1 # Highly time-resolved urban aerosol characteristics during

2 # springtime in Yangtze River Delta, China: Insights from soot

3 # particle aerosol mass spectrometry

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Abstract: In this work, the Aerodyne soot particle – aerosol mass spectrometer (SP-AMS) was deployed for the first time during the spring of 2015 in urban Nanjing, a megacity in the Yangtze River Delta (YRD) of China, for online characterization of the submicron aerosols (PM_1). The SP-AMS enables real-time and fast quantification of refractory black carbon (rBC) simultaneously with other non-refractory species (ammonium, sulfate, nitrate, chloride and organics). The average PM_1 concentration was found to be 28.2 μg m^{-3}, with organics (45%) as the most abundant component, following by sulfate (19.3%), nitrate (13.6%), ammonium (11.1%), rBC (9.7%) and chloride (1.3%). These PM_1 species together can reconstruct ~44% of the light extinction during this campaign based on the IMPROVE method. Chemically-resolved mass-based size distributions revealed that small particles especially ultrafine ones (<100 nm vacuum aerodynamic diameter) were dominated by organics and rBC, while large particles had significant contributions from secondary inorganic species. Source apportionment of organic aerosols (OA) yielded four OA subcomponents, including hydrocarbon-like OA (HOA), cooking-related OA (COA), semi-volatile oxygenated OA (SV-OOA), and low-volatility oxygenated OA (LV-OOA). Overall, secondary organic aerosol (SOA, equal to the sum of SV-OOA and LV-OOA) dominated the total OA mass (55.5%), but primary organic aerosol (POA, equal to the sum of HOA and COA) can outweigh SOA in early morning and evening due to enhanced human activities. High OA concentrations were often associated with high mass fractions of POA and rBC, indicating the important role of anthropogenic emissions during heavy pollution events. The diurnal cycles of nitrate, chloride and SV-OOA both showed good anti-correlations with air temperatures, suggesting their variations were likely driven by thermodynamic equilibria and gas-to-particle partitioning. On the other hand, in contrast to other species, sulfate and LV-OOA concentrations increased during afternoon, and showed no positive correlations with relative humidity (RH), likely indicating the contribution from photochemical oxidation is dominant over that of aqueous-phase processing for their formations. The bivariate polar plots show that the SV-OOA was formed locally, and

58 the variations of hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios in the

59 Van Krevelen space further suggests an evolution pathway of SV-OOA to LV-OOA.

60 Our findings regarding springtime aerosol chemistry in Nanjing may have important

61 implications for the air quality remediation in the densely populated regions.

62

1. Introduction

64   In recent years, high concentrations of fine particulate matter ($PM_{2.5}$) have been

65 frequently observed (Hu et al., 2015), in accompanying with the visibility impairment

66 and occurrence of haze events across large parts of China. $PM_{2.5}$ also affects human

67 health (e.g., Pope and Dockery, 2006;Cao et al., 2012), regional and global climate

68 directly by absorbing and scattering solar radiation or indirectly by acting as cloud

69 condensation nuclei and ice nuclei (e.g.,Ghan and Schwartz, 2007;Pöschl, 2005), and

70 the earth's ecosystem (Carslaw et al., 2010). These effects are predominantly

71 dependent upon the physical and chemical characteristics of fine particles, such as

72 mass concentration, chemical composition, size distribution, and hygroscopicity, all of

73 which are influenced by the emission sources and transformation and evolution

74 processes in the atmosphere.

75   The Yangtze River Delta (YRD) region is one of the most populated and

76 economically developed areas in China, but it is also facing with severe air pollution

77 lately. Nanjing, as one of the major megacities in this region, has a daily $PM_{2.5}$ mass

78 concentration varying between 33-234 μg m^{-3} during November 2011 - August 2012,

79 with an mean value of 106 μg m^{-3}, which is 4.2 times the WHO air quality standard of

80 25 μg m^{-3} (Shen et al., 2014). $PM_{2.5}$ pollution is significantly elevated during hazy

81 days, for example, a daily average of 282 μg m^{-3} was observed for a heavily polluted

82 day (Fu et al., 2008). A number of studies regarding aerosol chemistry in Nanjing

83 have been conducted, and identified various inorganic components (sulfate, nitrate,

84 ammonium and heavy metals, etc.) (e.g., Wang et al., 2003;Hu et al., 2012;Qi et al.,

85 2016) and hundreds of organic species (carboxylic/dicarboxylic acids, amines and

86 amino acids, polycyclic aromatic hydrocarbons, etc.) (Wang et al., 2011;Wang et al.,

87 2002;Yang et al., 2005;Wang et al., 2009) that contribute to the aerosol mass.

88 However, past studies mostly employed filter-based sampling technique, which due to

89 low time resolution (a few hours to days), is often incapable of capturing details of the

90 atmospheric evolution processes during the typical lifecycle of aerosols (Wexler and

91 Johnston, 2008). Subsequent offline analyses may also introduce artifacts as some

92 semi-volatile species can evaporate during sampling and storage (Dong et al., 2012).

93 On the other hand, in the past 15 years, the Aerodyne Aerosol Mass spectrometer

94 (AMS) (Canagaratna et al., 2007) has been widely used, and was proven to be

95 powerful for real-time online measurements of size-resolved chemical compositions

96 of submicron aerosols (PM_1) with very fine time resolution (seconds to minutes)

97 (Zhang et al., 2007a;Jimenez et al., 2009). The development of Aerodyne AMS began

98 with the invention of quadruple AMS (Q-AMS) (Jayne et al., 2000), following by the

99 compact time-of-flight AMS (C-ToF-AMS) (Drewnick et al., 2005), high resolution

100 time-of-flight AMS (HR-ToF-AMS) (DeCarlo et al., 2006) and the soot particle AMS

101 (SP-AMS) (Onasch et al., 2012). There are also an aerosol chemical speciation

102 monitor (ACSM) (Ng et al., 2011) and its updated version of ToF-ACSM (Fröhlich et

103 al., 2013), which are in particular designed for long-term unattended aerosol

104 measurements. SP-AMS is the most advanced version, which in principle incorporates

105 the single particle soot photometer (SP2) into the HR-ToF-AMS, and upgraded with a

106 laser vaporizer for detecting refractory black carbon (rBC) and associated/coated

107 species that cannot be measured by other types of AMS.

108 Recently, the Aerodyne AMS has been deployed widely in China (particularly

109 Beijing) (e.g., Xu et al., 2014 and references therein;Sun et al., 2014;Yeung et al.,

110 2014;Zhang et al., 2014;Li et al., 2015;Shen et al., 2015;Sun et al., 2015a;Sun et al.,

111 2015b;Yan et al., 2015;Zhang et al., 2015;Tang et al., 2016;Zhang et al., 2016a;Jiang

112 et al., 2015;Chen et al., 2015;Xu et al., 2015;Du et al., 2015;Sun et al., 2016;Wang et

113 al., 2015;Han et al., 2015;Wang et al., 2016b). However, only a few field campaigns

114 were conducted in the YRD region. Huang et al. (2012b) deployed an HR-ToF-AMS

115 together with an SP2 in Shanghai during the 2010 Shanghai World Expo, and in

Jiaxing during summer and winter of 2010 (Huang et al., 2012a). In urban Nanjing, an ACSM was applied for characterizing PM_1 during summer and autumn harvest seasons (Zhang et al., 2015), and during December 2013 to investigate a few heavy haze events (Zhang et al., 2016b). In addition, a Q-AMS was deployed in Nanjing to investigate the effects of PM_1 on visibility during January 2013 (Shen et al., 2015). Furthermore, a recent study by Wang et al. (2016a) reported the observation of fullerene soot in suburban Nanjing using an SP-AMS. Nevertheless, many questions remain unclear with regard to aerosol chemistry, sources, and processes in this region. Moreover, none of the previous AMS measurements studied the aerosol characteristics during springtime in Nanjing, yet the springtime aerosols may have different behaviors than those in other seasons, when aerosols are likely influenced significantly by emissions from biomass burning, coal burning etc. For these reasons, we reports in this work the real-time measurement results on urban fine aerosols in Nanjing using the SP-AMS during spring in 2015. The rich highly-time resolved, highly-chemical resolved mass spectral data, as well as chemically-resolved size distributions of different aerosol species obtained for the first time in Nanjing during this study, can allow us to conduct in-depth analyses, and better understand the characteristics, sources and relevant transformation processes of ambient aerosols. The findings for such a megacity are also valuable to the Pan-Eurasian Experiment (PEEX) infrastructure which aims to resolve the major uncertainties in Earth system science and global sustainability issues (Kulmala et al., 2015).

2. Experiments

2.1 Sampling site and instrumentation

The field campaign was conducted in the environment monitoring station of Nanjing Olympic center (32°0′33.00″N, 118°44′9.53″E, Fig. S1) from April 13 to 29, 2015. Details of the sampling site are shown in Fig. S1. The site was surrounded by residential buildings, close to a few urban arterial roads (~ 85 m northwest of Huangshan Road, ~ 200 m northeast to Mengdu Street and ~425 m southwest of

145 Xinglong Street). There are also a restaurant (~50 m), a student cafeteria (~300 m),

146 and the Nanjing Cigarette Factory (~480 m southeast) around the site.

147   The sampling inlet was installed outside the fifth floor of the building (~12 m

148 above the ground), with a $PM_{2.5}$ cyclone (URG Corp., Chapel Hill, NC, USA) to

149 remove coarse particles. Ambient particles were dried (RH <10%) via a diffusion

150 dryer filled with silica gel before entering into the SP-AMS. The sampling line (~2 m

151 long) was assembled using stainless steel tubing and proper fittings. Air flow was

152 controlled at around ~5 L min^{-1}, with a flow rate into the SP-AMS at ~80 cm^3 min^{-1}.

153   The SP-AMS can measure non-refractory (NR) PM_1 components including

154 ammonium, nitrate, sulfate, chloride and organics similar to other types of AMS via a

155 thermal tungsten heater. Moreover, it can also measure rBC and inorganic/organic

156 species that coated on the rBC cores, as it is equipped with an intracavity Nd:YAG

157 laser vaporizer (1064 nm) (Onasch et al., 2012). During this campaign, the instrument

158 was switched between "laser on" and "laser off" settings, and between V-mode (better

159 for mass quantification) and W-mode (better chemical resolution, ~5000 in this study),

160 with one cycle including six menu settings (M1: Laser on V-mode; M2: Laser off

161 V-mode; M3: Laser on W-mode; M4: Laser off W-mode; M7: Laser on PToF-mode;

162 M8: Laser off PToF-mode). Each menu was set to 2.5 min, thus a full running cycle

163 lasted for 15 mins. The PToF-mode was under V-mode, but was tuned in particular

164 for measuring particle sizes. The tungsten heater was always turned on and kept at

165 ~600°C.

166   The SP-AMS, in conjunction with a scanning mobility particle sizer (SMPS) (TSI

167 inc., Shoreview, MN, USA) was calibrated for mass quantification (e.g., ionization

168 efficiency) using size-selected (250 nm and 300 nm) monodisperse ammonium nitrate

169 particles following the procedures detailed in Jimenez et al. (2003). Pure ammonium

170 sulfate was used to determine the relative ionization efficiency (RIE) of sulfate

171 (Setyan et al., 2012). Quantification of rBC was calibrated using Regal Black

172 (REGAL 400R pigment black, Cabot Corp.) particles according to the procedures

173 reported in Onasch et al. (2012). Note that the solution of Regal Black was sonicated

174 during calibration to maintain a relative stable aerosol flow. RIEs of ammonium,

175 nitrate, sulfate, chloride, organics and rBC were determined to be 3.15, 1.05, 1.20, 1.3,

176 1.4 and 0.33, respectively. On the other hand, particle sizing was calibrated using

177 standard polystyrene latex (PSL) spheres (Duke Scientific Corp., Palo Alto, CA, USA)

178 across 100 - 700 nm range. Flow rate was also calibrated prior to the measurement.

179 Concentrations of gaseous species, e.g., carbon monoxide (CO) (Model T300,

180 Teledyne API, USA), ozone (O_3) (Model EC9810, Ecotech Pty Ltd, Australia),

181 nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) (Model LGH-01, Anhui Landun,

182 China), and meteorological data including air temperature (T), relative humidity (RH),

183 visibility (km), wind speed (WS) and wind direction (WD) were acquired at the same

184 site. $PM_{2.5}$ and PM_{10} mass concentrations were also recorded (BAM-1020, Met One

185 Instruments, Inc., USA), in parallel with the SP-AMS measurement.

186 **2.2 Data treatment and source analyses**

187 The SP-AMS data were post-processed by using the Igor-based standard

188 ToF-AMS Analysis Toolkit SQUIRREL v1.56D and PIKA v1.15D, available at:

189 http://cires1.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.htm

190 l. Note all mass concentrations reported here were calculated from the HR fitted

191 results on V-mode data. A collection efficiency is typically used to account for the

192 particles that aren't collected and measured by the instrument, due to the particles lost

193 during passage through inlet, time-of-flight chamber and bouncing from the vaporizer.

194 For the SP-AMS, the CE of laser vaporizer is mainly governed by particle divergence,

195 while for the tungsten vaporizer, the CE is governed mainly by the bouncing effects

196 (Matthew et al., 2008). A CE value of 0.5 is valid and used commonly for the AMS

197 measurements for most environments (Canagaratna et al., 2007). Nevertheless,

198 Middlebrook et al. (2012) further investigated this issue, and found that high aerosol

199 acidity, high ammonium nitrate, and high sampling line RH can increase the CE, and

200 provide composition-dependent CE parametrization. For our dataset, we found that

201 the composition-dependent CE rather than a constant CE=0.5 has negligible effects on

202 the quantification of aerosol species, as the particles were neutralized (Fig. 3a), the

mass fraction of ammonium nitrate were <40% in almost all cases, and also the sampling line RH was below 10%. And in fact, the PM_1 mass concentrations quantified by using the composition-dependent CE correlate a bit worse with the $PM_{2.5}$ concentrations than ones using CE=0.5. Thus, we a constant CE of 0.5, in consistent with many other AMS studies, was employed for this dataset.

Unless specified, the concentrations of ammonium, sulfate, nitrate, chloride and organics are from M2 setting (tungsten vaporizer only), while the rBC data is from M1 setting (dual-vaporizers: tungsten + laser) in this paper. The meteorological data (RH, T, WS, WD and visibility), concentrations of gas-phase species (CO, NO_2, SO_2 and O_3) and $PM_{2.5}$ were averaged into hourly data for comparisons with the SP-AMS data. The data reported are at local time, e.g., Beijing (BJ) Time.

Positive matrix factorization (PMF) (Paatero and Tapper, 1994) was applied on the high resolution mass spectra (HRMS) of organic aerosol (OA) obtained under laser off W-mode (M4 setting) to elucidate the OA sources/processes. We used the PMF Evaluation Tool version 2.08A (downloaded from: http://cires1.colorado.edu/jimenez-group/wiki/index.php/PMF-AMS_Analysis_Guide) (Ulbrich et al., 2009) to investigate the PMF results by varying the number of factors (from 2 to 8 factors) and rotations ("$f$peak", from -1 to 1 with an increment of 0.1). Only ions with m/z less than or equal to 180 were included in the analyses. Following the instruction detailed by Zhang et al. (2011), the 4-factor solution (at $f$peak = -0.1) was chosen as the optimal solution, as the 3-factor solution cannot separate the hydrocarbon-like OA (HOA) and cooking OA (COA) (Fig. S2). For the 5-factor solution (Fig. S3), Factor 2 and Factor 4 are clearly a split from the SVOOA from the 4-factor solution (r^2 = 0.89 and slope of 1.05); Factor 2 of 5-factor solution also shows much weaker correlations with nitrate than SVOOA of 4-factor solution does (r = 0.07 vs. 0.49). A summary of the key diagnostic plots are provided in Fig. S4. Detailed discussion of the PMF results is presented in Section 3.5. Note we found no significant differences between the PMF source apportionment results from the HRMS of OA (without rBC) obtained with dual-vaporizers setting (M3 setting) and

232   current results (M4 setting, tungsten vaporizer only), as the OA HRMS acquired under

233   these two circumstances were overall very similar (details in Section 3.4).

234   Note the elemental ratios shown throughout the paper were all calculated based

235   on the method proposed by Aiken et al. (2008) (referred to as A-A method). Recently,

236   Canagaratna et al. (2015) improved this methodology by using specific ion fragments

237   as markers to calculate the O/C and H/C ratios (referred to as I-A method). The I-A

238   method increased the O/C ratio, H/C ratio, and the OM/OC ratio from the values

239   calculated from the A-A method, on average, by 28%, 10% and 8%, respectively (Fig.

240   S5). In this work, we used the results from the A-A method for consistency and

241   comparisons with previous AMS measurements.

242

243   **3. Results and discussion**

244   **3.1 Mass concentrations, chemical compositions and diurnal changes**

245   The temporal variations of meteorological parameters, concentrations of the gas

246   pollutants, concentrations and mass fractions of different PM_1 components, and the

247   $PM_{2.5}$ mass loadings (from Met one BAM-1020) over the sampling period are

248   illustrated in Fig. 1. During this study, the mean temperature was 18.5 ^{o}C, RH on

249   average was 64%, and wind predominantly blew from southeast and southwest (Fig.

250   S6). The SP-AMS PM_1 concentrations ranged from 5.1 to 97.9 µg m^{-3}, with an

251   average of 28.2 µg m^{-3}. Note this average PM_1 concentration is significantly lower

252   than those observed during summer (38.5 µg m^{-3}), autumn (46.4 µg m^{-3}) and winter

253   (89.3 µg m^{-3}) (Zhang et al., 2015;Zhang et al., 2016b), showing that the air during

254   springtime in Nanjing is cleaner than in other seasons. The variations of PM_1

255   concentrations also match very well with $PM_{2.5}$ concentrations (Pearson's $r^2 = 0.72$),

256   and on average PM_1 accounts for ~ 54% of the $PM_{2.5}$ mass. This ratio appears to be a

257   bit low, likely due to the uncertainty of CE of the SP-AMS.

258   The average PM_1 composition is shown in Fig. 2a. The most abundant component

259   is found to be organics (45.0%), following by sulfate (19.3%), nitrate (13.6%),

260   ammonium (11.1%), rBC (9.7%) and chloride (1.3%). Fig. 2b further shows changes

261   of the PM$_1$ chemical compositions in different concentration bins. It can be seen that

262   although most PM$_1$ mass loadings are within 10 - 40 μg m^{-3}, high loading periods tend

263   to have higher mass contributions from organics and rBC, and less contributions from

264   secondary inorganic species, indicating that high PM events were influenced

265   significantly by local fresh emissions.

266   The molar ratio of inorganic anions (sulfate, nitrate and chloride) to cations

267   (ammonium) is 1.05 (Fig. 3a) (Zhang et al., 2007b). Considering that a small fraction

268   of sulfate, nitrate and chloride are possibly associated with metal cations, such as Na$^+$,

269   K$^+$ and Ca^{2+}, etc.,it can be concluded that the NR-PM$_1$ was overall neutral throughout

270   the study. On the other hand, the molar ratio of inorganic anions to ammonium is on

271   average 1.17 (Fig. 3b) when dual-vaporizers are on. This may be partially due to

272   variations of ionization/collection efficiencies of the measured species as the addition

273   of laser beam may change the distribution of vaporized species inside the ion chamber,

274   and also because of the detection of sulfate, nitrate and chloride bonded with metal

275   cations under the dual-vaporizers. These species don't evaporate on the tungsten

276   vaporizer under the laser-off mode. Indeed, more metal signals were observed with

277   the dual-vaporizers, as shown in Fig. S7.

278   Fig. 2c shows the average diurnal changes of organics, sulfate, nitrate, chloride

279   and rBC. Sulfate concentrations are slightly higher during daytime than during

280   nighttime, indicating a significant contribution from photochemical reactions. Sulfate

281   also shows the least variations among all species, reflecting its regional behavior.

282   Except for sulfate, all other species present a dual-peak pattern, with one peak in early

283   morning and another one in early evening. The peaks of rBC and organics are likely

284   due to local traffic/cooking activities (see details in Section 3.5), while the behavior of

285   nitrate is likely driven by the thermodynamic gas-particle partitioning: NH$_3$(g) +

286   HNO$_3$(g) $\leftrightarrow$ NH$_4$NO$_3$(p) as it shows good anti-correlations with the diurnal changes

287   of temperatures (r = -0.72 for nitrate $vs.$ T). The good correlations between the diurnal

288   cycles of nitrate and RH, in particular during nighttime, suggest a nighttime formation

289   pathway of nitrate, e.g., N$_2$O$_5$ + H$_2$O = 2HNO$_3$ and HNO$_3$ + NH$_3$ = NH$_4$NO$_3$.

290   Furthermore, we calculated the diurnal variations of the equilibrium constant of

291   NH_4NO_3 ($K_{p,AN}$) (Seinfeld and Pandis, 2006;Young et al., 2016) in Fig. 2c. The $K_{p,AN}$

292   displays a similar trend as nitrate ($r = 0.68$), providing strong evidence that nitrate

293   variations were governed mainly by the thermodynamic equilibrium. Chloride shows

294   similar behavior as nitrate, indicating it is driven by the equilibrium $NH_3(g) + HCl(g)$

295    $\leftrightarrow NH_4Cl(p)$ as well ($r = -0.76$ for chloride vs. T). Therefore, when temperature rises,

296   more NH_4NO_3 and NH_4Cl can dissociate into gaseous NH_3, HNO_3 and HCl, mass

297   loadings of particle-phase nitrate and chloride decrease correspondingly, and $vice$

298    $versa$.

299   In order to further elucidate the formation processes of sulfate, we calculated the

300   oxidation ratios of sulfur (f_S) (Fig. 4a), defined as $f_S = nSO_4^{2-}/(nSO_4^{2-} + nSO_2)$ (Xu et

301   al., 2014), indicating the conversion of SO_2 . Here nSO_4^{2-} and nSO_2 are the molar

302   quantities of particle-phase sulfate, and gas-phase SO_2, respectively. Diurnal

303   variations of f_S and RH are presented in Fig.4b, and Fig. 4c shows variations of sulfate

304   and nitrate concentrations with RH. The diurnal profile of f_S shows a negative

305   correlation with that of RH ($r = - 0.52$), and mass concentrations of sulfate even drop

306   under high RH conditions, indicating an insignificant role of aqueous-phase

307   processing for sulfate formation during this campaign. On the other hand, the f_S

308   reaches a maximum around 3 pm. Note the afternoon rise of fs and sulfate may be

309   affected by the down mixing of sulfate formed earlier, however, since concentrations

310   of all other aerosol species that mix with sulfate decrease significantly, we postulate

311   that the increase of fs likely suggest the photochemical production of sulfate in the

312   afternoon.

313

314   **3.2 Chemically-resolved size distributions**

315   The campaign-averaged mass-based size distributions, fractional contributions

316   and diurnal size distributions (image plots) of the major PM_1 species are depicted in

317   Fig. 5 (temporal variations of the mass-based size distributions of these PM_1 species

318   over the whole measurement period are provided in Fig. S8). Note the size

319   distribution of rBC in these plots were scaled from the size distribution of m/z 24

320   (C_2^+), as other major rBC ion clusters may be heavily influenced by other ions, such

321   as C^+ signal but from organics at m/z 12 (C^+), HCl^+ signal at m/z 36 (C_3^+), SO^+ signal

322   at m/z 48 (C_4^+), $C_2H_4O_2^+$ signal at m/z 60 (C_5^+). It also should be note that, although

323   the AMS is able to capture the bulk of atmospheric accumulation mode particles

324   (Canagaratna et al., 2007), right side of size distributions may be affected by the

325   incomplete transmission of larger particles limited by the SP-AMS inlet (in particular,

326   the supermicron ones).

327   As can be expected, all inorganic species (sulfate, nitrate, chloride and

328   ammonium) display a unimodal distribution with an accumulation mode peaking

329   ~550 nm (vacuum aerodynamic diameter, D_{va} (DeCarlo et al., 2004)), since they were

330   mainly formed from secondary reactions. The organics has a much broader size

331   distribution across from ultrafine (<100 nm) to supermicron meter range, with a small

332   sub-peak centering ~120 nm in addition to the major peak at ~440 nm, indicating

333   influences from both primary and secondary emissions. On the contrary, size

334   distribution of rBC behaves very differently from other components, which peaks at

335   90 - 200 nm range, reflecting clearly that it is mainly originated from primary

336   emissions. Overall, the small particles are predominantly consisted of organics and

337   rBC, which together account for more than 90% of the ultrafine particle mass. Mass

338   contributions from inorganic species increase significantly with the increase of

339   particle size, and they dominate masses of particles larger than 400 nm (Fig. 5b).

340   In line with the diurnal mass loadings of the PM_1 species shown in Fig. 2c, the

341   diurnal size distribution of sulfate is generally stable, with masses concentrating in the

342   400 - 700 nm range throughout the day (Fig. 5c); while the size distributions of nitrate,

343   chloride and organics present clear enhancements in the 300 - 700 nm range during

344   early morning and early evening due to increased mass concentrations of these species

345   during these two periods. The size distribution of rBC is also enhanced during the

346   morning and evening hours, but it extends to a much smaller size range (<100 nm).

347

3.3 PM₁ contributions on visibility impairment

348

349 In order to figure out the major species that are responsible for the visibility

350 degradation, here we employed the IMPROVE method to reconstruct the light

351 extinction coefficients (b_{ext}). b_{ext} values are derived from the measured visibility:

352 b_{ext}=3.91/V_s (Kong et al., 2015), where V_s stands for the visibility (in meter). The

353 following IMPROVE formula (Yang et al., 2007) was used:

354 $b_{ext} = 3f(RH)\{[(NH_4)_2SO_4] + [NH_4NO_3] + [NH_4Cl]\} + 4[OM] + 10[BC] + 1[soil]+10$

355 Where f(RH) is a RH-dependent empirical coefficient which considers the effects of

356 water uptake by inorganic salts on the light extinction; the f(RH) values used here

357 were taken from Malm and Day (2001), which were regressed from the Great Smoky

358 data set. $[(NH_4)_2SO_4]$, $[NH_4NO_3]$, $[NH_4Cl]$, [OM], and [BC] represent the mass

359 concentrations of ammonium sulfate, ammonium nitrate, ammonium chloride,

360 organics and black carbon directly from the SP-AMS measurements (in μg m⁻³)

361 ($[(NH_4)_2SO_4] = 1.375*[SO_4^{2-}]$, $[NH_4NO_3]=1.29*[NO_3^-]$ and $[NH_4Cl] = 1.51*[Cl^-]$).

362 Since the SP-AMS cannot accurately measure soil components (e.g., various

363 metals/metal oxides/metal salts), the term [soil] was set to zero during calculations.

364 By using this method, the reconstructed visibilities match reasonably well with

365 the measured values ($r^2 = 0.50$) as shown in Fig. 6a. Fig. 6b shows the time series of

366 the measured and reconstructed extinction coefficients throughout the whole sampling

367 period. It should be noted that, on average, the measured PM₁ species are only able to

368 explain ~44% of the light extinction. This is likely due to that: 1) as shown earlier, the

369 SP-AMS measured PM₁ only occupies ~54% of the PM₂.₅ mass; 2) we didn't include

370 contributions from soil components, coarse particles and also some gas-phase species

371 (such as NO₂); 3) although the influences of water are included in part through f(RH)

372 for inorganic salts, the water uptake by organic species are not considered explicitly,

373 which can be significant especially for the SOA under high RH conditions (Duplissy

374 et al., 2011;Denjean et al., 2015). Indeed, as shown in Fig. 6a, reconstructed

375 visibilities appear to deviate more significantly from the measured visibilities under

376 high RH than ones under low RH conditions, suggesting the importance of

377 particle-bounded water on visibility degradation. The pie chart in Fig. 6b presents the

378 average relative contributions of different components to the light extinction of PM_1.

379 The largest contributor is organics which accounts for 37.7%, followed by ammonium

380 sulfate (25.1%), rBC (20.7%), ammonium nitrate (15.1%) and a minor contributor of

381 ammonium chloride (1.4%).

382

383 **3.4 Chemical characteristics of OA**

384   The unique laser vaporizer of SP-AMS allows it to detect rBC and species coated

385 on the rBC core including both non-refractory and refractory organics, thus

386 comparison between the OA mass spectra obtained with dual-vaporizers and tungsten

387 vaporizer settings, can infer some information regarding the chemical features of

388 refractory organics, which were unable to be determined by any other types of AMS.

389 As shown in Fig. 7a and 7b, the OA obtained with dual-vaporizers setting have

390 slightly higher oxygen-to-carbon (O/C) ratio (0.28 vs. 0.27), nitrogen-to-carbon (N/C)

391 ratio (0.033 vs. 0.032) and lower hydrogen-to-carbon (H/C) ratio (1.50 vs. 1.52) than

392 the corresponding elemental ratios of OA obtained with the tungsten vaporizer only.

393 This result indicates that refractory organics are likely more oxygenated than the

394 non-refractory organics, and for this dataset it is mainly due to a higher fractional

395 contribution from $C_2H_3O^+$ (see the inset of Fig. 7a). This is different from the results

396 on laboratory-generated nascent soot, where larger fCO_2^+ (i.e., the fraction of total

397 organic signal contributed by CO_2^+) was observed with the dual-vaporizers setting,

398 indicating the variability of the chemical compositions of refractory organics.

399   It should be noted that, accurate determination of refractory organics is very

400 difficult, because: 1) A large portion of refractory organics cannot be detected by the

401 SP-AMS if they didn't coat on rBC cores; 2) To accurately measure the species only

402 coated on rBC cores, the tungsten vaporizer has to be physically removed, otherwise

403 the vaporizer temperature is still around 150^oC even its power is turned off, and the

404 non-refractory organics that don't coat on rBC cores can still be measured, and

405 complicates the analyses; 3) The CE and IE values for different species may vary

under different vaporizer settings, so that direct subtraction of organics measured under tungsten-only setting from the organics measured under dual-vaporizer setting may not represent the real refractory organics; 4) Some ions measured under dual-vaporizer setting are likely induced by the laser itself rather than the 70 ev electron impact. For example, a series of fullerene-like carbon clusters can be generated by the laser itself, even though they don't really exist in the atmosphere (Wang et al., 2016a;Onasch et al., 2015). This laser-induced ion formation scheme may work for other organics, thus makes it even more difficult for identifying the refractory organics. Further studies are essential to investigate this issue.

Overall, the O/C ratio (0.27) of OA in Nanjing during springtime is a bit lower than those observed at other urban locations in China – for instances, 0.30 in Shenzhen (He et al., 2011), 0.31 in Shanghai (Huang et al., 2012b), 0.33 in Lanzhou (Xu et al., 2014) and 0.34 in Beijing (Zhang et al., 2014), and much lower than those at rural sites – for instances, 0.47 in Kaiping (Huang et al., 2011) and 0.59 in Changdao (Hu et al., 2013). As O/C ratio is a good indicator of the aging degree of OA, the relatively low O/C level indicates a significant contribution from fresh emissions in Nanjing aerosols during springtime. Accordingly, the non-refractory OA (pie chart in Fig. 7b) is dominated in hydrocarbon $C_xH_y^+$ ions (51.2%) rather than the oxygen-containing ion fragments (37.4% of $C_xH_yO_1^+$ and $C_xH_yO_2^+$).

The scatter plot of $f44$ (mass fraction of m/z 44 to the total OA) $vs.$ $f43$ (mass fraction of m/z 43 to the total OA) (a.k.a., triangle plot) (Ng et al., 2010) was often used to investigate the oxidation degrees of OA. As presented in Fig. 8, most OA reside in the bottom end of the triangular region, again pointing out the less-oxygenated behavior of the OA. Since the HRMS can separate different ions at the nominal m/z, we also examined the fCO_2^+ $vs.$ $fC_2H_3O^+$ space and illustrated it in Fig. S9 - many OA locate outside the triangular region, yet still close to the bottom. Moreover, m/z 60 (mainly $C_2H_4O_2^+$) is a significant fragment ion of levoglucosan, which is well known as the biomass burning aerosol tracer (Alfarra et al., 2007). However, as $f60$ (mass fraction of m/z 60 to the total OA) is very low in OA (average

435 ± 1σ = 0.4 ± 0.06 %), indicating no biomass burning influences on the OA properties

436 during springtime in Nanjing.

437

438 **3.5 Sources and evolution processes of OA**

439 In order to further elucidate the sources and evolution processes of OA, we

440 performed PMF analyses and identified four OA components, including two primary

441 OA (POA) factors – a traffic-related hydrocarbon-like OA (HOA) and a

442 cooking-related OA (COA), and two secondary OA factors – a semi-volatile

443 oxygenated OA (SV-OOA) and a low volatility OOA (LV-OOA). Details about their

444 characteristics are discussed below.

445 **3.5.1 Mass spectral features of the OA factors**

446 The mass spectral profiles, time-dependent mass concentrations of the four OA

447 factors and corresponding tracer ions are presented in Fig. 9. The HOA mass spectrum

448 is overall dominated by the $C_xH_y^+$ ions (73.2%), such as $C_3H_7^+$, $C_4H_7^+$, $C_4H_9^+$, $C_5H_9^+$

449 etc., which are most likely produced from alkanes and cycloalkanes emitted from fuel

450 and lubricating oil burning (Canagaratna et al., 2004). This feature is in good

451 agreement with the mass spectral features of POA directly from vehicle

452 emissions(Collier et al., 2015), and the HOA factors determined in many other

453 locations (e.g., Ge et al., 2012b;Huang et al., 2010;Sun et al., 2011). HOA has the

454 lowest O/C ratio (0.10) and highest H/C ratio (1.75) among all factors, representing its

455 behavior as primary fresh emissions. The COA mass spectrum is also rich in $C_xH_y^+$

456 ions (64.7%), but having more oxygenated ions ($C_xH_yO_z^+$) than the HOA (26.5% *vs*.

457 15.4%), especially $C_3H_3O^+$ and $C_3H_5O^+$ ions. The significant contributions of $C_3H_3O^+$

458 and $C_3H_5O^+$ to *m/z* 55 and *m/z* 57 are a common feature of COA, that has been

459 reported in various urban locations around the world, for examples, Beijing (Sun et al.,

460 2015a), London (Allan et al., 2010), Fresno (Ge et al., 2012b), New York City (Sun et

461 al., 2011) and Barcelona (Mohr et al., 2012;Mohr et al., 2015). These

462 oxygen-containing ions are in part generated from the fragmentation of fatty acids in

463 the cooking aerosols (Ge et al., 2012b). As a result, COA has a higher O/C ratio of

464 0.16 and a lower H/C ratio of 1.67 than those of HOA. The O/C and H/C levels of

465 COA in this work are also close to those identified in other locations aforementioned.

466 The consistency of the chemical characteristics of COA from such different locations

467 suggests that ambient COA is more relevant to the cooking oil rather than the different

468 types of food, which was postulated earlier by Allan et al. (2010).

469   Unlike the two POA factors, SV-OOA and LV-OOA are both abundant in

470 oxygen-containing fragments ($C_xH_yO_z^+$ ions), which are 46.4% and 54.8%,

471 respectively. The higher O/C ratio (0.55 *vs.* 0.32) and more $C_xH_yO_2^+$ ions (18.8% *vs.*

472 11.8%) in the LV-OOA mass spectrum than those of the SV-OOA, reflecting the fact

473 that LV-OOA went through more aging/oxidation reactions than SV-OOA. The O/C

474 ratio of SV-OOA is 0.32, which is within the O/C range of SV-OOA observed

475 worldwide (Jimenez et al., 2009). The LV-OOA O/C ratio of 0.55 is in the lower end

476 compared to the O/C levels of LV-OOA observed in other China sites, for examples,

477 0.64 in Kaiping (Huang et al., 2011), 0.65 in Shanghai (Huang et al., 2012b), 0.68 in

478 Lanzhou (Xu et al., 2014), 0.78 in Changdao (Hu et al., 2013) and 0.80 in Hong Kong

479 (Lee et al., 2013).

480   Consistently, in the *f*44 *vs.* *f*43 space (Fig. 8), SV-OOA situates near the bottom

481 side while LV-OOA approaches to the upper part of the triangular region, because of a

482 much larger fractional contribution of CO_2^+ in the LV-OOA mass spectrum. HOA and

483 COA, as POA factors, both reside in the bottom end of the plot, away from SV-OOA

484 and LV-OOA; while they locate outside the triangle in the *f*CO_2^+ *vs.* *f*$C_2H_3O^+$ space

485 (Fig. S9), indicating that the HRMS acquired by the SP-AMS is better in

486 differentiating POA factors from other SOA factors than the unit mass resolution

487 (UMR) data.

488   In order to justify the OA factors identified in this study, we compared the

489 spectral similarities of the OA factor spectral profiles (in both HR and UMR) with

490 those separated during wintertime in Beijing (Sun et al., 2015a), summertime in

491 Lanzhou (Xu et al., 2014), and wintertime in Fresno (Ge et al., 2012b;Ge et al.,

492 2012a). The results are listed in Table 1. Indeed, the HOA, COA and LV-OOA mass

493 spectra are highly similar to the corresponding factors identified in Bejing, Lanzhou

494 and Fresno ($r^2 > 0.87$); SV-OOA also correlates fairly well with Bejing and Lanzhou

495 SV-OOA too, but with relative low r^2 (0.68 – 0.75), mainly because of one or two ion

496 fragments, namely, higher CO^+ and CO_2^+ signals in Beijing SV-OOA and higher

497 $C_2H_3O^+$ signal in Lanzhou SV-OOA than those in Nanjing SV-OOA. The SV-OOA on

498 the other hand, correlates very well with the Fresno OOA ($r^2 = 0.90$ and 0.91).

499   Moreover, as presented in Fig. 9a, the HOA mass spectrum contains relatively

500 higher fraction of ions with large m/z values ($m/z > 100$) than that of COA (14.0% *vs.*

501 8.2%), and most of these ions are $C_xH_y^+$ ions, probably from fuel burning emitted

502 long-chain alkanes, etc. The SV-OOA also includes more large m/z ion fragments ($m/z>$

503 100) than those in the LV-OOA mass spectrum (10.5% *vs.* 5.3%), likely suggesting

504 that further oxidation of SOA species may lead to the fragmentation of high molecular

505 weight species and formation of small molecules – a mechanism verified by both

506 lab-scale experiments (e.g., Yu et al., 2014) and field measurements (e.g., Lee et al.,

507 2012).

3.5.2 Temporal variations, diurnal patterns and relative contributions of the OA

factors

510   The temporal variations of different OA factors and their corresponding tracer

511 ions are displayed in Fig. 9b. $C_4H_9^+$ ion, a.k.a., the HOA mass spectral tracer (Zhang

512 et al., 2005) indeed varies very closely to the HOA ($r^2= 0.94$). Time series of the COA

513 tracer ion $C_6H_{10}O^+$ (and also $C_5H_8O^+$, $C_7H_{12}O^+$) (Sun et al., 2011;Ge et al., 2012b)

514 match very well with that of COA too ($r^2 = 0.90$). SV-OOA correlates better with

515 $C_2H_3O^+$ ($r^2 = 0.90$) than with CO_2^+ ($r^2 = 0.66$). Although LV-OOA doesn't correlate

516 very well with CO_2^+ ($r^2 = 0.12$) mainly due to the mismatch during April 23 - 26, the

517 correlation is still much better than it with $C_2H_3O^+$ ($r^2 < 0.001$). In Table 2, we

518 tabulate the correlation coefficients (r) of the four OA factors with the gas-phase

519 species, BC and inorganic species. Note we used Pearson's r not r^2 here since some

520 correlation coefficients are negative. From the table, it is clear that the traffic-related

521 gaseous species, CO and NO_2, correlate best with HOA among all OA factors;

522 SV-OOA correlates better with nitrate ($r = 0.49$) than it with sulfate ($r = 0.11$);

523 LV-OOA correlate better with sulfate ($r = 0.23$) that it with nitrate ($r = 0.11$). All these

524 results are consistent with the traffic origin of HOA, the semi-volatile and

525 low-volatility behaviors of SV-OOA and LV-OOA.

526 Accordingly, diurnal cycles of the OA factors are presented in Fig. 10a.

527 Correlation coefficients (r) of the diurnal variations between OA factors with

528 gas-phases and inorganic species are provided in Table 2, as well. HOA

529 concentrations show an early morning peak, and it overall remains at high levels

530 during nighttime. Besides the impacts of boundary layer height, this is also due to

531 enhanced emissions from construction vehicles around the site, which were in fact

532 much more active during nighttime than during daytime because of the restrictions of

533 Nanjing government. Most of those vehicles used low-quality diesel fuel, and could

534 emit a large amount of rBC particles. The rBC diurnal pattern is indeed almost

535 identical to that of HOA ($r =0.99$), indicating that the HOA during this campaign was

536 apparently associated with the construction vehicle emissions. COA concentrations

537 increase during noon (12 pm – 1 pm) and early evening, in response to the lunchtime

538 and dinnertime cooking activities. SV-OOA concentrations decreases from 9 am, and

539 reach a minimum during afternoon (3 pm – 4 pm), oppositely to the variation of

540 temperatures ($r = -0.85$) but similar to that of nitrate ($r = 0.53$), corroborating its

541 semi-volatile feature. Different from other factors, LV-OOA concentrations increase

542 during daytime and shows positive correlation with temperature ($r = 0.76$); it also has

543 negative correlation with the diurnal cycle of RH ($r = -0.75$). Both behaviors are

544 similar to those of sulfate ($r = 0.72$ for the diurnal cycle of LV-OOA *vs.* sulfate),

545 indicating the leading role of photochemical oxidation for LV-OOA formation as well.

546 As shown in Fig. 10b, due to mainly the increase of LV-OOA mass loading, OA is

547 overwhelmingly dominated by the SOA (SV-OOA + LV-OOA) during afternoon (80.2%

548 at 3 pm); POA (HOA + COA) only dominates the OA mass during morning (53.2% at

549 7 am) and early evening (56.9% at 8 pm) in response to the enhanced traffic and

550 cooking emissions. On average, the OA is composed of 27.6% of HOA, 16.9% of

551 COA, 27.4% of SV-OOA and 28.1% of LV-OOA (Fig. 10c), with SOA outweighing

552 POA (55.5% *vs.* 44.5%). However, as shown in Fig. 10d, with the increase of OA

553 mass loadings, the fractional contribution of POA increases, highlighting the

554 important and direct influences of anthropogenic emissions on the heavy pollution

555 haze events.

556

557 **3.5.3 Local/regional influences and evolution processes of the OA factors**

558   Combining WS, WD and mass loadings, the bivariate polar plots of the four OA

559 factors, rBC, total OA, nitrate, sulfate and the total PM_1 are shown in Fig. 11. These

560 plots provide an effective graphical method for showing the potential influences of air

561 masses from different directions with different wind speeds to the receptor site

562 (Carslaw and Beevers, 2013). Clearly, high mass loadings of HOA and rBC mostly

563 link with low WS (< 1 m s^{-1}), indicating they are mainly from local vehicle emissions.

564 High COA concentrations occur mainly under low WS as well, but with some high

565 concentrations accompanied with air masses from southeast under higher WS.

566 SV-OOA appears to be mainly formed locally, except for a concentration hotspot in

567 the southeast – likely due to emissions from the tobacco factory that resides in that

568 direction. Nitrate, as a semi-volatile species, behaves overall similar to the SV-OOA.

569 High concentrations of LV-OOA are distributed in all directions under higher WS,

570 similar to that of sulfate, representing their regional behaviors. Overall, high PM_1

571 mass loadings occur mainly under low WS, indicating that the PM_1 is heavily affected

572 by local emissions rather than pollutants in a regional scale.

573   The aging of OA can be described in general by the increase of O/C and decrease

574 of H/C. In this regard, we plotted the Van Krevelen diagram (Heald et al., 2010) (Fig.

575 12a) to show the relationships between H/C and O/C ratios for all OA as well as the

576 four OA factors. Overall, in this study, the H/C and O/C ratios of OA data are

577 correlated linearly with a slope of -1.04 ($r^2 = 0.93$). Interestingly, the two OOA factors

578 lie very well on the fitted straight line. This trend may suggest that the evolution of

579 secondary OA during this campaign follows a transformation pathway of SV-OOA to

580 LV-OOA. The diurnal cycle of LV-OOA varies oppositely to that of SV-OOA ($r =$

581 -0.86), probably supporting this hypothesis. In addition, SV-OOA and LV-OOA mass

582 concentrations, and O/C ratios of OA all show no obvious correlations with the RH as

583 shown in Fig. 12b and Fig. 12c, indicating that aqueous-phase processing is

584 insignificant compared to the photochemical processing for the oxidation of OA.

585

4. Conclusions

587   We present for the first time the real-time measurement results using the SP-AMS

588 on submicron aerosols in urban Nanjing during springtime (April 13 - 29, 2015). The

589 dynamic variations of SP-AMS determined PM_1 mass loadings, agreed well with the

590 $PM_{2.5}$ measured by the Met One $PM_{2.5}$ analyzer. The average PM_1 concentration was

591 28.2 μg m^{-3}, lower than previously ACSM-determined PM_1 concentrations during

592 summer and winter in Nanjing. Organics on average comprised the largest fraction

593 (45%) of PM_1, and its fractional contributions increased in case of high PM_1 mass

594 loadings. The diurnal cycles of mass concentrations of organics, rBC, nitrate and

595 chloride all presented a similar behavior, which was high in early morning and

596 evening, but low in the afternoon. Concentrations of sulfate, on the contrary, increased

597 during afternoon. Further investigations of f_S, sulfate concentrations and its

598 relationship with RH suggest that photochemical processing contributed significantly

599 to sulfate formation compared to the aqueous-phase processing, while nitrate (and

600 chloride) formation was mainly governed by the thermodynamic equilibrium. The

601 chemically-resolved mass-based size distribution data showed that rBC occupied a

602 large fraction of ultrafine particles, while secondary inorganic species could dominate

603 the mass of particles larger than 400 nm (D_{va}). In addition, by using the IMPROVE

604 method, we found that the observed PM_1 components were able to reproduce ~44% of

605 the light extinction during this study.

606   PMF analyses resolved four OA factors, e.g., HOA, COA, SV-OOA and LV-OOA.

607 Mass spectral profiles of these factors agree very well with the corresponding factors

608 identified at other locations. The springtime OA showed no influences from biomass

burning emissions. On average, the OA is dominated by SOA (55.5%), but POA appeared to be more important when the OA mass loadings are high, and can be dominant in early morning and evening. Diurnal cycle of SV-OOA varied similarly to that of nitrate, reflecting its semi-volatile behavior. Diurnal variations of LV-OOA showed great resemblance to that of sulfate. The bivariate polar plots indicate that SV-OOA was formed locally, and the Van Krevelen diagram further suggests a transformation from SV-OOA to LV-OOA in Nanjing. Generally, our highly time-resolved SP-AMS measurement results may offer useful insights into the aerosol chemistry, and have important implications for the PM control and reduction in this densely populated region.

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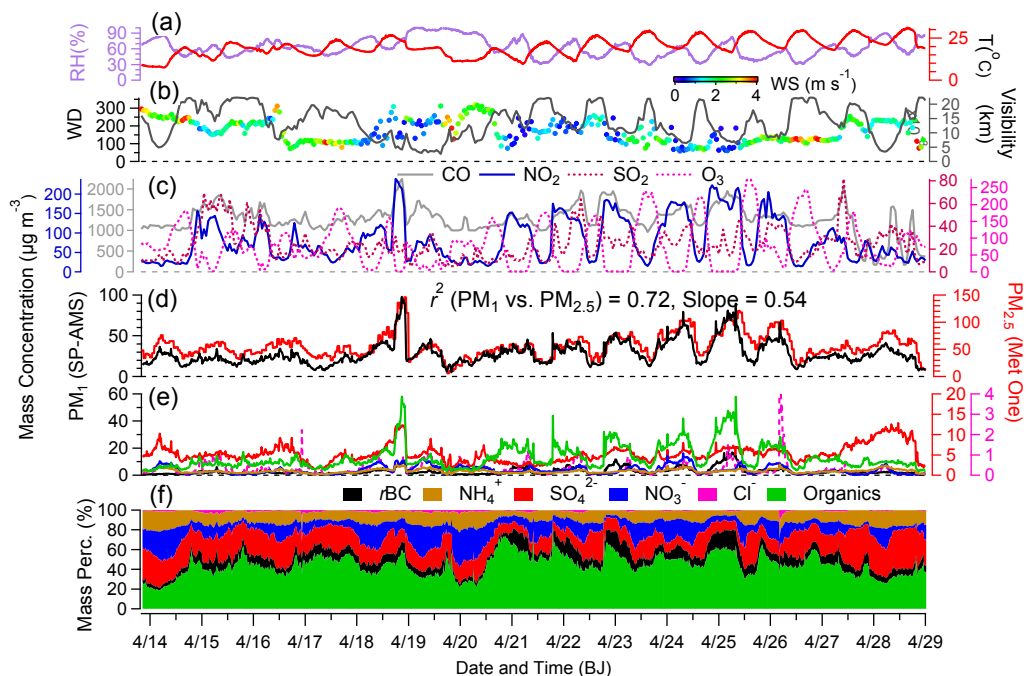
Figure 1. Time series of (a) relative humidity (RH) and temperature (T), (b) wind direction (WD) colored by wind speed (WS, m s^{-1}) and visibility (km), (c) mass concentrations of CO, NO$_2$, SO$_2$ and O$_3$ (hourly data), (d) mass concentrations of PM$_1$ measured by the SP-AMS, and PM$_{2.5}$ measured by the co-located Met One PM$_{2.5}$ analyzer, (e) mass concentrations of rBC, ammonium, sulfate, nitrate, chloride and organics, and (f) mass contributions (%) of the six PM$_1$ components (BJ, Beijing).

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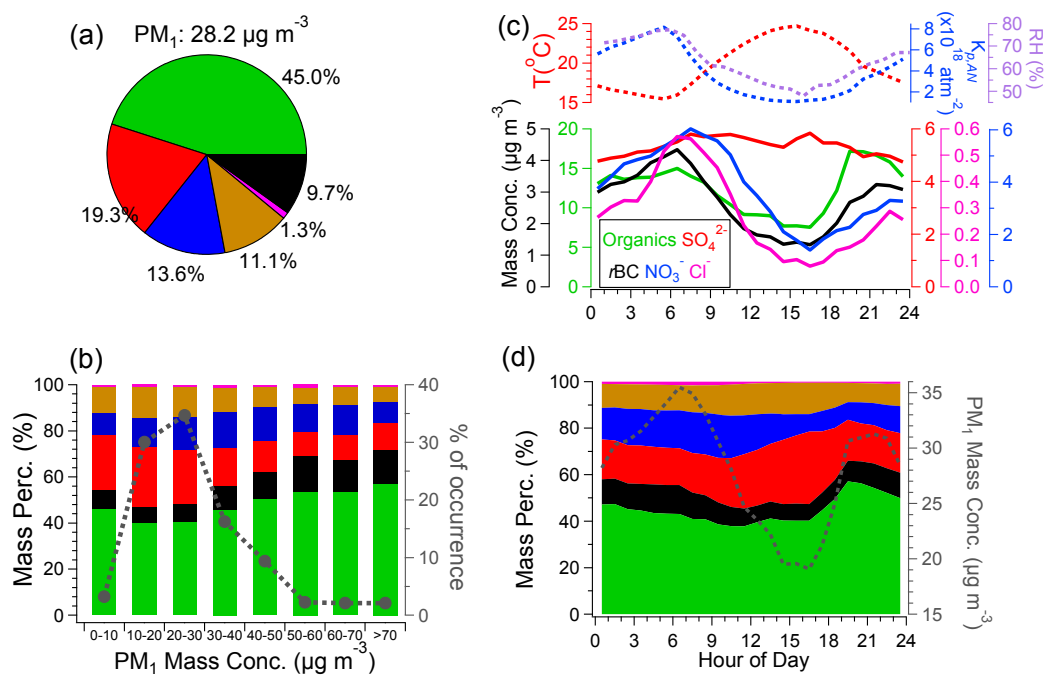
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1006 Figure 2. (a) Campaign-averaged mass contributions of organics, sulfate, nitrate,
1007 ammonium, chloride and rBC to the total PM$_1$, (b) mass percentages of the six PM$_1$
1008 species (left y-axis) and, fractions of the number of data points to the total number of
1009 data points for PM$_1$ at different concentration bins (right y-axis), (c) diurnal patterns
1010 of mass concentrations of the major PM$_1$ species (bottom panel), temperature (top
1011 panel, left y-axis), relative humidity (RH) (top panel, right y-axis), and the equilibrium
1012 constant ($K_{p,AN}$) of NH$_4$NO$_3$ (top panel, right y-axis)

1013 ($K_{p,AN} = K_{p,AN}(298)exp\left\{a\left(\frac{298}{T}-1\right)+b\left[1+ln\left(\frac{298}{T}\right)-\frac{298}{T}\right]\right\}$, for reaction

1014 NH$_4$NO$_3$(p) $\leftrightarrow$ NH$_3$(g) + HNO$_3$(g). $K_{p,AN}$(298) is the equilibrium constant at 298 K
1015 (3.36×10^{16} atm^{-2}), a = 75.11, and b = -13.5 (Seinfeld and Pandis, 2006)), (d) diurnal
1016 variations of mass fractional contributions of the six PM$_1$ species (left y-axis), and the
1017 PM$_1$ mass concentrations (right y-axis).

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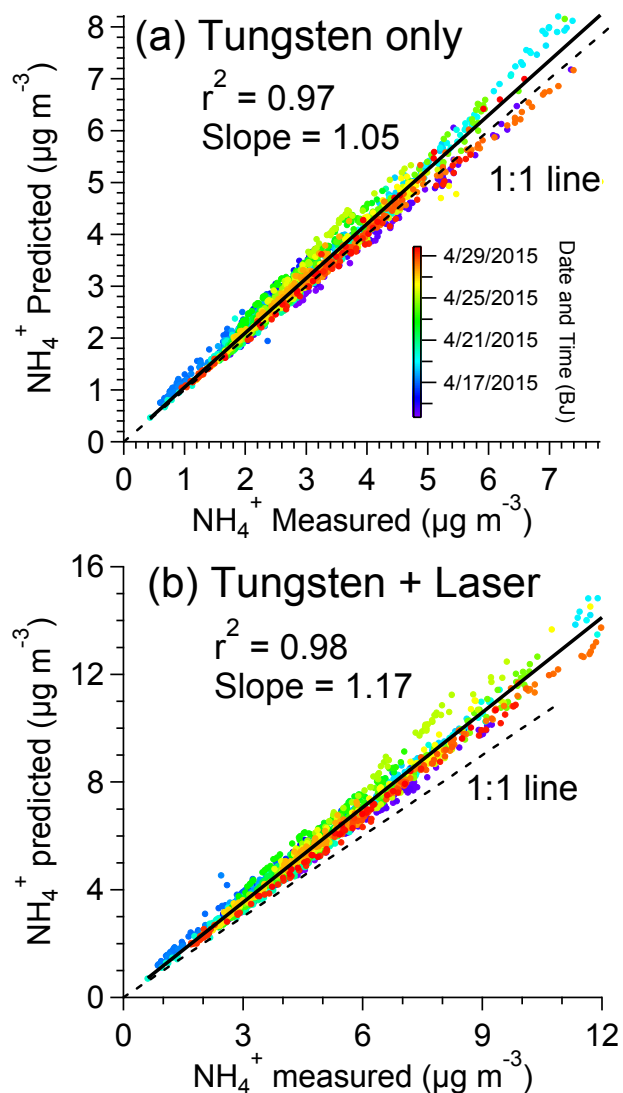
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1021 Figure 3. Scatter plots of the predicted NH_4^+ *vs.* measured NH_4^+ concentrations
1022 (colored by time), in the case of (a) tungsten vaporizer only, and (b) dual-vaporizers
1023 (tungsten + laser). The predicted values were calculated according to the formula:
1024 NH_4^+ predicted = $18 \times (2 \times SO_4^{2-}/96 + NO_3^-/62 + Cl^-/35.5)$ (Zhang et al., 2007b).

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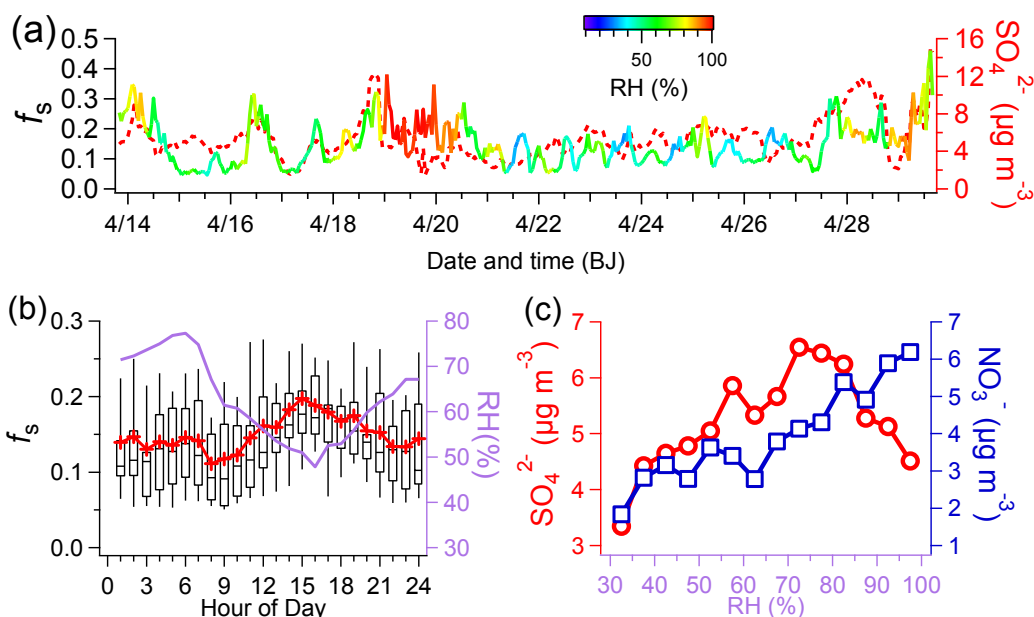
1029   Figure 4. Time series of (a) sulfur oxidation ratio, $f_S = nSO_4^{2-}/(nSO_4^{2-} + nSO_2)$, and
1030   sulfate, (b) diurnal variations of f_S and RH (the lines and cross symbols indicate the
1031   mean values, the lines in the boxes indicate the median values, the upper and lower
1032   boundaries of the boxes indicate the 75th and 25th percentiles, and the whiskers above
1033   and below the boxes indicate the 90th and 10th percentiles), (c) Sulfate and nitrate
1034   concentrations *vs*. RH, the circles or squares represent the average concentrations
1035   within different RH bins (5% increment) for sulfate and nitrate, respectively.

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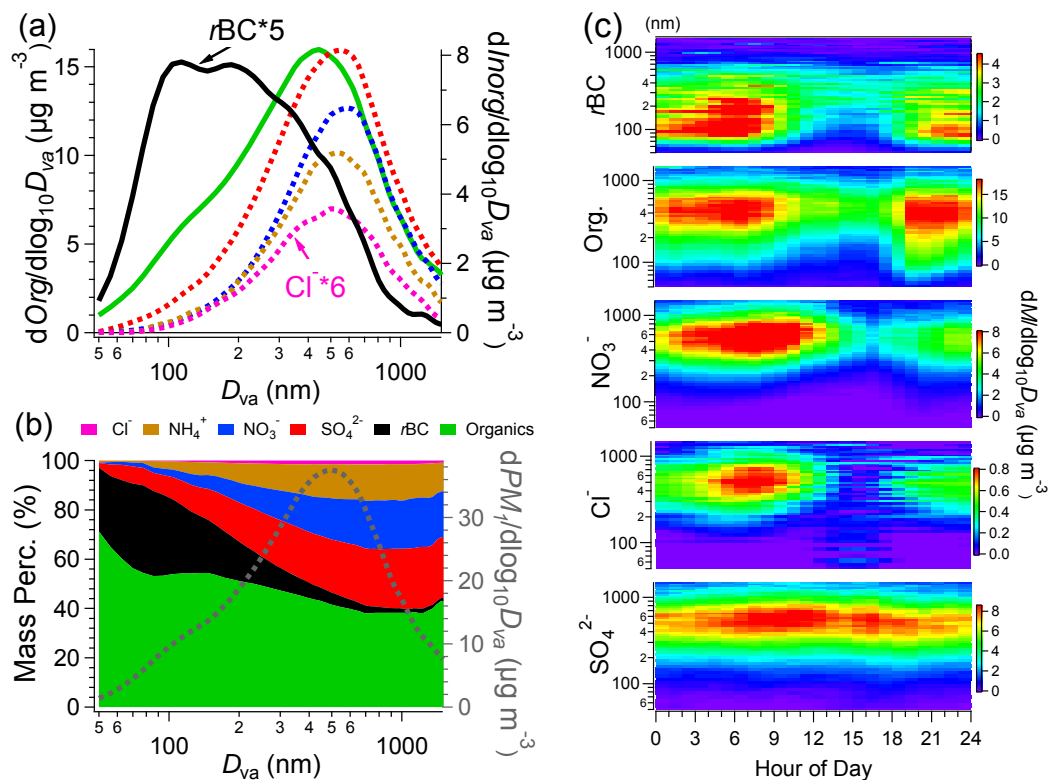


Figure 5. (a) Mass-based average size distributions of organics, rBC (left y-axis), sulfate, nitrate, chloride and ammonium (right y-axis) (D_{va}, vacuum aerodynamic diameter), (b) fractional contributions of the six PM_1 species as a function of particle size (left y-axis), and size distribution of total PM_1 (right y-axis), (c) diurnal profiles of the size distributions of rBC, organics, nitrate, chloride and sulfate.

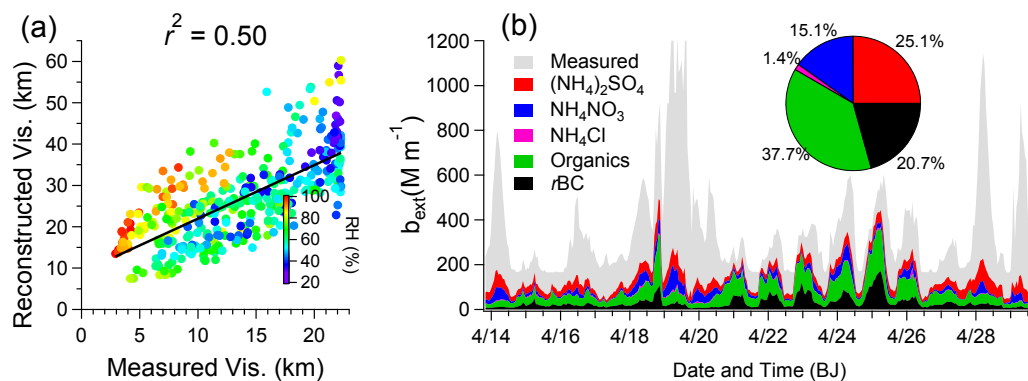



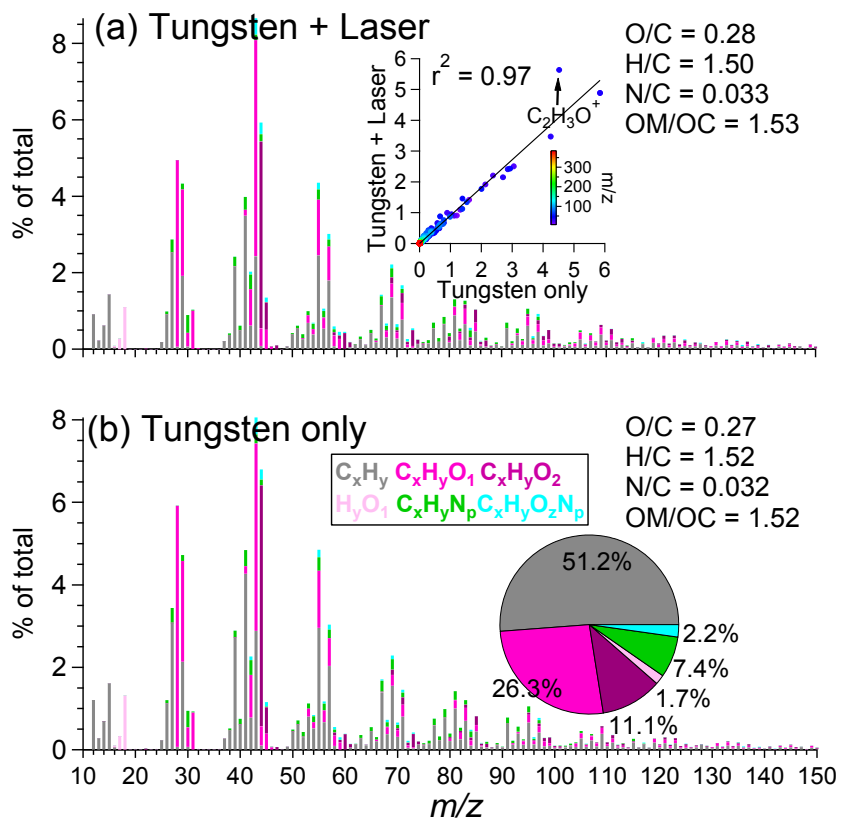
Figure 6. (a) Scatter plot of reconstructed *vs.* measured visibility (colored by RH), (b) light extinction coefficients derived from measured visibility (grey), and reconstructed from SP-AMS measured ammonium sulfate, ammonium nitrate, ammonium chloride, organics and *r*BC using the IMPROVE method. The inset pie shows the relative contributions of the five species to the light extinction of PM_1.

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Figure 7. Campaign-averaged high resolution mass spectra of OA colored by six ion categories, in the case of (a) dual-vaporizers (tungsten + laser) (the inset scatter plot compares the spectral similarity between (a) and (b)), and (b) tungsten vaporizer only (the inset pie shows the relative contributions of six ion categories to the total OA).

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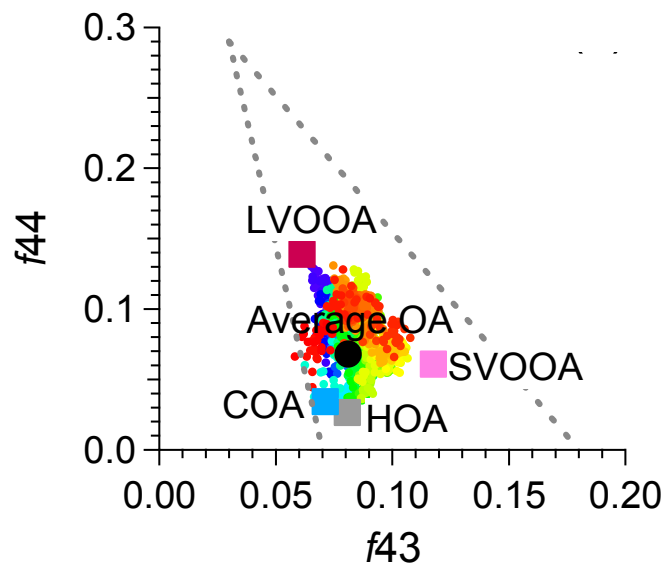
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Figure 8. Triangle plot of *f*44 *vs*. *f*43 for all OA (colored by time), and the four OA
factors identified by the PMF analyses.

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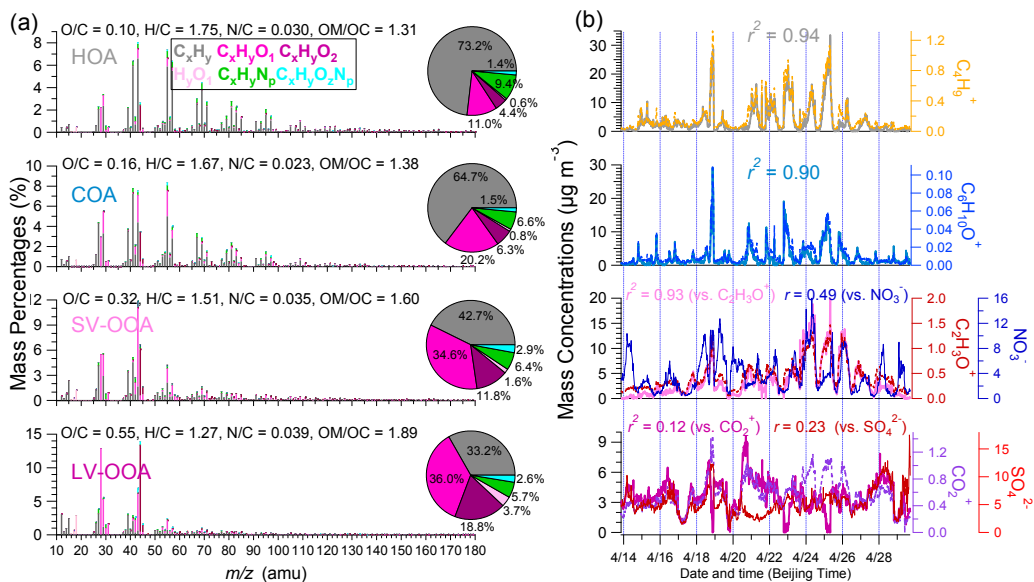
Figure 9. (a) High resolution mass spectra of hydrocarbon-like OA (HOA), cooking-related OA (COA), semi-volatile oxygenated OA (SV-OOA), and low volatility oxygenated OA (LV-OOA) colored by six ion categories (the four inset pies show the relative contributions of the six ion categories to the four OA factors, respectively), (b) time series of the four OA factors, corresponding tracer ions, nitrate and sulfate.
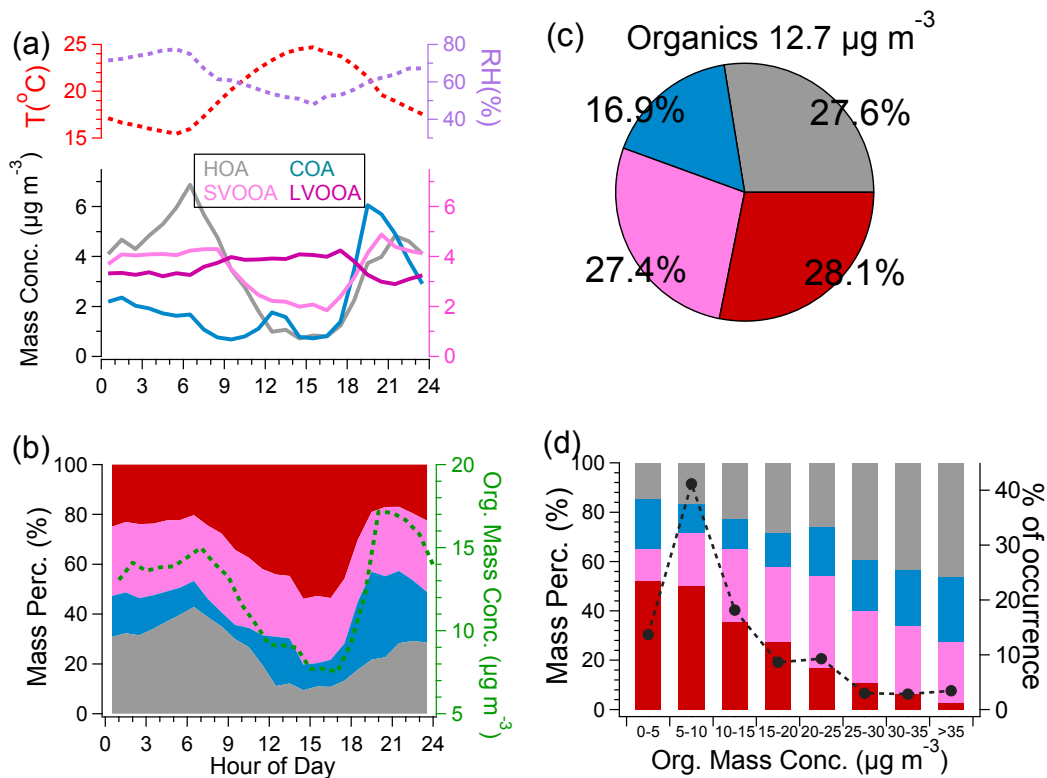
Figure 10. (a) Diurnal cycles of mass concentrations of the four OA factors (bottom panel), temperature (top panel, left *y*-axis) and RH (top panel, right *y*-axis), (b) diurnal variations of mass contributions of the four OA factors (left *y*-axis), and the total OA mass concentrations (right *y*-axis), (c) campaign-averaged mass contributions of the four OA factors to the total OA mass, and (d) mass contributions of the four OA factors (left *y*-axis), and the fractions of the number of data points to the total number of data points for the OA at different concentration ranges (right *y*-axis).
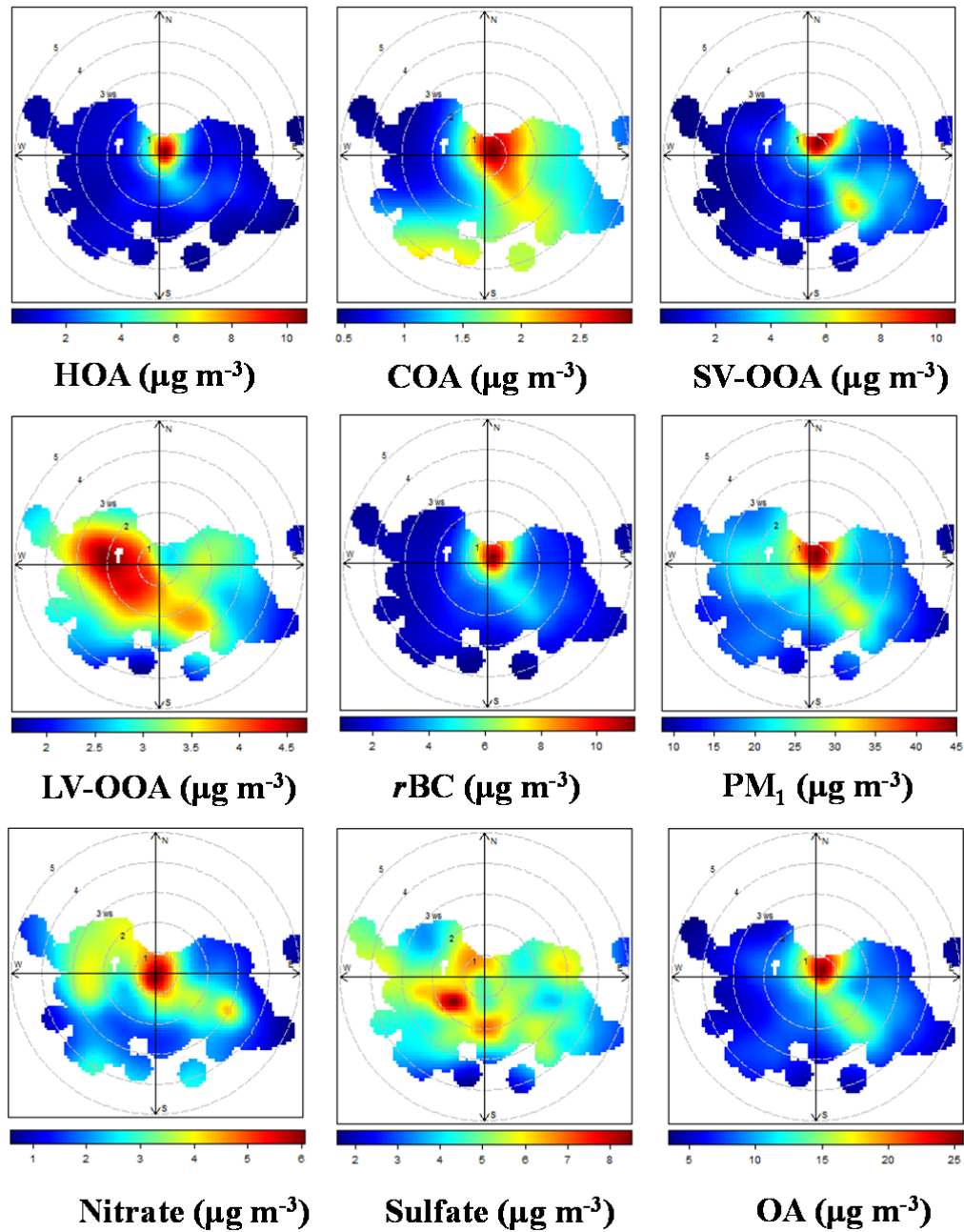
Figure 11. Bivariate polar plots of HOA, COA, SV-OOA, LV-OOA, rBC, PM$_1$, nitrate, sulfate and the total OA (the color scale shows the concentration of each species, and the radical scale shows the wind speed that increases outward from the center).

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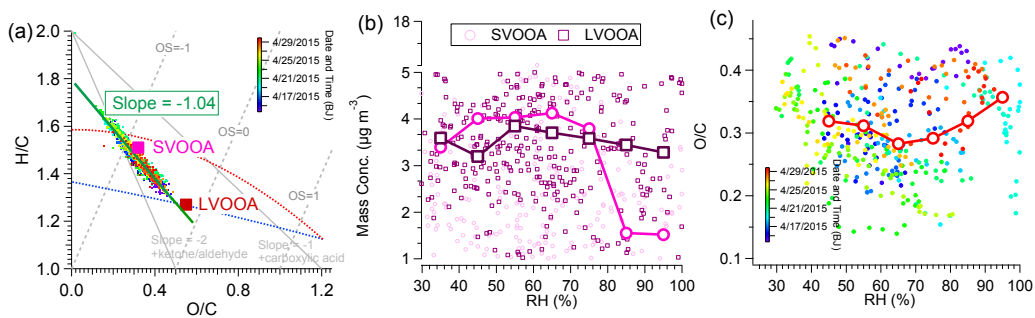
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1099 Figure 12. (a) Van Krevelen diagram of H/C *vs.* O/C ratios for all OA data colored by
1100 time, the blue and red dashed lines correspond to the right and left grey dashed lines
1101 in the *f*44 vs. f43 triangle plot of Fig. 8, the grey lines represents the addition of a
1102 particular functional group to an aliphatic carbon (Heald et al., 2010), (b) scatter plot
1103 of SVOOA and LVOOA mass concentrations *vs.* RH, the circles or squares represent
1104 the average mass concentrations within different RH bins (10% increment) for
1105 SVOOA and LVOOA, respectively, (c) scatter plot of O/C *vs.* RH (colored by time),
1106 the circles represent the average O/C values within different RH bins (10%
1107 increment).

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1109 Table 1. Correlation coefficients (Pearson's r^2) between the mass spectral profiles of
1110 the OA factors identified in this work with the corresponding factors identified in
1111 Beijing (2013 Winter) (Sun et al., 2015a), Lanzhou (2014 Summer) ((Xu et al., 2014)),
1112 and Fresno (2010 Winter) (Ge et al., 2012b).

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Nanjing	High resolution MS (r^2)		
(2015 Spring)	Beijing (2013 Winter)	Lanzhou (2012 Summer)	Fresno (2010 Winter)*
HOA	0.92	0.90	0.98
COA	0.93	0.94	0.93
SV-OOA	0.68	0.75	0.90
LV-OOA	0.91	0.98	0.87
	Unit mass resolution MS (r^2)		
HOA	0.92	0.91	0.99
COA	0.96	0.96	0.95
SV-OOA	0.70	0.74	0.91
LV-OOA	0.90	0.98	0.89

1114 *Note the Fresno (2010 Winter) study only identified one OOA factor, we thus
1115 compared both SV-OOA and LV-OOA in this study with it.

1116 Table 2. Correlation coefficients (Pearson's r) between the time series of the four OA
1117 factors with the gas-phase species (hourly data) and other PM_1 components (15-min
1118 data), and the correlation coefficients between the diurnal data.

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Pearson's r	Temp.(T)	CO	NO_2	SO_2	O_3	SO_4^{2-}	NO_3^-	Cl^-	rBC
		Hourly data				15-min data			
HOA	-0.14	0.71	0.77	0.13	-0.54	0.15	0.26	0.45	0.92
COA	0.11	0.50	0.58	-0.06	-0.22	0.19	0.07	0.08	0.61
SVOOA	0.19	0.41	0.70	0.14	-0.21	0.11	0.49	0.25	0.70
LVOOA	0.069	-0.2	-0.18	0.06	0.14	0.23	0.11	0.01	-0.22
		Diurnal data							
HOA	-0.94	0.86	0.86	0.66	-0.96	-0.35	0.72	0.82	0.99
COA	-0.15	0.28	0.59	-0.24	-0.24	-0.57	-0.33	-0.25	0.19
SVOOA	-0.85	0.86	0.94	0.58	-0.90	-0.51	0.53	0.61	0.89
LVOOA	0.76	-0.58	-0.83	-0.27	0.77	0.72	-0.26	-0.33	-0.75

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