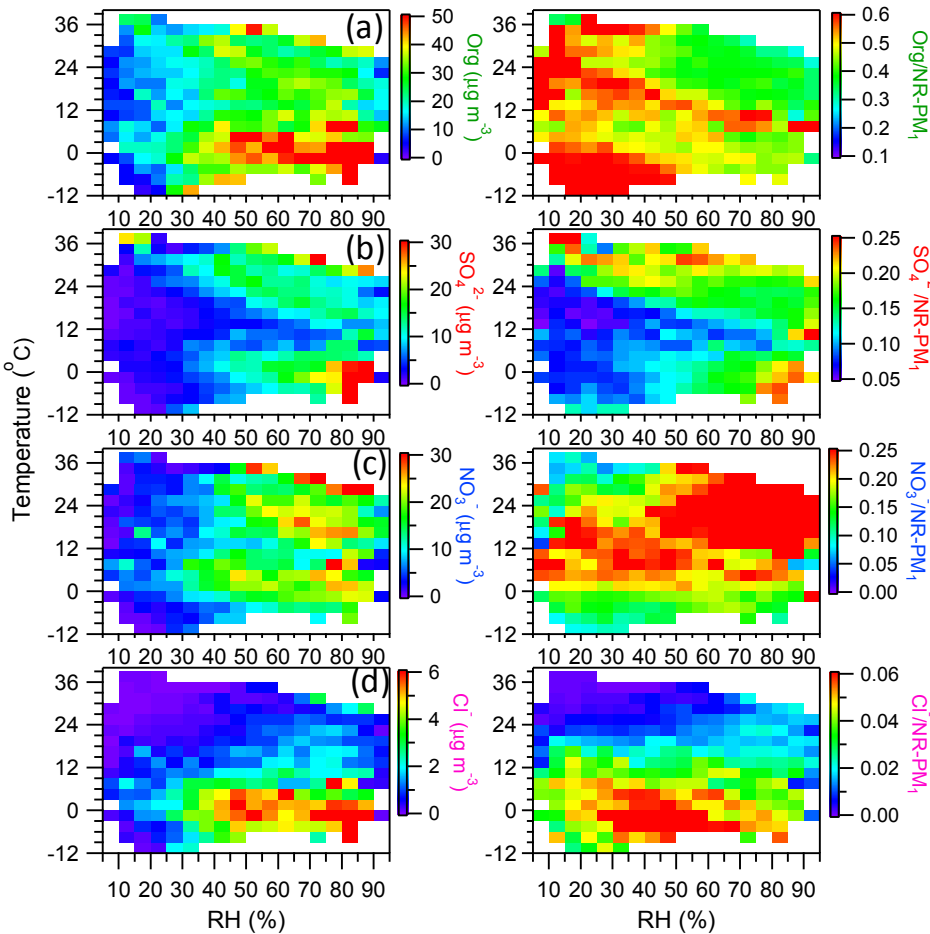
916  
 917 Fig. 7. Monthly average diurnal cycle of (a) organics, (b) sulfate, (c) nitrate, and (d)  
 918 chloride during the four seasons.



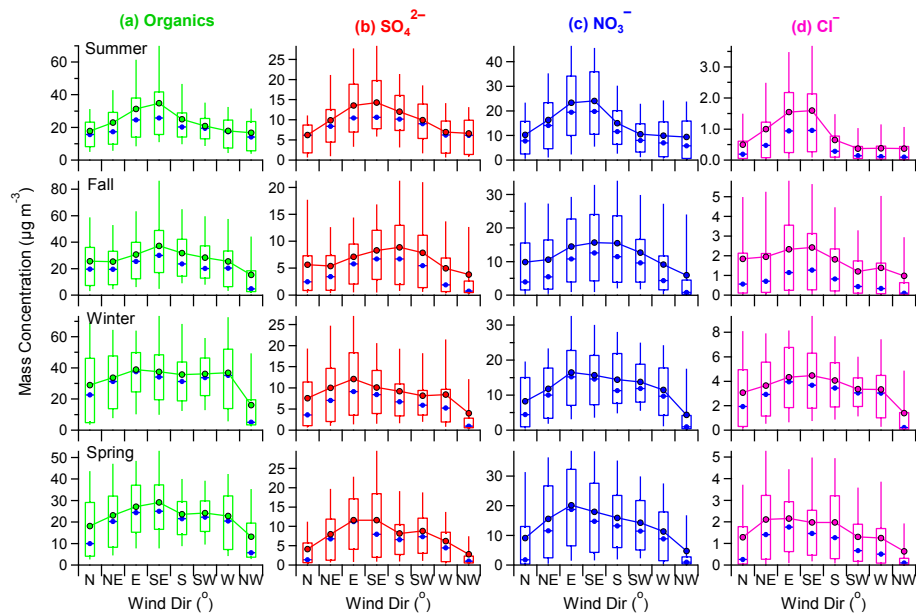
919  
 920 Fig. 8. Comparison of the average diurnal cycles of (a) organics, (b)  $\text{SO}_4^{2-}$ , (c)  $\text{NO}_3^-$ , and  
 921 (d)  $\text{Cl}^-$  between weekdays and weekends during the four seasons. Note that the periods  
 922 with  $\text{NR-PM}_{10} < 20 \mu\text{g m}^{-3}$  are excluded.  
 923



924  
 925 Fig. 9. RH/T dependence of (a)  $\text{NR-PM}_{10}$  mass concentration and (b) WS for a whole  
 926 year. The data are grouped into grids with increments of RH and  $T$  being 5% and  $3^\circ\text{C}$ ,  
 927 respectively. Grids cells with the number of data points fewer than 10 are excluded.

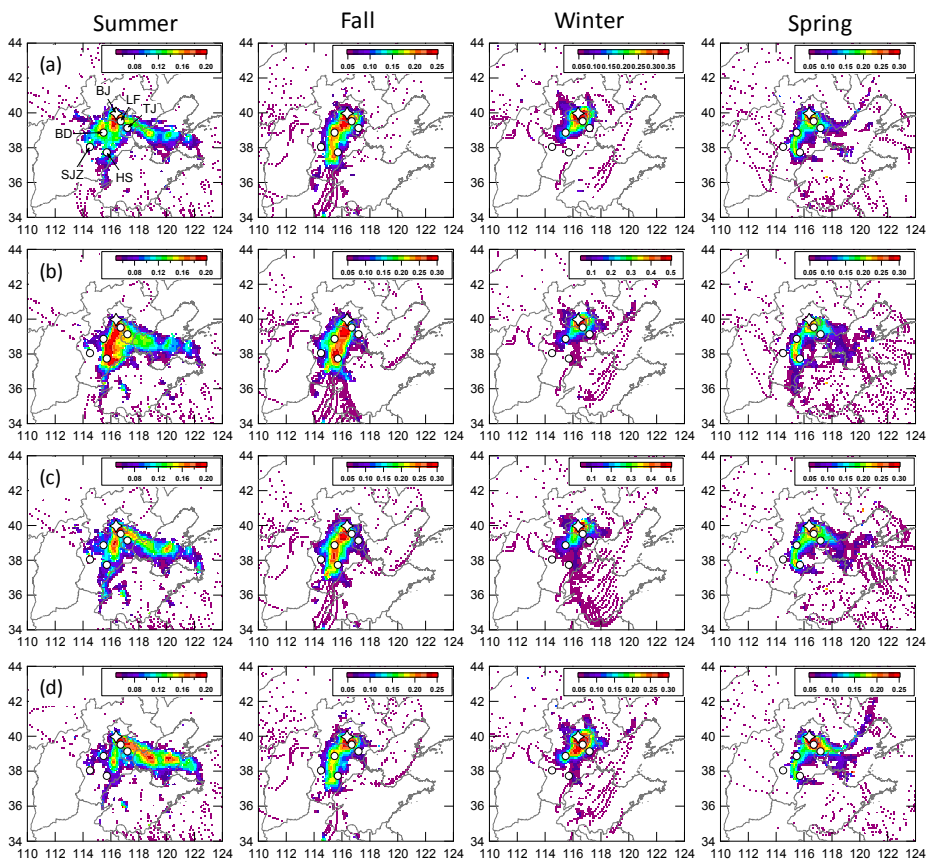


928  
 929 Fig. 10. RH/ $T$  dependence of mass concentrations and mass fractions of aerosol species  
 930 for a whole year: (a) organics; (b) sulfate; (c) nitrate; (d) chloride. The data are grouped  
 931 into grids with increments of RH and  $T$  being 5% and 3°C, respectively. Grids cells with  
 932 the number of data points fewer than 10 are excluded.



933

934 Fig. 11. Box plots of mass concentrations of (a) organics, (b)  $\text{SO}_4^{2-}$ , (c)  $\text{NO}_3^-$ , and (d)  $\text{Cl}^-$   
 935 as a function of wind directions sectors. All the data were segregated into eight wind  
 936 sectors representing north (N), northeast (NE), east (E), southeast (SE), south (S),  
 937 southwest (SW), west (W), and northwest (NW). The mean (cross), median (horizontal  
 938 line), 25th and 75th percentiles (lower and upper box), and 10th and 90th percentiles  
 939 (lower and upper whiskers) are shown.



940

941 Fig. 12. PSCF of NR-PM<sub>1</sub> species during four seasons: (a) organics; (b) sulfate; (c)  
 942 nitrate; (d) chloride. The cities marked in each panel are Beijing (BJ), Tianjing (TJ),  
 943 Langfang (LF), Baoding (BD), Shijiazhuang (SJZ), and Hengshui (HS). The color scales  
 944 indicate the values of PSCF.