

1 **Characteristics of aerosol pollution during heavy haze events**
2 **in Suzhou, China**

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15

16 **Abstract**

17 Extremely severe haze weather events occurred in many cities in China, especially in
18 the east part of the country, in January 2013. Comprehensive measurements including
19 hourly concentrations of PM_{2.5} and its major chemical components (water-soluble
20 inorganic ions, OC, and EC) and related gas-phase precursors were conducted via
21 on-line monitoring system in Suzhou, a medium size city of Jiangsu province, just
22 east of Shanghai. PM_{2.5} frequently exceeded 150 $\mu\text{g m}^{-3}$ on hazy days, with the
23 maximum reaching 324 $\mu\text{g m}^{-3}$ on Jan. 14, 2013. Unfavorable weather conditions
24 (high RH, and low rainfall, wind speed and atmospheric pressure) were conducive for
25 the haze formation. High concentrations of secondary aerosol species (including SO₄²⁻,
26 NO₃⁻, NH₄⁺, and SOC) and gaseous precursors were observed during the first two
27 haze events, while elevated primary carbonaceous species emissions were found
28 during the third haze period, pointing to different haze formation mechanisms. OM,
29 (NH₄)₂SO₄, NH₄NO₃ were found to be the major contributors to visibility impairment.
30 High concentrations of sulfate and nitrate might be explained by homogeneous
31 gas-phase reactions under low RH conditions and by heterogeneous processes under
32 relatively high RH conditions. Analysis of air mass trajectory clustering and potential
33 source contribution function manifested that aerosol pollutions in the studied areas
34 were mainly caused by local activities and surrounding sources transported from
35 nearby cities.

36

37 **1. Introduction**

38 Haze is defined as visibility lower than 10 km when relative humidity < 80%. Rapidly
39 increased air pollution in China in the past several decades have resulted in frequent
40 occurrences of haze events, which have caused great concern to the scientific
41 community as well as the public (Zhang et al., 2012). Haze events have adverse
42 effects on human health, traffic, climate, and other important aspects (Zhang et al.,
43 2015; Charlson et al., 1987; Ramanathan and Vogelmann, 1997; Tegen et al., 2000; Yu
44 et al., 2002; Tie et al., 2009a; Tie et al., 2009b). Fine particles (PM_{2.5}, aerosols with an

45 aerodynamic diameter of 2.5 microns or less) are largely responsible for haze
46 formation due to their ability in light extinction including scattering and absorbing
47 solar and infrared radiation (Yu et al., 2014). Light extinction of PM_{2.5} is highly
48 associated with its chemical composition (Tao et al., 2014). Water-soluble inorganic
49 ions and carbonaceous species often account for major fractions of PM_{2.5} and are
50 important contributors to visibility impairment (Tan et al., 2009; Pathak et al., 2009),
51 and thus have been investigated extensively (Yang et al., 2005; Jansen et al., 2014;
52 Pathak et al., 2009). Most existing studies were based on filter sampling and off-line
53 analysis and had limitations in providing detailed insight into the roles the major
54 chemical species played during shorter haze periods.

55 High contributions of secondary inorganic aerosols (SIA, including sulfate,
56 nitrate and ammonium), the predominant water-soluble ionic species in PM_{2.5}, to
57 visibility reduction have been observed in many cities in China (Huang et al., 2014).
58 Gas- or liquid-phase reactions of sulfur dioxide and nitrogen oxides are the primary
59 mechanisms forming aerosol sulfate and nitrate. For the formation of sulfate,
60 homogeneous gas phase reaction of SO₂ with OH radical, and heterogeneous reactions
61 in the aqueous surface layer of pre-existing particles and in-cloud processes are the
62 primary mechanisms (Wang et al., 2006). The rates of gas-phase and liquid-phase
63 reactions of SO₂ were similar in summer while the heterogeneous processes were
64 responsible for the oxidation in winter (Hewitt, 2001). Nitric acid can be formed from
65 homogeneous gas-phase reactions of NO₂ with OH or O₃ and from heterogeneous
66 hydrolysis of N₂O₅, which occurred predominantly during daytime and nighttime,
67 respectively (Khoder, 2002). Both sulfuric acid and nitric acid react with alkaline
68 substance in the atmosphere, mostly ammonia under ambient conditions to produce
69 salts (Hewitt, 2001). The neutralization of sulfuric acid by ammonia has been found to
70 be preferred over the formation of ammonium nitrate (Warneck, 1999). Thus, the
71 formation of ammonium nitrate in fine particles is usually under significantly
72 neutralized or ammonium-rich conditions (Pathak et al., 2009). There are various
73 factors influencing the formation of aerosol sulfate and nitrate, such as the levels of

74 gaseous precursors (SO_2 , NH_3 , NO_x) and oxidants, the characteristics of pre-existing
75 aerosols, and meteorological conditions. These factors may vary by location, resulting
76 in different formation mechanism in different areas. For instance, different formation
77 pathways had been reported for nitrate in ammonia-rich and ammonia-deficient areas
78 (Pathak et al., 2009).

79 In January 2013, extremely severe, persistent and widespread haze weather
80 occurred in 10 provinces in central and eastern China. These serious pollution events
81 not only had great adverse effects on human health, as seen in a sharp increase in
82 respiratory diseases, but also caused immeasurable economic loss (Huang et al., 2014;
83 Chen et al., 2013). High secondary inorganic and organic aerosol contributions to
84 particulate pollution during these haze events were reported in a recent study based on
85 the measurements at urban sites in Beijing, Shanghai, Guangzhou and Xi'an, which
86 located in the northern, eastern, southern and western regions of China, respectively
87 (Huang et al., 2014). In addition to investigating primary particulate emissions, the
88 formation mechanisms of these secondary species and related affecting factors also
89 need to be understood in order to controlling $\text{PM}_{2.5}$ levels in China.

90 The Yangtze River Delta (YRD), the Pearl River Delta,
91 Beijing–Tianjin–Tangshan, and the Sichuan Basin are the four regions with heaviest
92 haze influence in China. The characteristics and formation mechanisms of haze in the
93 YRD are different from other haze regions, such as Beijing and the Pearl River Delta
94 (Fu et al., 2008). Suzhou is located in the heartland of YRD region and is an important
95 city. It suffered from the extremely serious aerosol pollution in Jan. 2013. With the
96 tremendous economic growth over the past 30 years, Suzhou has experienced high
97 levels of air pollution as reflected in the frequency of haze occurrence. The annual
98 haze days in Suzhou increased from only two days to more than 150 days from 1956
99 to 2011, i.e. over 40% of days were hazy in 2011. The low visibility, particularly the
100 haze, has become a major concern of the city. However, only a few studies have
101 focused on haze events in Suzhou and little is known about the chemical
102 characteristics and sources of fine particles in this city. To fill these knowledge gaps,

103 an intensified monitoring campaign was launched from December 2012 to January
104 2013 to collect high temporal resolution chemical and meteorological data. The
105 objectives of this study are to (1) identify the dominant species in PM_{2.5} and
106 responsible for the visibility reduction; (2) explore the formation mechanism of the
107 aerosol pollution; (3) study the impact of local, nearby and remote sources on the
108 formation of haze in urban Suzhou.

109

110 **2. Methodology**

111 **2.1 Field observations**

112 The sampling station was set up at the roof of one building in Suzhou Institute of
113 Environmental Sciences (31°20'N, 120°36'E) (Fig. 1), about 300 m west to Nanyuan
114 South Road and 360 m north to S Ring Road Elevated Bridge. There is no industrial
115 source nearby and the site is representative of an urban residential and commercial
116 environment. Suzhou is located in the center of Yangtze River Delta (YRD) and about
117 80 km east of Shanghai and 200 km west of Nanjing.

118 On-line hourly PM_{2.5} mass concentrations were measured using tapered element
119 oscillating microbalance (TEOM1405, Thermo Scientific Corp., MA, US) with the
120 heating temperature of 50 °C. Some of the volatile particulate matter might be lost at
121 50 °C, but comparisons with collocated filters showed that the loss was less than
122 10%-20% of the gravimetric mass (Chow et al., 2008).

123 Hourly real-time concentrations of five cations (Na⁺, K⁺, NH₄⁺, Ca²⁺, and Mg²⁺)
124 and four anions (F⁻, Cl⁻, NO₃⁻, and SO₄²⁻) in PM_{2.5} were determined by URG Series
125 9000 Ambient Ion Monitor (AIM, URG Corporation, Chapel Hill, NC). The system
126 consists of a particle collection unit and two ion chromatograph analyzers for cation
127 and anion analyses. PM_{2.5} was separated by a sharp-cut cyclone inlet operating at a
128 flow rate of 3 L/min. The air was drawn through a liquid diffusion parallel-plate
129 denuder to remove the interfering acidic and basic gases. A Steam-Jet Aerosol

130 Collector was placed downstream of the denuder for collection and extraction of
131 particles. The water extract was subsequently injected into the two ICs once an hour.
132 The estimated uncertainties of the AIM measurements were approximately less than
133 15% (Trebs et al., 2004; Pathak et al., 2011). Some measures were taken out to reduce
134 error, for instance, standards solutions were periodically injected to check the
135 consistency of sensitivity of the detectors and air flow rate is frequently checked using
136 a calibrated flow meter.

137 A semi-continuous OC/EC analyzer (Sunset Laboratory, Forest Grove, Oregon,
138 USA) was applied to determine the carbonaceous species in PM_{2.5}. This instrument
139 used the thermal-optical transmittance method based on NIOSH Method 5040.
140 Organic compounds were vaporized in pure helium and then oxidized to CO₂ in a
141 manganese dioxide oxidizing oven. CO₂ was then quantified by non-dispersive
142 infrared detector. EC was then desorbed in an oxygen blend carrier gas and then
143 oxidized and quantified using the same method as for OC. The split point between the
144 pyrolyzed carbon formed from the organic carbon during the heating and EC that was
145 originally in the sample was determined by measuring the transmission of a laser
146 beam through the filter. Known volume of methane was injected, oxidized and
147 quantified as an internal standard. Good correlations were found between the data
148 measured by this instrument and filter-based laboratory analyses (Bae et al., 2004).

149 Visibility was monitored using the Belfort Model 6000 Visibility Sensor (Belfort
150 Instrument Corp., MD, US). Trace O₃, SO₂, NO-NO₂-NO_x and CO gases were
151 obtained with a resolution of 1 h by applying online analyzers (Thermo Instruments,
152 TEI 49i, 43i, 42i and 48i, respectively). Meteorological parameters were collected
153 using Met Station One (Met One Corp., OR, US).

154

155 **2.2 Data analysis methods**

156 **2.2.1 Reconstruction of the light extinction coefficient**

157 The light extinction (b_{ext}) which is the sum of light scattering by particle ($b_{\text{s,p}}$),
 158 absorption by particle ($b_{\text{a,p}}$), scattering by gas ($b_{\text{s,g}}$), and absorption by gas ($b_{\text{a,g}}$), is
 159 reconstructed according to the revised IMPROVE algorithm as following (Pitchford et
 160 al., 2007):

$$\begin{aligned}
 161 \quad b_{\text{ext}} &= b_{\text{s,p}} + b_{\text{a,p}} + b_{\text{a,g}} + b_{\text{s,g}} \\
 162 \quad &\approx 2.2 \times f_{\text{s}}(\text{RH}) \times [\text{Small } (\text{NH}_4)_2\text{SO}_4] + 4.8 \times f_{\text{L}}(\text{RH}) \times [\text{Large } (\text{NH}_4)_2\text{SO}_4] \\
 163 \quad &+ 2.4 \times f_{\text{s}}(\text{RH}) \times [\text{Small } \text{NH}_4\text{NO}_3] + 5.1 \times f_{\text{L}}(\text{RH}) \times [\text{Large } \text{NH}_4\text{NO}_3] \\
 164 \quad &+ 2.8 \times [\text{Small OM}] + 6.1 \times [\text{Large OM}] \\
 165 \quad &+ 1 \times [\text{Fine Soil}] + 1.7 \times f_{\text{ss}}(\text{RH}) \times [\text{Sea Salt}] \\
 166 \quad &+ 0.6 \times [\text{Coarse Mass}] + 10 \times [\text{EC Mass}] \\
 167 \quad &+ 0.33 \times [\text{NO}_2 \text{ (ppb)}] + \text{Rayleigh Scattering} \quad (1)
 \end{aligned}$$

168 where $f_{\text{s}}(\text{RH})$ and $f_{\text{L}}(\text{RH})$ are the water growth factors for small- and large-sized
 169 distribution of sulfate and nitrate, respectively, and $f_{\text{ss}}(\text{RH})$ is the water growth factor
 170 for sea salt. Water growth factors are adopted according to Pitchford et al. (Pitchford
 171 et al., 2007). The constant numbers in the above equation are extinction efficiencies
 172 for each chemical species under dry condition. $(\text{NH}_4)_2\text{SO}_4$ mass is estimated as 1.38
 173 times of SO_4^{2-} mass and NH_4NO_3 mass 1.29 times of NO_3^- mass assuming that SO_4^{2-}
 174 and NO_3^- are fully neutralized by NH_4^+ in the forms of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 ,
 175 respectively, according to the revised IMPROVE method. Organic matter (OM) is
 176 estimated as 1.8 times of OC concentration to account for unmeasured fractions.

177 The concentrations of sulfate, nitrate, and OM are divided into small- and
 178 large-sized fractions in this algorithm. The size modes are described by log-normal
 179 mass size distributions with geometric mean diameter and geometric standard
 180 deviations. Concentrations of sulfate, nitrate, and OM in the large- and small-mode
 181 are estimated using the following equations (taking sulfate as an example):

$$182 \quad [\text{Large } (\text{NH}_4)_2\text{SO}_4] = [\text{Total } (\text{NH}_4)_2\text{SO}_4]^2/20, \text{ for } [\text{Total } (\text{NH}_4)_2\text{SO}_4] < 20 \mu\text{g m}^{-3} \quad (2)$$

$$183 \quad [\text{Large } (\text{NH}_4)_2\text{SO}_4] = [\text{Total } (\text{NH}_4)_2\text{SO}_4], \text{ for } [\text{Total } (\text{NH}_4)_2\text{SO}_4] > 20 \mu\text{g m}^{-3} \quad (3)$$

184 $[\text{Small } (\text{NH}_4)_2\text{SO}_4] = [\text{Total } (\text{NH}_4)_2\text{SO}_4] - [\text{Large } (\text{NH}_4)_2\text{SO}_4]$ (4)

185

186 **2.2.2 Air mass back trajectory**

187 To study the impact of local and regional sources on the aerosol pollution in Suzhou,
188 48-h back trajectories starting at 100 m from the sampling site were calculated using
189 the NOAA HYSPLIT model (http://ready.arl.noaa.gov/HYSPLIT_traj.php). The back
190 trajectories were calculated four times per day at starting times of 04:00, 10:00, 16:00,
191 and 22:00 UTC, i.e. 12:00, 18:00, 00:00, and 06:00 local times, respectively. The
192 trajectory cluster analysis was based on the GIS-based software TrajStat (Wang et al.,
193 2009).

194

195 **2.2.3 Potential source contribution function**

196 The potential source contribution function (PSCF) method is based on the results of
197 HYSPLIT model and can be used to identify the regional sources. The zone of
198 concern is divided into $i \times j$ small equal grid cells. The PSCF value for the ij th grid
199 cell is calculated as: $\text{PSCF}_{ij} = m_{ij}/n_{ij}$, where n_{ij} is designated as the number of
200 trajectory segment endpoints that fall in the ij th cell and m_{ij} is defined as the number
201 of trajectory endpoints with pollutants concentrations higher than an set criterion
202 (Ashbaugh et al., 1985; Wang et al., 2009). In present study, the average
203 concentrations were treated as the criterion (Hsu et al., 2003). The PSCF values were
204 multiplied by a weighting function W_{ij} to reduce the effect of small values of n_{ij} and to
205 better reflect the uncertainty in the values for the cells with small n_{ij} values. The
206 weighting function W_{ij} is defined as follows (Polissar et al., 1999):

207
$$W_{ij} = \begin{cases} 1.00, & 80 < n_{ij} \\ 0.70, & 20 < n_{ij} \leq 80 \\ 0.42, & 10 < n_{ij} \leq 20 \\ 0.05, & n_{ij} \leq 10 \end{cases}$$

208

209 The PSCF value can be interpreted as the conditional probability that air masses
210 with pollutants concentration greater than the set criterion pass through the *ij*th cell
211 during transport to the receptor site (Wang et al., 2009). That is, cells with high PSCF
212 values are indicative of regions having high potential contributions to the pollution at
213 the receptor site.

214

215 **3. Results and discussion**

216 **3.1 General characteristics of haze events**

217 As illustrated in Fig. 2, the visibility varied from a few hundred meters to more than
218 50 km with a minimum value of only 322 m on Jan. 15, 2013, which was
219 accompanied by high RH (82%). During the 2-month observation period, there were a
220 total of ten periods when visibility was below 10 km. Excluding the five periods
221 accompanied by precipitation, the other five periods were identified as haze events
222 and all of these events occurred in January 2013. During the haze occurrence, hourly
223 concentrations of PM_{2.5} often exceeded 150 $\mu\text{g m}^{-3}$, with a maximum concentration of
224 324 $\mu\text{g m}^{-3}$ observed on Jan. 14, 2013. These concentrations were generally higher
225 than those in normal periods. The daily concentrations of PM_{2.5} on haze days varied
226 from 148 to 196 $\mu\text{g m}^{-3}$, which were 1.97 to 2.61 times the Grade II criteria of the
227 national ambient air quality standard (75 $\mu\text{g m}^{-3}$). These values were comparable to
228 that observed in Nanjing where the average PM_{2.5} was 175.6 $\mu\text{g m}^{-3}$, but slightly
229 higher than those in some other cities in YRD where mean values were generally
230 lower than 147.3 $\mu\text{g m}^{-3}$ when haze occurred in Jan. 2013 (Wang et al., 2014a; Wang
231 et al., 2014d). The aerosol pollution happened in northeast China such as in Beijing,
232 Tianjin, and Shijiazhuang were much severer, for instance, the daily and hourly
233 concentrations of PM_{2.5} were up to 368 $\mu\text{g m}^{-3}$ and 462 $\mu\text{g m}^{-3}$ in Tianjin in January 9
234 to 13, 2013, and the maximum hourly value of approximately 1000 $\mu\text{g m}^{-3}$ was
235 recorded in Beijing and Shijiazhuang in Jan. 2013 (Ji et al., 2014; Han et al., 2014;
236 Wang et al., 2015).

237 Approximately 40% of the time in January 2013 met haze weather criteria,
238 whereas no haze appeared in December 2012. Low amount of rainfall in January
239 might be one of the factors causing the long duration of haze. Relative humidity (RH)
240 was reported to be an important contributor to the visibility reduction. In the present
241 study, visibility decreased with increasing RH, e.g. when RH increased from 42% to
242 78%, visibility decreased from 42 km at 2:00 p.m. on 17 January to 4 km at 7:00 a.m.
243 on 19 January. Statistically, RH was relatively higher during haze occurrence than
244 clear periods. Low wind speed, smaller than 5 m s^{-1} , was frequently observed during
245 this winter. Furthermore, wind speed was mostly less than 1 m s^{-1} during the haze
246 events, lower than those in Beijing (Yang et al., 2015). Besides, atmospheric pressure
247 was also found to be relatively low during the haze occurrences. The stagnant air, due
248 to low wind speed and pressure, was unfavorable for aerosol horizontal transport or
249 vertical diffusion, and therefore resulted in aerosol accumulation. Therefore,
250 unfavorable weather conditions (high RH, and low rainfall, wind speed and
251 atmospheric pressure) were among the causes forming haze in January 2013 in
252 Suzhou as well as in many other cities (Wang et al., 2014b; Wang et al., 2014c; Wang
253 et al., 2014d; Han et al., 2014; Yang et al., 2015).

254 In order to get more insights of the haze formation in this region, three haze
255 events, which occurred on Jan. 19, from Jan. 21 to 26, and on Jan. 30, respectively,
256 were further discussed below. Generally, the meteorological parameters and aerosol
257 pollution level were comparable during these three haze occurrences, except for the
258 relatively lower RH and higher temperature in the third haze events.

259

260 **3.2 PM_{2.5} chemical composition and light extinction**

261 **3.2.1 PM_{2.5} chemical composition**

262 The temporal variations of the concentrations of water-soluble inorganic ions (WSIIs)
263 are illustrated in Fig. 3. The mean concentration of WSIIIs (including four anions and

264 five cations) was $48.8 \pm 24.6 \mu\text{g m}^{-3}$, accounting for 40% of $\text{PM}_{2.5}$ mass concentration,
265 slightly lower than that in Beijing which was $69.4 \pm 55.8 \mu\text{g m}^{-3}$ and accounted for
266 43% of $\text{PM}_{2.5}$ (Tao et al., 2015). SO_4^{2-} was the most abundant species in WSIs, with
267 averaged value of $21.1 \pm 13.5 \mu\text{g m}^{-3}$, followed by NH_4^+ ($13.9 \pm 5.69 \mu\text{g m}^{-3}$) and
268 NO_3^- ($10.7 \pm 6.75 \mu\text{g m}^{-3}$), accounting for 43%, 29% and 21% of WSIs, respectively.
269 These secondary inorganic components in total constitute 93% of total WSIs, close to
270 the result in Beijing (Gao et al., 2015; Tao et al., 2015). The rest of ions, Na^+ ($1.36 \pm$
271 $0.43 \mu\text{g m}^{-3}$), K^+ ($0.85 \pm 0.45 \mu\text{g m}^{-3}$), Cl^- ($0.54 \pm 1.28 \mu\text{g m}^{-3}$), Ca^{2+} ($0.34 \pm 0.27 \mu\text{g}$
272 m^{-3}), F^- ($0.06 \pm 0.72 \mu\text{g m}^{-3}$), Mg^{2+} ($0.05 \pm 0.07 \mu\text{g m}^{-3}$), each had minor contribution
273 ($< 3\%$) to WSIs.

274 NO_3^- and SO_4^{2-} are mainly formed from the transformation of their respective
275 gaseous precursor of NO_x and SO_2 (Wang et al., 2005). The emission ratio of NO_x to
276 SO_2 was 17.2–52.6 for motor vehicles and 0.527–0.804 for stationary sources in the
277 Yangtze River Delta, which means that the emissions of SO_2 from motor vehicles
278 were much less than NO_x , but the emissions of SO_2 from stationary sources such as
279 power plants, industrial boilers and furnaces were relatively higher than NO_x (Fu et
280 al., 2008). Thus, the mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ could be used as an indicator of the
281 relative importance of mobile and stationary sources of sulfur and nitrogen in the
282 atmosphere (Arimoto et al., 1996). In the present study, the averaged ratios of
283 $\text{NO}_3^-/\text{SO}_4^{2-}$ and NO_x/SO_2 were 0.59 and 5.68, respectively, indicating that emissions
284 from vehicles and stationary sources were both important in Suzhou. The ratio of
285 $\text{NO}_3^-/\text{SO}_4^{2-}$ in this study was lower than that in Beijing, but higher than those in
286 Shanghai (0.43), Qingdao (0.35), Taiwan (0.20), and Guiyang (0.13) (Wang et al.,
287 2006; Yao et al., 2002; Hu et al., 2002a; Fang et al., 2002; Xiao and Liu, 2004).

288 The $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio was relatively higher for 20% worst visibility hours (0.58)
289 than 20% best visibility hours (0.54), suggesting that vehicle emission might play an
290 important role in haze pollution. This was in agreement with the result in Guangzhou,
291 where the $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio was 1.02 under stagnation and 0.55 in normal days, but
292 contrary to that in Beijing, where the ratio in haze days (0.89) was lower than in

293 normal days (0.96) (Tan et al., 2009; Wang et al., 2006). In present study, NO_x
294 concentration greatly exceeded that of SO₂ during haze period, coincided with the
295 result in Guangzhou, but disagreed with that in Beijing (Tan et al., 2009). Previous
296 studies have indicated that high NO_x emission may reduce the formation of OH and
297 H₂O₂, and further decrease the possibility of SO₄²⁻ formation (Tan et al., 2009). Thus,
298 the elevation of NO₃⁻ concentration under worse visibility conditions was greater than
299 that of SO₄²⁻ in both Suzhou and Guangzhou. The ratios of (NO₃⁻/SO₄²⁻) to (NO_x/SO₂)
300 were lower for worse visibility period, in accordance with that in Beijing, showing
301 that the nitrate concentrations may be also greatly affected by the re-volatilization of
302 NH₄NO₃ (Tan et al., 2009).

303 The carbonaceous species, constituting 22% of PM_{2.5}, were dominated by
304 organic carbon, which was $22.8 \pm 10.6 \mu\text{g m}^{-3}$ and 3 to 29 times of that of elemental
305 carbon ($2.79 \pm 2.58 \mu\text{g m}^{-3}$), similar to those in Beijing (Tao et al., 2015). The
306 relatively high ratios of OC/EC (10.6 ± 4.29), which were higher than the ratios in
307 Beijing (7.1 ± 0.5) and Jinan (7.15 ± 1.78), demonstrated the existence of secondary
308 organic carbon (SOC) (Ji et al., 2014; Zhang et al., 2014). The concentrations of SOC
309 were estimated by applying the EC tracer method, which has been widely used to
310 estimate the secondary organic aerosol contribution to PM_{2.5} concentrations (Castro et
311 al., 1999; Yang et al., 2005). The minimum ratio of OC/EC was 3.09 in the present
312 study. The estimated SOC was $14.2 \pm 5.69 \mu\text{g m}^{-3}$, contributing 65% on average to
313 OC. The SOC/OC was higher than 0.5 during almost the whole sampling period
314 except on Jan. 30 when the third haze event occurred. This ratio was higher than most
315 of the results found in other areas such as in Beijing and Guangzhou (Yang et al.,
316 2005; Tan et al., 2009).

317 Major components in PM_{2.5} were found to be SO₄²⁻ (17%), SOC (14%), NH₄⁺
318 (12%), NO₃⁻ (8%), and POC (6%). The top four components were mainly from
319 secondary sources. PM_{2.5} was significantly correlated with these secondary species,
320 revealing that gas to particle conversion was severe in winter and had great impact on
321 aerosol pollution in this region. It's worth noting that the aerosol composition in the

322 third haze event was distinct from the other two (Fig. 3) as seen from the higher
323 proportion of carbon species from primary emissions (POC and EC) and lower
324 fraction of secondary formation components (SIA and SOC), indicating different haze
325 formation mechanism in the third haze event.

326

327 **3.2.2 Light extinction coefficient**

328 In order to determine the contribution of PM_{2.5} constituents to the visibility
329 degradation, light extinction (b_{ext}) was reconstructed based on the revised IMPROVE
330 algorithm. In the present study, the impact of fine soil and coarse mass were not
331 included because of the lack of metal elements and coarse matter concentrations. The
332 estimated b_{ext} was $664 \pm 288 \text{ Mm}^{-1}$ and was significantly correlated with PM_{2.5}
333 concentrations ($r = 0.94$, $p < 0.001$), demonstrating the strong influence of fine
334 aerosols on visibility degradation.

335 The reconstructed light extinction coefficient was compared with that derived
336 from visibility and that calculated using a regression model developed by Chen.
337 Extinction coefficient is inversely correlated with visibility according to the
338 Koschmieder equation ($\text{Vis} = K/b_{\text{ext}}$) (Seinfeld and Pandis, 2012). By using a K value
339 of 3.912, the calculated b_{ext} was $371 \pm 234 \text{ Mm}^{-1}$, much lower than the coefficients
340 obtained from IMPROVE algorithm. Nevertheless, they were significantly correlated
341 with each other ($r = 0.71$, $p < 0.001$). Another method applied here to estimate b_{ext}
342 was a 2-factor parameterization regression model based on RH and aerosol volume
343 concentration (Chen et al., 2012). The volume concentration can be acquired from the
344 mass concentration divided by an average particle density of 1.7 g cm^{-3} (Wehner et al.,
345 2008). A comparison of b_{ext} reconstructed by IMPROVE algorithm and the regression
346 model is presented in Fig. 4. Generally, a strong correlation was evident with a
347 correlation coefficient higher than 0.97 ($R^2 = 0.952$), confirming that the reconstructed
348 b_{ext} from the IMPROVE algorithm was reliable. The majority of b_{ext} was clustered
349 near the 1:1 line for $b_{\text{ext}} < 500 \text{ Mm}^{-1}$, with the corresponding RH mainly below 75%.

350 However, for $b_{\text{ext}} > 500 \text{ Mm}^{-1}$, the dispersion of b_{ext} gradually increased, and most of
351 the corresponding RH was higher than 75%. There are two possibilities causing these
352 deviations. The first one is the ignorance of the impact of particle size distribution on
353 light extinction in the 2-factor parameterization model applied here, as the variation of
354 aerosol mass or volume fractions of different size particles can influence b_{ext} value
355 especially under high RH (Chen et al., 2012). The second one is from the
356 uncertainties of in situ measurements since RH sensor may have large errors under
357 high RH condition. The regression model result was directly controlled by the RH
358 value, and the hygroscopic growth factor in the IMPROVE algorithm depends on RH.

359 The light extinction was mostly influenced by aerosol light scattering as the
360 estimated $b_{\text{s,p}}$ was $609 \pm 277 \text{ Mm}^{-1}$, accounting for 91% of b_{ext} , while $b_{\text{a,p}}$ and the
361 extinction coefficient by gaseous were only $27.9 \pm 25.8 \text{ Mm}^{-1}$ and $26.6 \pm 4.87 \text{ Mm}^{-1}$,
362 respectively. The largest contributor to b_{ext} from the reconstructed chemical species in
363 fine particles was organic matter (OM), accounting for 40%, followed by $(\text{NH}_4)_2\text{SO}_4$,
364 34%, NH_4NO_3 , 16%, and EC, 4%. However, the percentage contributor varied greatly
365 during the study period, e.g. the contributions of NH_4NO_3 ranged from only 3% to up
366 to 40%. Generally, the contributions of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 were higher under
367 low visibility period, increased from 30% and 11%, respectively, during the 20% best
368 visibility periods to 39% and 19%, respectively, during the 20% worst visibility
369 period. Correspondingly, the contributions of OM and EC reduced from 46% and 5%,
370 respectively, to 35% and 4%, respectively, during the same periods. These results
371 indicated the important role sulfate and nitrate played on haze formation.

372 The percentage contribution to light extinction from individual aerosol
373 components also varied with haze event and visibility conditions. The percentage
374 contributions of individual components during the best and worst 20% visibility hours
375 in each of the three haze events are compared and shown in Fig. 5. During the first
376 haze event (on Jan. 19), the contribution of NH_4NO_3 was 8% and 24% during the 20%
377 best and worst visibility hours, respectively, while the corresponding numbers are
378 48% and 37% for OM. There were no significant differences between the two

379 visibility categories for the contributions of $(\text{NH}_4)_2\text{SO}_4$ or EC. During the second haze
380 event (from Jan. 21 to 26), the fractions were 1.8, 1.5 and 1.3 times higher for
381 NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$ and EC respectively but 1.2 times lower for OM under 20%
382 worst visibility condition than those under 20% best visibility condition during this
383 time. Overall, $(\text{NH}_4)_2\text{SO}_4$ made great contribution to the light extinction and NH_4NO_3
384 had largest difference between 20% best and worst visibility conditions during these
385 two haze events. Therefore, secondary inorganic aerosols especially NH_4NO_3 was
386 likely the key component for the impaired visibility for these two haze events. The
387 elevated proportion of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 during the heavy polluted period was
388 also observed in Beijing (Tao et al., 2015; Wang et al., 2015; Zheng et al., 2015). A
389 different trend of comparison between the best and worst visibility periods was found
390 in the third haze event (on Jan. 30) than in the first two. In the third event, the
391 percentage contributions of OM and EC increased during the worst visibility period
392 compared to the best visibility period (from 40% to 49% and 6.8% to 11%,
393 respectively), while that of $(\text{NH}_4)_2\text{SO}_4$ decreased (from 28% to 19%). Carbonaceous
394 components played a more important role for visibility reduction in the third event.
395 Therefore, there seems to be different formation mechanisms for haze events in
396 Suzhou.

397

398 **3.3 Conversion from gas to particle phase**

399 **3.3.1 Variations of aerosol particles and precursors**

400 Fig. 6 diagrammed the diurnal variations of meteorological parameters, various
401 aerosol components, gaseous precursors, and some other important gaseous species
402 under three different visibility conditions: (1) all data, (2) visibility ≤ 10 km, and (3)
403 visibility > 10 km. The daily variations of gas-phase compounds were different
404 between species and were mainly controlled by the direct surface emissions (such as
405 NO_x , SO_2 , and CO) or photochemical process (O_3). There were a distinct morning
406 peak and a less distinct afternoon peak, consistent with morning and afternoon rush

407 hours for NO_x and CO. This might be related to the heavy traffic emissions in the
408 rush hours and the strong elevation of the Planetary Boundary Layer heights at noon.
409 In contrast, there was only one mid-day peak for SO₂. This diurnal profiles were
410 similar to those observed in Guangzhou (Hu et al., 2002b) and Maryland (Antony
411 Chen et al., 2001). In the latter study, the dominant source of SO₂ was considered to
412 be the long range transport from the industrialized Midwest and with the deep
413 boundary layer around noon; SO₂ aloft mixed more effectively down to the surface
414 and thus caused the mid-day peak of SO₂. The reasons for the diurnal variation of SO₂
415 observed in the present study need further investigation. Similar to the diurnal
416 distribution of SO₂, O₃ also showed one distinct peak around noon due to the strong
417 photochemistry at that time (Quan et al., 2014).

418 For the aerosol components, EC which was also produced by the surface
419 emissions showed a profile similar to NO_x and CO. Furthermore, EC had
420 significantly positive correlation with NO_x and CO, demonstrating that they had
421 common sources, mainly from vehicular exhaust. The diurnal profiles of the
422 secondary species were similar to their precursors but obviously affected by other
423 factors such as solar radiation, which could promote the oxidation of the precursors.
424 For instance, there was a 2-hour delay for sulfate to reach its peak compared to SO₂
425 due to the transformation processes. This pattern was also observed in Guangzhou
426 (Hu et al., 2002b). NO₃⁻ and SOC exhibited similar diurnal variation as their
427 precursors had common sources and they both formed from secondary photochemical
428 oxidation. The daily profiles of NO₃⁻, NH₄⁺ and SOC showed lower concentrations
429 around 15:00 (local time) probably due to the high boundary layer and/or low
430 concentration of precursors. Besides, for NO₃⁻ and NH₄⁺, high temperature, which
431 enhanced the evaporative loss, and low relative humidity may also be responsible for
432 the low levels.

433 Fig. 6 also suggested that both gas-phase compounds and aerosol components all
434 showed similar patterns of diurnal variations but had different magnitudes of
435 concentrations for different visibility levels. These components except for O₃ all

436 showed relatively higher concentrations under low visibility especially for the
437 secondary inorganic species, indicating the important impact of the formation of
438 secondary components on the visibility reduction. The relatively low levels of O₃
439 under low visible conditions might be due to the decreased photochemical production
440 and the chemical conversions of SO₂ and NO_x to sulfate and nitrate. It is worth noting
441 that the relatively high humidity which favored the formation of sulfate and nitrate
442 was observed under low visibility conditions. In addition, it seemed that low visibility
443 was associated with southwest wind. This might related to the topography. There are
444 mountains located on the southwest which is not conducive to the diffusion of
445 pollutants.

446 In consideration of the distinct aerosol composition during the third haze, the
447 comparison of gaseous pollutants between the third and the first two haze episodes
448 were made. The concentrations of SO₂ and O₃ were comparable for these three haze
449 event. Contrarily, much higher levels of NO, CO and NO₂ were evident during the
450 third haze, in accordance with the high concentrations of POC and EC. These species
451 (NO, CO, NO₂, POC and EC) had good correlations with each other. Furthermore,
452 they had similar diurnal variations and exhibited extremely high levels in the morning
453 rush hours on January 30 when the third haze occurred. These results implied that
454 there were common sources for these species, mainly from vehicle exhaust emission.

455

456 **3.3.2 Formation mechanisms of sulfate and nitrate**

457 As discussed earlier, the chemical formation of sulfate and nitrate from SO₂ and NO₂
458 respectively, should play important roles for visibility reduction, especially for the
459 first two haze events. The sulfur oxidation ratio, defined as $SOR = n\text{-SO}_4^{2-} / (n\text{-SO}_4^{2-} +$
460 $n\text{-SO}_2)$ and the nitrogen oxidation ratio, defined as $NOR = n\text{-NO}_3^- / (n\text{-NO}_3^- + n\text{-NO}_2)$
461 were used as indicators of the secondary transformation processes. The daily
462 variations of NOR showed similar patterns as those of NH₄⁺ and NO₃⁻. Likewise,
463 SOR had similar diurnal changes as SO₄²⁻. The values of SOR and NOR increased

464 more than 1.3 and 2.0 times, respectively, during the first two haze periods compared
465 to clear periods, implying greater oxidation of gaseous species and more elevated
466 secondary aerosols. This was supported by the evidently higher concentrations of
467 SO_4^{2-} , NH_4^+ , and NO_3^- in the first two haze events. Almost no elevating levels of SOR,
468 NOR or SIA were observed in the third haze, again confirming that the SIA formation
469 may not be the predominant factor controlling the occurrence of this haze event.

470 The formation of SO_4^{2-} from SO_2 was mainly ascribed to the gas-phase oxidation
471 by OH and H_2O_2 radical or heterogeneous oxidation (Wang et al., 2006; Zhao et al.,
472 2013). The gas-phase reaction is a strong function of temperature and heterogeneous
473 reactions always associated with high RH (Sun et al., 2006; Sun et al., 2014; Sun et al.,
474 2013a). However, weak correlations were found between SOR and either temperature
475 ($r = 0.174$, $p < 0.01$) or RH ($r = 0.150$, $p < 0.01$) in the present study, indicating the
476 complex formation mechanism of sulfate.

477 Many studies suggested that sulfate from aqueous SO_2 oxidation catalyzed by
478 transition metals was more significant during winter haze rather than gas-phase
479 oxidation (Li et al., 2011; Sun et al., 2013b; Zhao et al., 2013). Our measurement also
480 found that the heterogeneous oxidation was an important sulfate formation pathway in
481 this study area. As shown in Fig. 7, high concentrations of NO_2 accompanied with
482 ultralow level of O_3 less than 10 ppb and low amount of solar radiation were observed
483 during most of the time in the haze period, such as from 12 PM to 10 AM on 19
484 January and from 21 to 34 January. These results revealed the rather weak
485 photochemical activities during these time windows. The high levels of NO_2 and
486 weak photochemical activities could result in insufficient production of oxidants (OH
487 and H_2O_2 radicals) for gas-phase oxidation (Hua et al., 2008). Thus, other oxidation
488 reactions other than gas-phase oxidation likely explained the formation of abundant
489 secondary sulfates during the haze episode. The high RH ($> 70\%$) during these haze
490 period was a beneficial factor for aqueous-phase oxidation of SO_2 to sulfate. Besides,
491 the calculation results using the Extended AIM Aerosol Thermodynamic Model
492 (E-AIM, Model II) (Clegg et al., 1998) (<http://www.aim.env.uea.ac.uk/aim/aim.php>)

493 showed a significant increase of the liquid water content when $RH > 70\%$. These
494 results highlight the importance of aqueous-phase reaction to the secondary
495 transformation of SO_2 .

496 The concentrations of O_3 were not extremely low during the whole haze period,
497 such as during daytime on January 23 and 25; the O_3 levels were as usual and had
498 obvious diurnal variations with one distinct peak around noon. RH was lower than
499 70% and sulfate was primarily in the solid phase at these times, indicating that
500 gas-phase oxidation was probably the dominant pathway for sulfate formation.
501 Aqueous-phase oxidation likely became predominant at night. This could explain the
502 high SOR in the afternoon and the sustained high level at night.

503 Nitrate formation is mainly through gas-phase oxidation of NO_2 by OH during
504 daylight and the heterogeneous reactions of nitrate radical during nighttime (Seinfeld
505 and Pandis, 2012). Fig. 8 showed the nitrate-to-sulfate molar ratio ($[NO_3^-]/[SO_4^{2-}]$) as
506 a function of the ammonium-to-sulfate molar ratio ($[NH_4^+]/[SO_4^{2-}]$), which can
507 provide an insight into the formation pathway of the secondary species (Jansen et al.,
508 2014; Pathak et al., 2009; He et al., 2012). The relative abundance of nitrate linearly
509 increased with the increasing ammonium-to-sulfate molar ratio. Fitting a linear
510 regression line resulted in an intercept of $[NH_4^+]/[SO_4^{2-}]$ -axis of 1.51, indicating that
511 nitrate formation via homogeneous reaction of HNO_3 with NH_3 became significant at
512 $[NH_4^+]/[SO_4^{2-}] > 1.51$ (Pathak et al., 2009; Jansen et al., 2014; He et al., 2012). Pathak
513 et al. (2009) also reported an intercept value of 1.5 for several cities worldwide while
514 Jansen et al. (2014) found a slightly smaller intercept value of 1.38 for Hangzhou. The
515 ammonium concentration in excess of the amount at which nitrate formation became
516 evident was defined as excess ammonium ($[NH_4^+]_{exc} = ([NH_4^+]/[SO_4^{2-}] - 1.51) \times [SO_4^{2-}]$).
517 The concentrations of excess ammonium were always higher than 0 and linearly
518 correlated with nitrate concentration, as shown in Fig. 8. This indicated that the
519 formation of nitrate was strongly associated with ammonium formation. In other
520 words, when the excess ammonium was > 0 , the gas-phase homogeneous reaction
521 between the ambient ammonia and nitric acid was responsible for forming nitrate

522 (Pathak et al., 2009; Jansen et al., 2014). The slope of 0.37 for the regression and the
523 scattering of the data indicated that the excess ammonium was bound to species other
524 than nitrate, such as chloride, bisulfate, etc. The significance of gas-phase
525 homogeneous reaction to nitrate formation has been reported for many cities (Jansen
526 et al., 2014; Pathak et al., 2009). However, as mentioned above, in some cases during
527 haze period, the conditions (ultralow ozone concentrations, low solar radiation and
528 high NO₂) were not favorable for the gas-phase oxidation. Relatively high RH were
529 often observed in those cases, which may have favored the gas to particle partitioning
530 of nitrate acid and ammonia (Sun et al., 2011). Furthermore, the E-AIM calculation
531 results manifested that the nitrate partly or completely existed in the aqueous phase
532 during those conditions. Therefore, we assumed that heterogeneous chemistry, such as
533 heterogeneous hydrolysis of N₂O₅ (N₂O₅ + H₂O (aq) → 2HNO₃) or equilibrium
534 partitioning (HNO₃ (g) + NH₃ (g) ↔ NH₄⁺ (aq) + NO₃⁻ (aq)) also contributed to the
535 formation of nitrate under high RH conditions. This was supported by the fact that in
536 Fig. 8 more plots were deviated from the regression line when RH were relatively
537 high. The importance of heterogeneous reactions for nitrate formation were also
538 reported in other studies (Sun et al., 2011; Zheng et al., 2015).

539

540 **3.4 Regional sources deduced from trajectory and PSCF analyses**

541 The regional sources and transport of air pollutants exert a profound impact on local
542 air quality in YRD region as it is located in the typical monsoon region (Ding et al.,
543 2013). Therefore, trajectory clustering method was employed to examine the pathway
544 of air masses and to look into the chemical composition and light extinction
545 coefficients among the air masses with different origination. The calculated 48-h back
546 trajectories were clustered into six clusters (Fig. 9 and Table 1), i.e. six air mass
547 transport pathways. As can be seen, air masses reaching at Suzhou mainly came from
548 local areas, the nearby provinces (cluster 2, accounting 31.7%), and the northwestern
549 areas (cluster 1 and 3, both accounted for 20.6%).

550 High aerosol concentrations were associated with these trajectories. This was
551 reasonable considering that these air masses passed over some highly industrialized
552 cities, such as Hefei, Nanjing, and Hangzhou (Fig. 1). Relatively low levels of PM_{2.5}
553 were related to clusters 5 and 6. Based on the pathways and origins, these air masses
554 were expected to bring in relatively clean air from the East China Sea and the Yellow
555 Sea and consequently reduced the aerosol pollution in Suzhou.

556 Aerosols had high fractions of secondary inorganic ions (39%-42%) and
557 relatively low contributions of OC (15%-16%) when the air masses fell in the C1, C3
558 and C4, while had relatively high percentage of OC (36%) when the air masses fell
559 into the C5. These differences of aerosol concentrations and composition in different
560 clusters may result in distinct light extinction coefficients and species contributions to
561 visibility reduction when air masses originated from different directions (Fig. 9).
562 Similar to PM_{2.5}, the reconstructed b_{ext} was the highest when air masses originated
563 from the Northwest area (C3) and was relatively low when air masses fell into C5 and
564 C6 areas. However, the lowest value of b_{ext} was in the C6 instead of C5 for the lowest
565 PM_{2.5} level, because of the higher contribution of OM in the C5. AS and OM were the
566 dominant species determining the light extinction for all clusters. However, AS was
567 the predominant contributor to light extinction for trajectories from north and
568 northwest (C1, C3, C4), while in other cases the light extinction was primarily
569 affected by OM. AN was the third highest contributor in all trajectory clusters with
570 the largest contribution when air masses originated from northwest.

571 The origins of air masses in different haze events were further analyzed to
572 interpret the relative contributions of chemical species to visibility reduction that
573 differed between haze events. Most air masses fell into C1 and C3 (air masses from
574 north and northwest, respectively) in the first two haze occurrence while all air mass
575 trajectories were in C2 (air masses from local and nearby areas) for the third haze
576 event. The contribution of OM to the total light extinction was higher in the third haze
577 event than in the first two as discussed early, consistent with the results for cluster
578 analysis that the light extinction was primarily impacted by AS for C1 and C3 but by

579 OM for C2. These results manifested that the third haze event was mainly contributed
580 by the primary emission of carbon species from the local and/or surrounding areas.

581 It should be noted that air mass back trajectory analysis only suggests the
582 originations and pathways of air masses but does not directly reveal the exact sources.
583 Based on the results of trajectory analysis, the PSCF method was applied to explore
584 the likely regional sources of major components in PM_{2.5}, including sulfate, nitrate,
585 OC, and EC, as illustrated in Fig. 10. Generally, PM_{2.5} and the five aerosol species in
586 Suzhou were mainly affected by local sources and nearby cities. Specifically, the
587 higher value for PM_{2.5} and the aerosol components were all localized in northwest to
588 the south, covering surrounding cities in Jiangsu and near the border of Anhui and
589 Zhejiang provinces. Additionally, these species were all affected by pollutions from
590 Anhui province. Sulfate, nitrate and ammonium had similar spatial distributions, and
591 relatively more affected by the north and northwest cities in Shandong, Jiangsu and
592 Anhui provinces while pollutions from south cities in Zhejiang province had more
593 impact on OC and EC in studied area than sulfate, nitrate and ammonium.

594

595 **4. Conclusions**

596 Heavy aerosol pollution occurred in Suzhou in January 2013 with daily PM_{2.5}
597 concentrations on haze days 1.97 to 2.61 times higher than Grade II criteria of the
598 national ambient air quality standard (75 $\mu\text{g m}^{-3}$) and maximum value of 324 $\mu\text{g m}^{-3}$
599 on Jan. 14, 2013. Unfavorable weather conditions (high RH, low rainfall, wind speed
600 and atmospheric pressure) especially high RH together with increased air pollutants
601 produced from local and nearby sources were responsible for these haze formation.

602 During the first two haze periods, the major aerosol components were SO₄²⁻,
603 NO₃⁻, NH₄⁺, and SOC, which were mainly from secondary sources. Furthermore,
604 SOR and NOR both increased under worst visibility conditions, revealing efficient
605 gas to particle conversion. Additionally, the contributions of (NH₄)₂SO₄ and NH₄NO₃
606 to the reconstructed b_{ext} based on IMPROVE were higher under low visibility

607 conditions while those of OM and EC were higher under high visibility conditions,
608 indicating that secondary inorganic aerosols especially NH_4NO_3 seemed to be very
609 important for the impaired visibility. Gas-phase homogeneous reaction might
610 dominate the formation of sulfate and nitrate under low RH conditions while
611 heterogeneous process might be responsible when RH were relatively high.

612 Distinctively, high proportion of carbon species from primary emission and
613 lower fraction of secondary formation components were observed in the third haze.
614 The SOR and NOR during the third haze episode were comparable to clean days.
615 Moreover, increasing proportions of OM and EC accompanied with decreasing
616 percentage of $(\text{NH}_4)_2\text{SO}_4$ were found under worst visibility conditions when the third
617 haze occurred. These results suggested that the carbon components from the primary
618 emission might be relatively important for the visibility reduction for this haze event.

619 Trajectory clustering analysis showed that the air quality in Suzhou was mostly
620 affected by air masses originating from North and Southwestern areas which were
621 associated with high aerosol concentrations. Distinct aerosol composition profiles,
622 light extinction coefficients and species contributions to visibility reduction were
623 observed when air masses originated from different directions, e.g. AS was the
624 predominant contributor to light extinction for trajectories from north and northwest,
625 while in other cases the light extinction was primarily affected by OM.

626 The likely sources of aerosol and the major species based on the PSCF method
627 were mainly from local anthropogenic activities and source emissions transported
628 from nearby cities. The northwestern to southern regions may be important sources of
629 aerosols and the major components. The northern and northwestern areas were
630 predominant source regions for sulfate, nitrate and ammonium aerosols, whereas the
631 southern area could be the common source region for carbonaceous species. This
632 information has the implications for the importance of collaborative air pollution
633 control strategy in the Yangtze River Delta Region.

634

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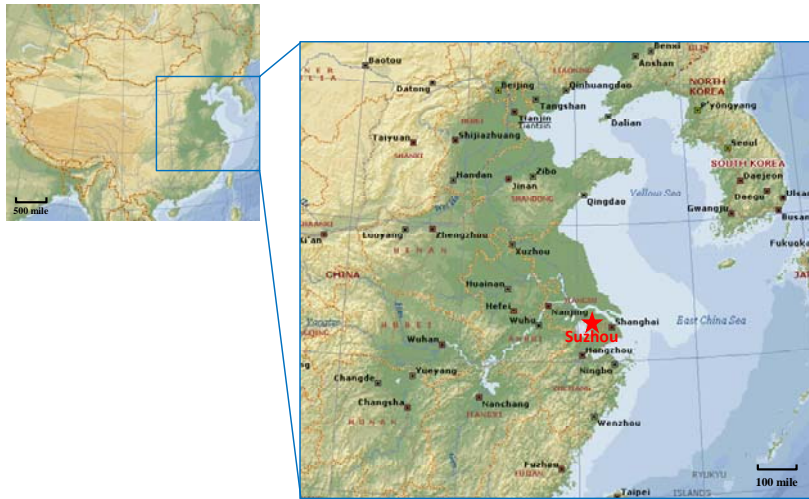
889

890 Table 1. The percentages of air masses from each trajectory cluster and associated
 891 mean concentrations ($\mu\text{g m}^{-3}$) of $\text{PM}_{2.5}$ and its major chemical components, and mean
 892 b_{ext} (Mm^{-1}).

	1	2	3	4	5	6
Percent (%)	20.6	31.7	20.6	12.7	6.3	7.9
$\text{PM}_{2.5}$	129	117	167	103	84.0	87.4
OC	21.1	22.8	25.3	16.4	30.5	20.3
EC	2.05	3.87	2.21	1.45	3.90	1.86
Sulfate	22.9	18.2	32.4	23.1	8.85	8.39
Nitrate	11.5	10.0	16.9	7.84	3.26	7.91
Ammonium	15.2	12.3	18.9	12.4	7.93	9.88
b_{ext}	675	597	921	556	548	463

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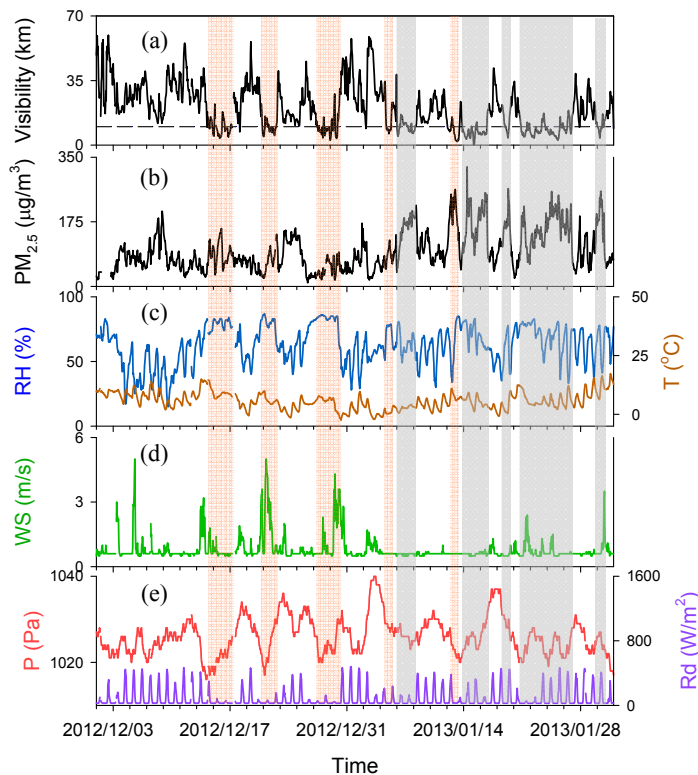
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896 Figure 1. The sampling site in Suzhou. The locations of major cities with a population
 897 of more than 1 million (such as Qingdao, Nanjing and Hangzhou) are marked with a
 898 square symbol. The topographical map was derived from Microsoft® Encarta® 2009
 899 © 1993 – 2008.

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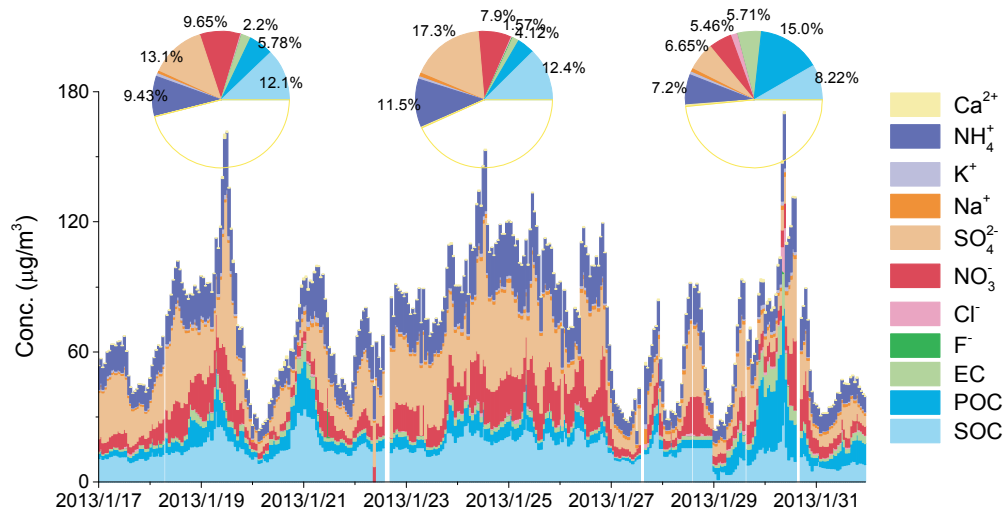


901

902 Figure 2. Time series of (a) visibility; (b) $PM_{2.5}$ concentration; (c) relative humidity
 903 (RH) and temperature (T); (d) wind speed (WS) and pressure (P); and (e) solar
 904 radiation (Rd). The shaded areas in orange represent periods when visibility were

905 lower than 10 km and accompanied by precipitation. The shaded areas in grey
 906 represent haze periods.

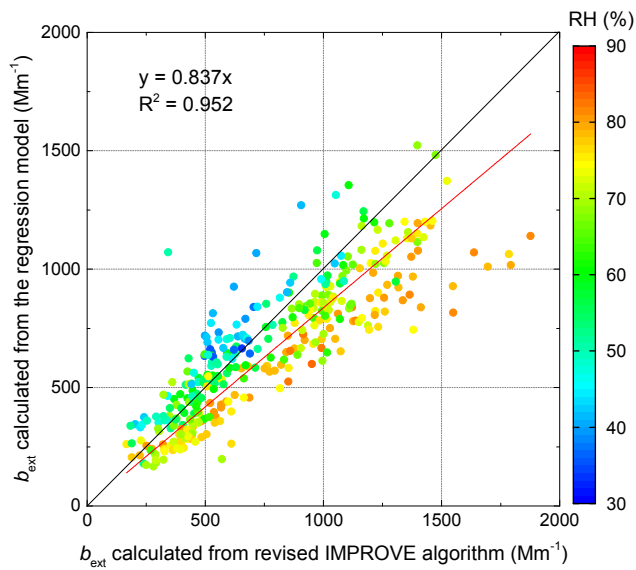
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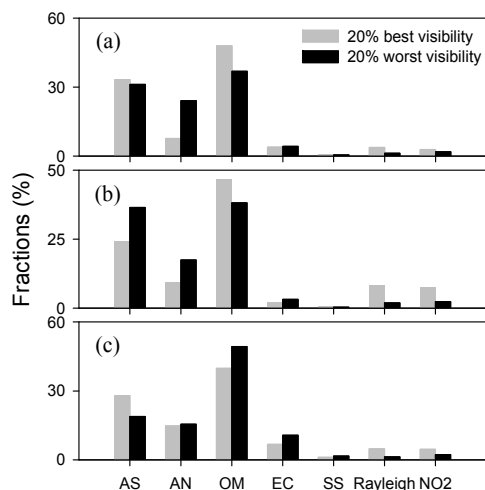
909 Figure 3. Temporal distribution of water soluble inorganic ions and carbonaceous
 910 species. The aerosol composition in the three haze events was also illustrated in the
 911 pie chart.

912



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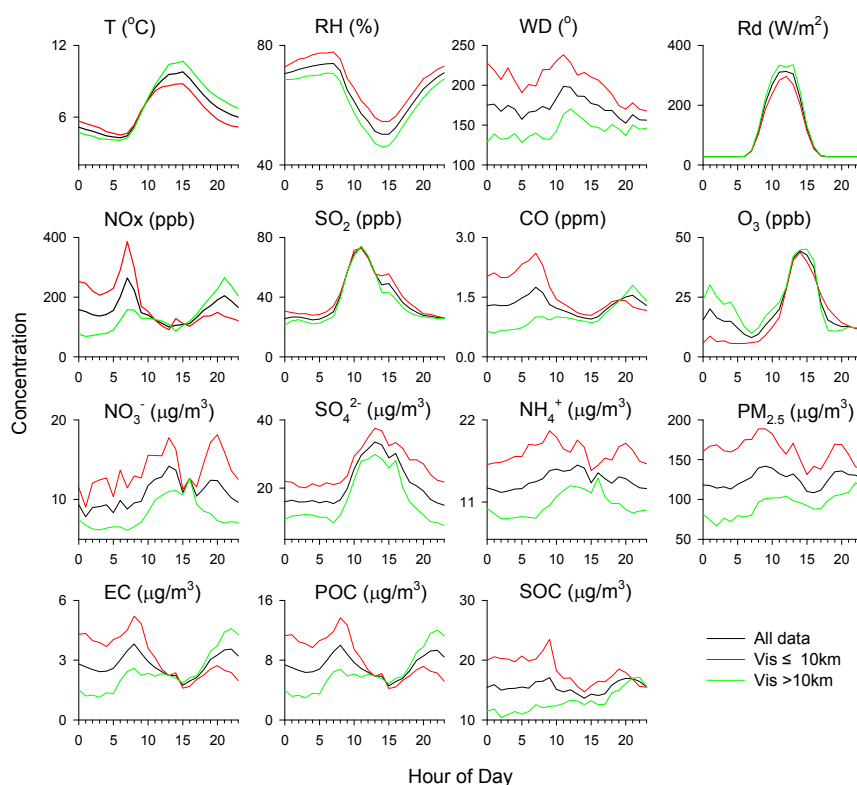
914 Figure 4. Comparison of the calculated b_{ext} between those obtained from the
 915 regression equation and those from the IMPROVE algorithm.



916

917 Figure 5. Relative contributions of various chemical components in PM_{2.5}
 918 (ammonium sulfate (AS), ammonium nitrate (AN), OM, and EC) to the total light
 919 extinction under 20% best and 20% worst visibility conditions during the first (a),
 920 second (b), and third (c) haze events.

921

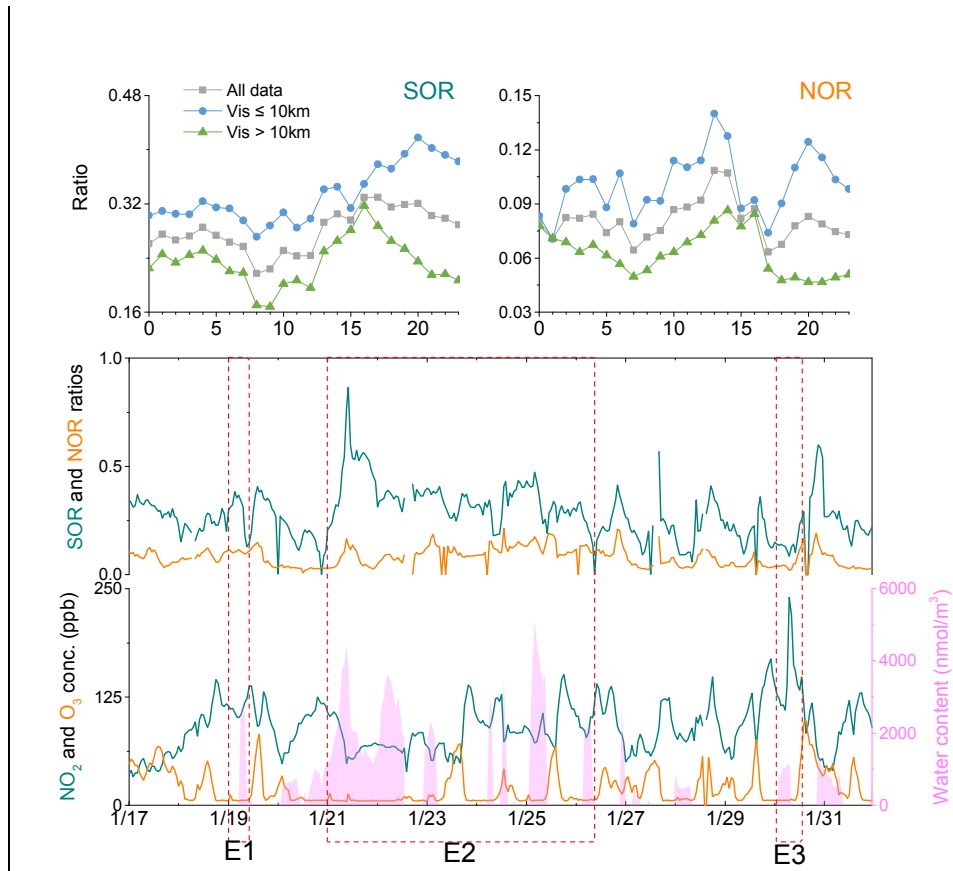


922

923 Figure 6. Diurnal profiles of meteorological variables, aerosol precursors (NO_x, SO₂),
 924 CO, O₃, PM_{2.5}, and major aerosol compounds (NO₃⁻, SO₄²⁻, NH₄⁺, EC, POC, SOC)

925 under different visibility conditions.

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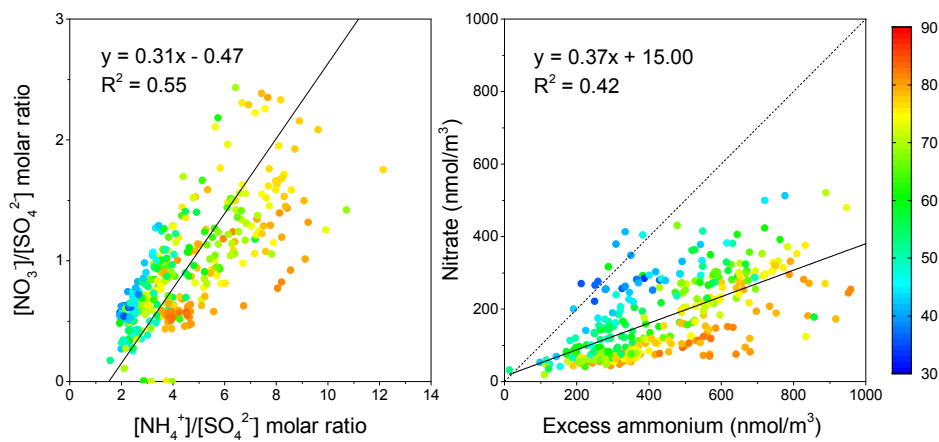


927

928 Figure 7. Temporary distributions of SOR, NOR, NO₂, O₃ and aerosol water content.

929 Diurnal profiles of NOR and SOR ratios under different visibility conditions.

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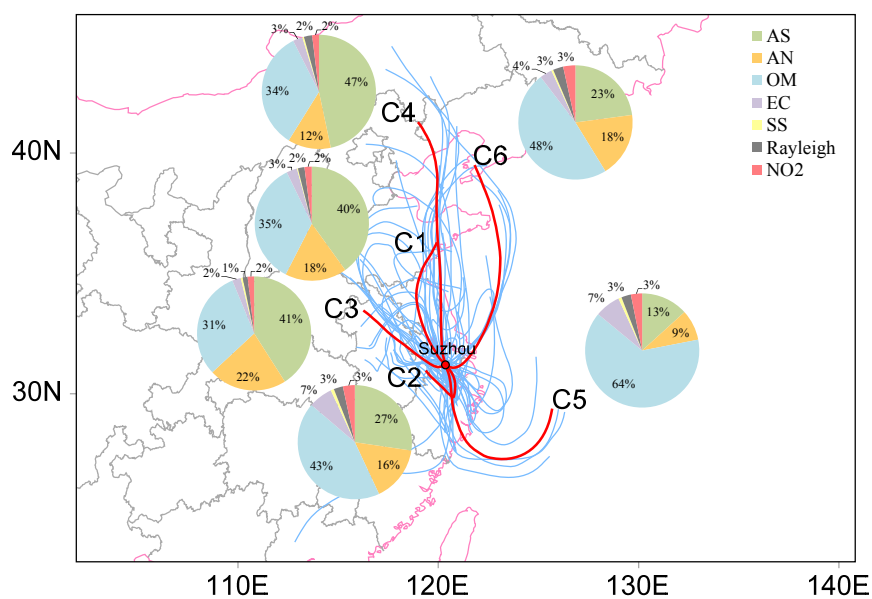
931

932 Figure 8. Nitrate to sulfate molar ratio as a function of ammonium to sulfate molar

933 ratio (left) and relationship between molar concentrations of nitrate and excess

934 ammonium (right).

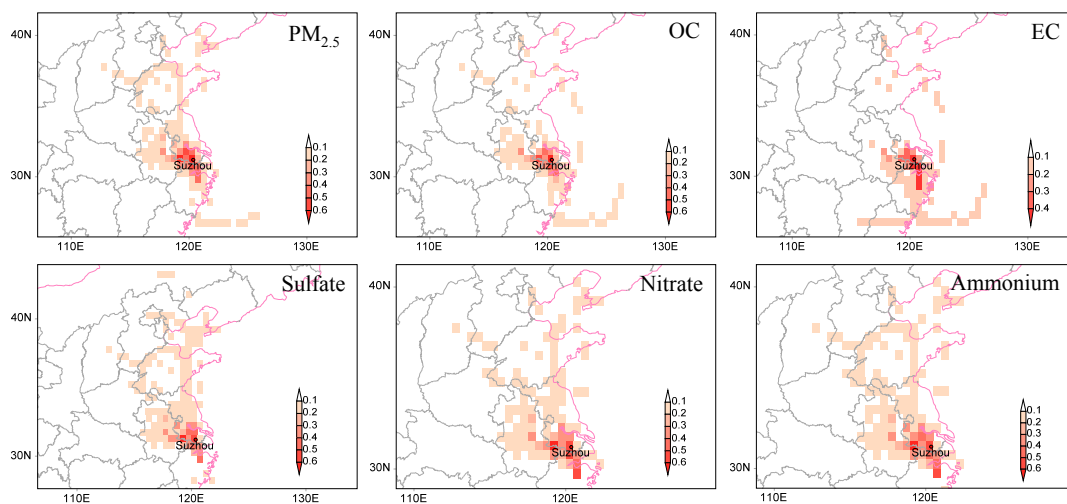
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937 Figure 9. Backward air mass trajectories and six mean trajectories after the cluster
938 analysis at the sampling site during Jan. 17 to 31. Relative contributions of various
939 chemical components to the total light extinction in different clusters are illustrated.

940



941

942 Figure 10. The PSCF maps for PM_{2.5}, OC, EC, sulfate, nitrate, and ammonium.

943