

1 ***Anonymous Referee #1***

2
3 *This contribution presents number size distribution and concentration of non-volatile*
4 *particle fractions and the volatile composition of ambient aerosols based on VTDMA*
5 *data. In particular, even though volatility analysis of ambient aerosols in general have*
6 *been intensively studied in different fields, it is the first time to provide the chemical*
7 *composition based on volatility of aerosols in PRD region with a different synoptic*
8 *condition.*

9
10 ***Major comments: (we have indexed the comments for easy reference)***

11
12 *1. The volatility information of studied site, which this work strives to provide, could*
13 *be written out more explicitly both in the introduction and results.*

14 *1.1 According to this, the main goals of the study, given in the end of the introduction,*
15 *should be revised. At least, more discussion about how the results obtained in this*
16 *study would contribute to, e.g., estimating the chemical composition of size*
17 *segregated aerosols and the mixing state of the non-volatile residuals, should be*
18 *added, because this is given as a motivation for this work in the introduction.*

19 *1.2 In addition, the discussion of the mixing state of the non-volatile residuals is far*
20 *too simplified. Please consider adding more materials from either total number*
21 *size distribution measurements or chemical composition data from other*
22 *instruments, or air masses origins information. Also, the literature could be*
23 *rechecked for the last 2-3 years.*

24
25 *2. It is highlighted in the manuscript that in urban areas “non-volatile” aerosol*
26 *fraction consists mainly of soot. This statement guides the reader to think that there*
27 *are no other important non-volatile aerosol compounds. However, as it is*
28 *concluded the non-volatile fraction may actually consist of some extremely low-*
29 *volatility organic material that does not evaporate even at 300 °C. More discussion*
30 *on the effectively non-volatile organics should be added to the manuscript; what*
31 *are these organics?*

- 34 3. *The author wrote the VTDMA measurements were performed at 25, 100 and 300 °C,*
35 *while in the discussion section; only the results at 300 °C were present. The*
36 *definition of VSF, LV, MV, HV and all relevant quantities actually were based on*
37 *number size distribution after heating at 300 °C. The author did not write clearly in*
38 *the methodology part, please revise it.*
39
- 40 4. *Conventionally, ammonium sulfate can be considered to be of low-volatility and it*
41 *tends to evaporate at around 200 °C. It seems that in this manuscript low volatile*
42 *refers to material that is elsewhere referred to as extremely low volatile or*
43 *effectively non-volatile (see recent literature, e.g. Donahue et al., 2013 in Faraday*
44 *Discussions; Murphy et al., 2014 in ACP).*
45
- 46 5. *The author should avoid using too many abbreviations or use them in cautions*
47 *especially they are not conventionally used elsewhere.*
48
- 49 6. *The discussion of the fraction of low volatile, medium volatile and high volatile*
50 *materials on the non-volatile cores as well as the complete volatile materials was*
51 *mainly related to meteorological conditions and traffic emissions. I thus strongly*
52 *recommend that the general meteorological parameters, e.g. temperature, relative*
53 *humidities as well as traffic densities are given, since all results only represent*
54 *concurrent conditions. For example, plot time series or diurnal variations of air*
55 *mass origins and traffic densities around by can also help for the discussion.*
56
- 57 7. *Concerning the number fractions, isn't it possible that the finest particles (initial*
58 *diameter of 40 nm) get below the detection limit of the instrument upon heating? If*
59 *so, it cannot be assumed that these particles would be completely evaporated.*
60 *These particles may include an extremely low volatility "non-volatile" fraction,*
61 *which cannot be detected because of the small size of the remaining particles after*
62 *the heating. This issue should be discussed in the manuscript.*
63
- 64 8. *Please provide the residence time in your heating unit; is it long enough for all the*
65 *volatile material to evaporate? Please add this information to the manuscript.*
66

67 9. *If available, the particle number size distribution from DMPS or SMPS during the*
68 *whole campaign should be given. Was new particle formation seen in this site?*
69 *How does the number size distribution vary during day and night?*

70

71 **Response:**

72 We thank the reviewer for the useful comments. Below please find our response to
73 each of the points above. [Major changes to the manuscript are shown in blue.](#)

74

75 **1.** In the introduction, we have revised the background of VTDMA studies, volatility
76 of organics and goals of this work, which were:

- 77 i) To characterize the volatility of ambient aerosols at a suburban site in
78 Guangzhou, a mega city in China; and
79 ii) To better characterize the composition of non-volatile materials in VTDMA
80 measurements at 300 °C.

81

82 In the results and discussion section, we have added the following new materials
83 and discussions to achieve the goals above:

- 84 i) Meteorological conditions including wind speed, wind direction, temperature,
85 and relative humidity;
86 ii) Particle number size distribution from the SMPS;
87 iii) Time series and diurnal variations in OC and EC concentrations; and
88 iv) Back trajectory analysis

89

90 With the addition of the new materials, the subsections in the results and discussion
91 section of the revised manuscript are re-organized:

- 92 - 3.1 Overview
93 - 3.2 Diurnal variations
94 - 3.3 Back trajectory analyses
95 - 3.4 New particle formation
96 - 3.5 Closure analysis for LV and MV residuals at 300 °C, OC and EC

97

98 The response below will focus on the new materials added. We do not have time
99 series data of traffic density at the sampling site, but we cited Zhang et al. (2015)

100 for the diurnal traffic pattern measured in a tunnel experiment in Guangzhou to aid
101 the discussion.

102

103 **1.1 Revised Introduction**

104 **1.1.1 Background of VTDMA studies and volatility of organics**

105 Philippin et al. (2004) later developed a VTDMA capable of evaporating volatile
106 materials in aerosols at temperatures up to 300 °C. Non-volatile materials at 300 °C,
107 such as EC, non-volatile organics and sea salt can externally or internally mix (or be
108 coated) with volatile materials. Note that the terms “volatile” and “non-volatile” are
109 defined at the heating temperature of 300 °C in the VTDMA. They are different from
110 the volatilities defined under ambient conditions (Donahue et al., 2009; Murphy et al.,
111 2014) or in other measurement techniques (Twomey, 1968; Pinnick et al., 1987;
112 Huffman et al., 2009). The composition of these non-volatile residuals can vary
113 spatially and temporally in VTDMA measurements. Previous studies have
114 demonstrated good agreement between the mass of black carbon and the mass of
115 particles with small volatile fractions, which experienced size reductions of 5 to 10%
116 upon heating at 300 °C in the VTDMA. Various studies have also used a VTDMA to
117 estimate the mixing states of soot particles. Particles with small volatile fractions are
118 often assumed to be soot particles externally mixed with particles with volatile
119 materials at 300 °C. Particles with larger volatile fractions, which experienced size
120 reductions of more than 10% upon heating at 300 °C in the VTDMA, were assumed to
121 represent soot particles internally mixed (coated) with the volatile materials (Philippin
122 et al., 2004; Cheng et al., 2006; Frey et al., 2008; Wehner et al., 2009; Rose et al., 2011;
123 Levy et al., 2014; Zhang et al., 2016).

124

125 Organics also contribute to light absorption by atmospheric particles (Bond 2001;
126 Kirchstetter et al. 2004; Chen and Bond 2010). Laboratory studies have shown that
127 organic aerosols may form low volatility oligomers after aging for a long time (e.g.
128 Kalberer et al., 2004). Huffman et al. (2009) showed that highly oxygenated, aged
129 organic aerosols exhibited similar or lower volatility than the primary organic aerosols
130 or the less oxygenated ones. Recently, Häkkinen et al. (2012) found that the mass
131 fraction remaining of non-BC residuals, i.e. the difference between the residual mass
132 derived from a volatility differential mobility particle sizer at 280 °C and the black

133 carbon mass derived from an aethalometer, is positively correlated with the mass
134 fraction of organics measured with an aerosol mass spectrometer.

135

136 **1.1.2 Goals of this study**

137 In this study, simultaneous measurements of aerosol volatility and carbonaceous matter
138 were made at a suburban site in Guangzhou, China during wintertime in February and
139 March 2014 using a VTDMA and a semi-continuous OC/EC analyzer, respectively.
140 Volatility measurements were made for ambient aerosols ranging from 40 nm to 300
141 nm in diameter. Residuals remaining after heating at 300 °C in the VTDMA are referred
142 to as non-volatile in this study. We report the average values, time series and diurnal
143 variations in the number and volume fractions of the volatile and non-volatile materials,
144 as well as the OC and EC concentrations. We examine the relationships of the non-
145 volatile materials upon heating at 300 °C to EC and to the non-volatile OC, based on
146 analyses of the diurnal patterns and mass closures of the OC/EC and VTDMA data.
147 Finally, we discuss the influence of air mass origins on the volatility of the sampled
148 aerosols and concentrations of OC and EC based on back trajectory analysis.

149

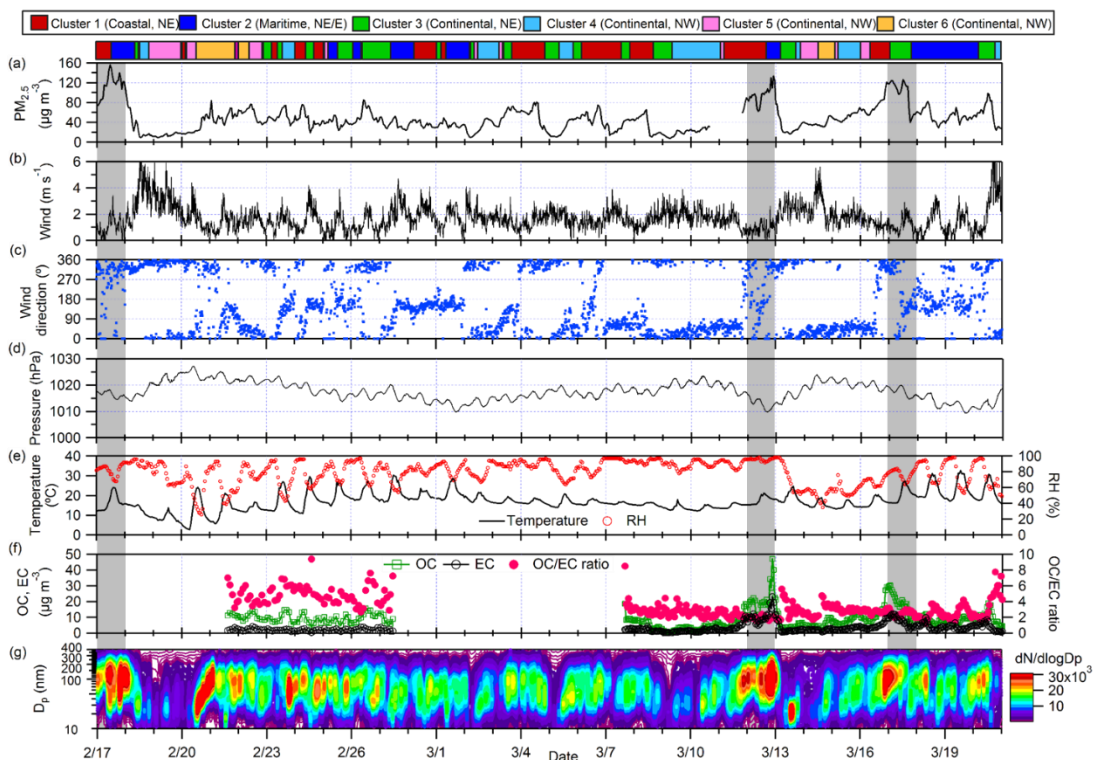
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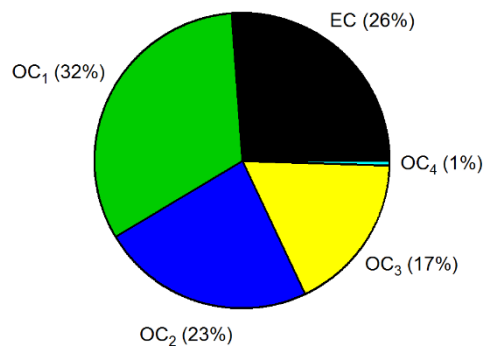
152 **1.2 Revised Results and Discussions (with new materials added)**

153 **1.2.1 Meteorological conditions, SMPS and OC/EC data**

154 The time series of meteorological conditions, particle number size distribution, $PM_{2.5}$,
 155 OC and EC concentrations during the campaign are presented in Fig. R1. Overall, the
 156 campaign came under the influence of the prevailing northerly wind with an average
 157 wind speed and temperature (\pm one standard deviation) of $1.73 \pm 0.95 \text{ m s}^{-1}$ and $14.8 \pm$
 158 $5.1 \text{ }^\circ\text{C}$, respectively. The average $PM_{2.5}$ concentration was $48 \pm 26 \text{ } \mu\text{g m}^{-3}$. A few cold
 159 front periods were observed, during which the wind speed increased and the
 160 temperature decreased. In general, the low wind speed favored the accumulation of
 161 $PM_{2.5}$. OC concentrations ranged from 0.5 to $47.0 \text{ } \mu\text{g m}^{-3}$ with an average of 9.0 ± 6.0
 162 $\text{ } \mu\text{g m}^{-3}$, while EC concentrations ranged from 0.2 to $23.0 \text{ } \mu\text{g m}^{-3}$ with an average of $3.4 \pm$
 163 $3.0 \text{ } \mu\text{g m}^{-3}$. OC_1 , the most volatile group among OC_1 to OC_4 in OC/EC analysis,
 164 accounted for one-third of the total carbon mass (Fig. R2).
 165



166 Fig. R1. Overview of major meteorological parameters, $PM_{2.5}$, OC and EC
 167 concentrations, OC/EC ratio and particle number size distributions in the campaign. Air
 168 mass clusters are depicted at the top and the shaded areas indicate days with daily-
 169 averaged $PM_{2.5}$ concentrations exceeding $95 \text{ } \mu\text{g m}^{-3}$.
 170
 171



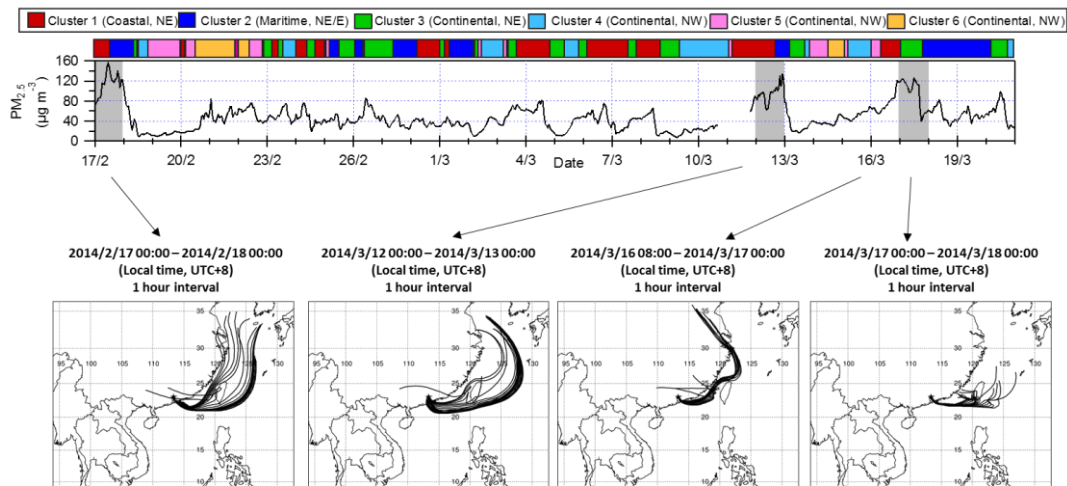
172

173 Fig. R2. Average mass fractions of EC, OC₁, OC₂, OC₃ and OC₄ in PM_{2.5}.

174

175 On Feb 17, and Mar 12 and 17, the daily-averaged PM_{2.5} concentrations exceeded 95
 176 $\mu\text{g m}^{-3}$; they were nearly twice the daily-averaged values on other days (Fig. R1, shaded
 177 area in grey). Results of 72 h back trajectories (Stein et al., 2015; Rolph, 2016) showed
 178 that air masses arriving at the site on or before these three days mostly originated from
 179 the continental or oceanic area close to Eastern China (Fig. R3). The SMPS data also
 180 showed a mode near 100 nm with a high particle number concentration (Fig. R1).

181



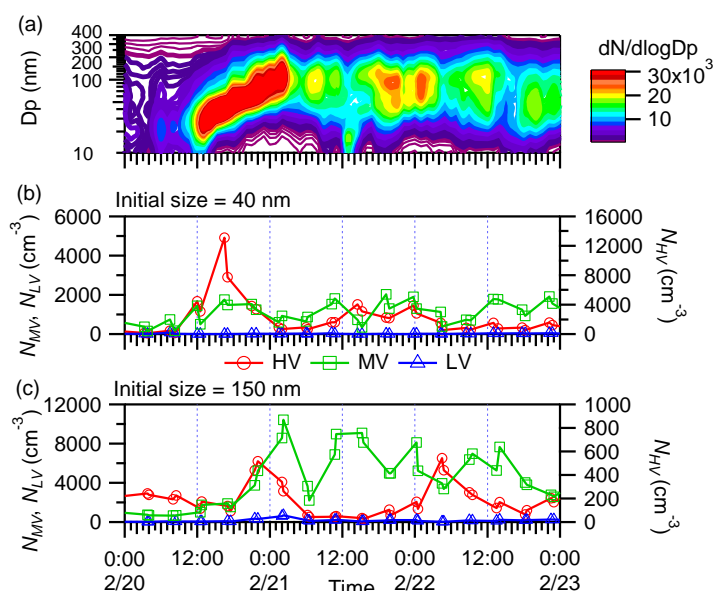
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183 Fig. R3. Time series of PM_{2.5} concentrations and 72 h back trajectories at hourly
 184 intervals on Feb 17, and Mar 12, 16 and 17.

185

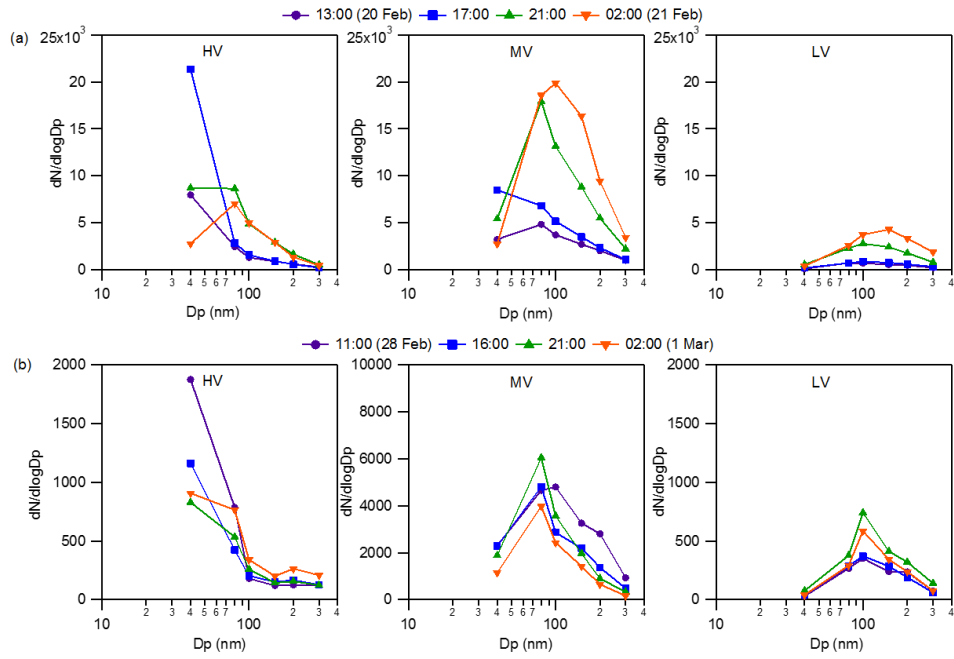
186

187 Two new particle formation (NPF) events were observed in the campaign on Feb 20
 188 and Mar 13 (Fig. R1). Since VTDMA data were not available during the NPF event on
 189 Mar 13, we only focus on the NPF event on Feb 20 which happened after a cold front
 190 under a low $PM_{2.5}$ concentration. On Feb 20, a sub-20 nm particle mode was first
 191 observed at 12:00. This particle mode grew continuously until it reached 120 nm at
 192 02:00 on Feb 21. In VTDMA measurements, a sharp increase in the number
 193 concentration of HV particles having an initial diameter of 40 nm was observed at
 194 17:00 on Feb 20 (Fig. R4). This event is likely related to the growth of the newly
 195 formed particles when they mixed with the volatile materials via condensation or
 196 adsorption. As these particles aged further, they grew larger as reflected in the increase
 197 in number concentrations of larger MV particles and the increase in $PM_{2.5}$ mass (Fig.
 198 R4). The growth of the newly formed particles can also be observed from the number
 199 size distributions of HV, MV and LV particles at different times on Feb 20 and 21 (Fig.
 200 R5). The mode of HV particles increased from 40 nm at 17:00 to 80 nm at 21:00 on
 201 Feb 20 Feb. The mode stayed at 80 nm while the corresponding number concentration
 202 decreased at 02:00 on Feb 21 Feb. In contrast, the number concentrations of MV
 203 particles grew continuously. The HV and MV particle concentrations and diameter
 204 modes underwent much smaller changes on the non-event day of Feb 28 (Fig. R5).
 205



206

207 Fig. R4. Time series of (a) particle number size distribution, (b) number concentrations
 208 of HV, MV and LV in 40 nm particles and (c) number concentrations of HV, MV and
 209 LV in 150 nm particles.



210

211 Fig. R5. Particle number size distribution of (columns from left to right) HV, MV and

212 LV particles (a) at 13:00, 17:00, 21:00 on 20 Feb and 02:00 on 21 Feb and (b) at 11:00,

213 16:00, 21:00 on 28 Feb and 02:00 on 1 Mar.

214

215 **1.2.2 Comparison of the diurnal variations in OC/EC and VTDMA data**

216 The diurnal variations in the mass fractions of OC and EC in PM_{2.5} are compared with
217 the volume fractions of CV, HV residual, MV residual, LV residual and VM in particles
218 of dry initial diameters of 40, 150 and 300 nm. The OC and EC data on Mar 12 and 17
219 were excluded since they were more than two standard deviations higher than those on
220 other days. Subtle morning peaks between 06:00 and 10:00 were observed for the
221 volume fraction of LV residuals (Fig. R6). A similar peak was observed for the mass
222 fraction of EC in PM_{2.5} in the morning (Fig. R7). This suggests that LV particles may
223 be related to the EC from vehicle emissions in the morning. This EC was relatively
224 less aged and externally mixed with other volatile materials. In the late afternoon, LV
225 residuals showed another peak between 17:00 and 19:00 whereas the mass fraction of
226 EC in PM_{2.5} exhibited a minimum at 15:00, after which it increased continuously. The
227 continuous increase in EC at night is likely related to the increase of heavy-duty diesel
228 vehicles (Zhang et al., 2015), which was restricted during daytime (Bradsher, 2007).

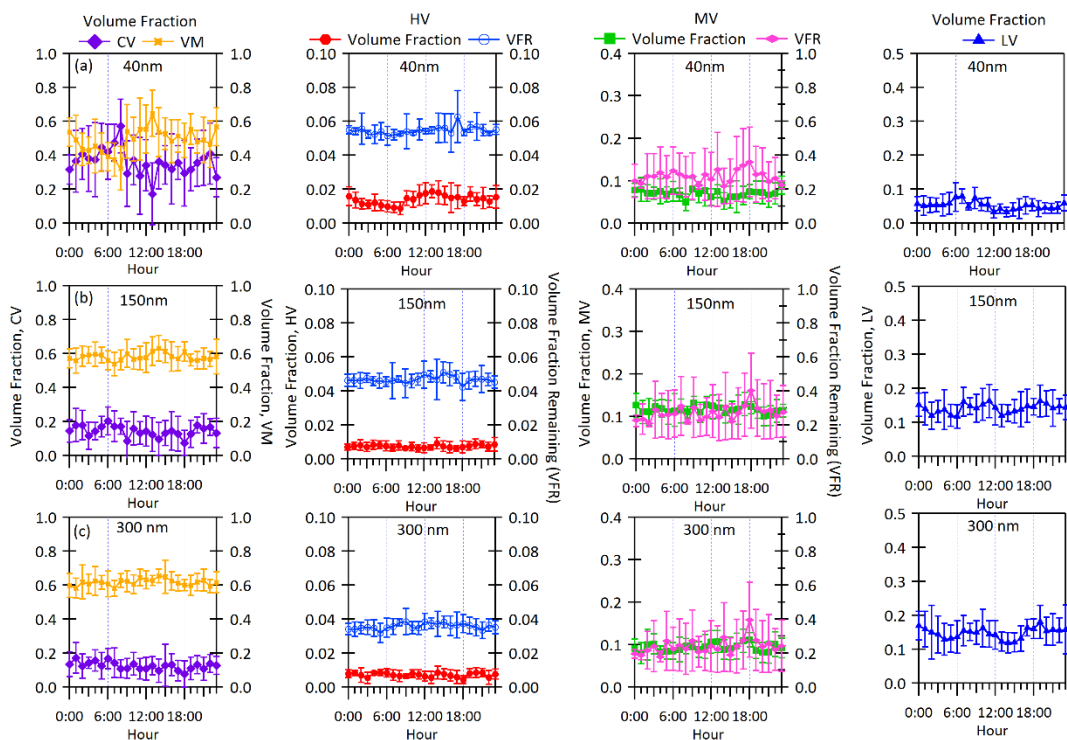
229

230 Although OC₁ contributed to about half of the total OC mass, the diurnal variation in
231 the mass fraction of OC in PM_{2.5} was driven by the total mass of OC₂, OC₃ and OC₄
232 (OC₂₋₄), which reached a minimum between 05:00 and 09:00 and increased until 19:00.
233 OC can be attributed to both primary and secondary sources. The increased mass
234 fraction of OC in PM_{2.5} and OC-to-EC ratio in the afternoon suggest that the sources
235 of OC were less related to traffic but more to the aging and formation of secondary
236 organic aerosols (Turpin et al., 1990; Chow et al., 1996). These OC₂, OC₃ and OC₄
237 may be highly oxygenated species or oligomers that are less volatile than primary or
238 less oxygenated organics (Kalberber et al., 2004; Huffman et al., 2009).

239

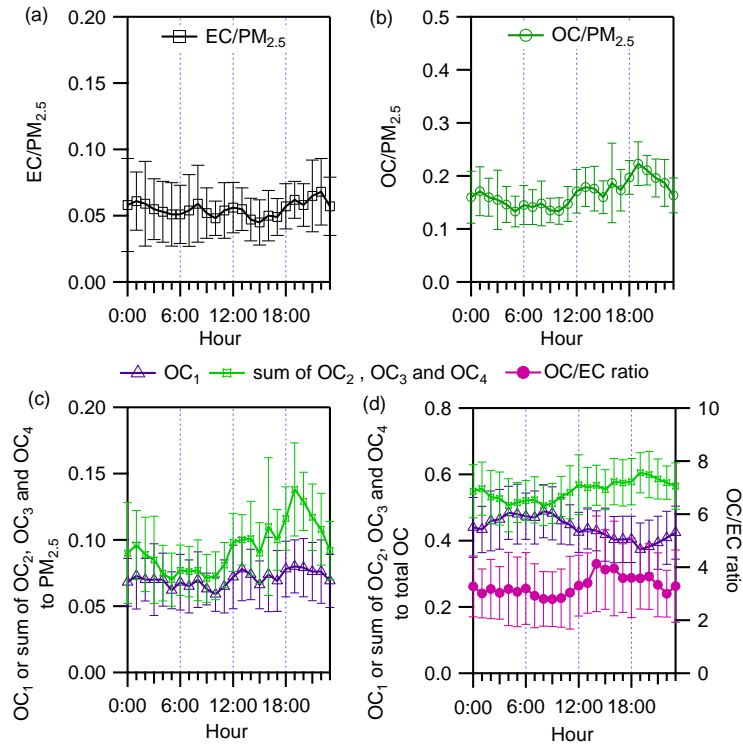
240 It is interesting to note that the volume fraction of LV residuals and the *VFR* of MV
241 particles at different sizes showed a dip in the afternoon (Fig. R6, third column from
242 the left). The *VFR* of 40 nm MV particles showed a dip at 14:00 while those in 150 nm
243 and 300 nm particles showed a dip at 15:00. The volume fraction of LV residuals in
244 150 nm and 300 nm particles reached a minimum at 13:00 and 15:00, respectively.
245 Because EC decreased between 12:00 and 15:00, the increase in the volume fraction
246 of LV residuals in 150 nm particles since 13:00 and the *VFR* of 40 nm MV particles

247 since 14:00 may be related to the increased presence of aged organics as well as the
 248 EC particles which aged via coagulation and condensation.
 249



250
 251 Fig. R6. Diurnal variations in volume fractions of (columns from left to right) CV, VM,
 252 HV residual, MV residual and LV residual in (a) 40 nm, (b) 150 nm and (c) 300 nm
 253 particles. Diurnal variations in the volume fraction remaining (*VFR*) of HV and MV
 254 particles are plotted on the right axis. Error bars represent one standard deviation.

255
 256

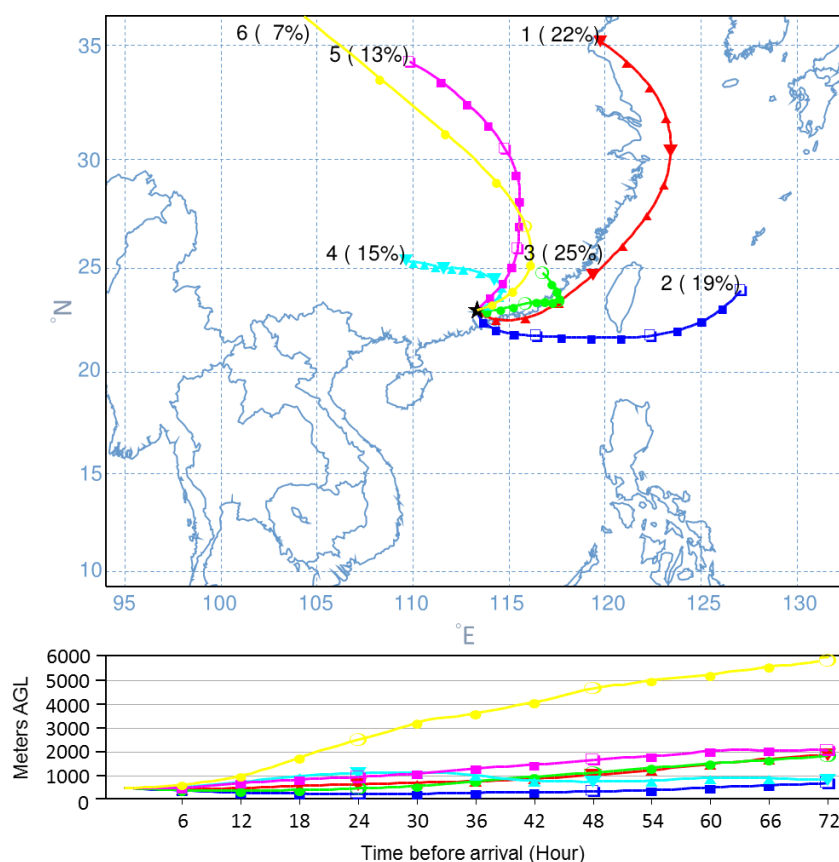


257

258 Fig. R7. Diurnal variations in the mass fractions of EC, OC, OC₁ and the sum of OC₂,
 259 OC₃ and OC₄ in PM_{2.5}, the ratio of OC to EC, mass fractions of OC₁ and the sum of
 260 OC₂, OC₃ and OC₄ to total OC in February and March. Error bars represent one
 261 standard deviation.

262 **1.2.3 Back trajectory analyses**

263 We calculated the 72 h back trajectories of the air masses arriving at the sampling site
264 (23°00 N, 113°25'' E) at 4 h intervals (at 00:00, 04:00, 08:00, 12:00, 16:00 and 20:00
265 local time, UTC +8) using the PC version of the HYSPLIT4 (Hybrid Single Particle
266 Lagrangian Integrated Trajectory, version 4) model (Stein et al., 2015; Rolph, 2016).
267 Archived meteorological data from the Global Data Assimilation System (GDAS) 1-
268 deg was employed and the receptor height was set at 500 m above ground level (a.g.l.).
269 The 191 back trajectories calculated were grouped into six clusters based on their
270 spatial distribution (Fig. R8).
271



272
273 Fig. R8. Mean back trajectories of the six types of air masses arriving at the sampling
274 site.
275

276 Overall, the sampling site was mostly affected by northwesterly and northeasterly air
277 masses. Cluster 1 and 3 are coastal and continental air masses, respectively, although
278 both originated from the northeast. Clusters 4, 5 and 6 represent continental air masses
279 originating from the northwest. Cluster 2 is a group of maritime air masses originating
280 from the East China Sea northeast or east of Guangzhou. While air masses in cluster 6
281 were transported at relatively high speeds and altitudes (over 3000 m a.g.l.), air masses
282 in all the other clusters were transported at an altitude below 1500 m a.g.l. for over 40
283 h before arriving at the site. Nevertheless, air masses in cluster 6 only persisted for less
284 than three days. Since the corresponding VTDMA and OC/EC data were sometimes
285 unavailable, cluster 6 will be excluded from the following discussion.

286

287 The average PM_{2.5}, OC and EC concentrations associated with air masses from the
288 northeast of Guangzhou (clusters 1, 2 and 3) were higher than those from the northwest
289 (clusters 4 and 5, Table R1). Days associated with coastal and maritime air masses
290 were more polluted than days associated with continental air masses for several reasons.
291 First, south China as a region is often affected by the high pressure system moving
292 eastward or southward from the continent out to sea in winter. When the maritime or
293 coastal air streams entered from the southeast of the sampling site at Panyu, the
294 atmosphere at the sampling site became more stable with low local wind speeds (e.g.
295 the polluted days on Feb 17 and Mar 12, 16 and 17, Fig. R1 and R3). Local pollutants
296 accumulated and the city was also affected by pollutants from the southeastern areas
297 of the site (e.g. Shenzhen, Nansha and Dongguan). Second, land-sea breeze cycles
298 were observed when the sampling site was under the influence of maritime air masses
299 from Mar 18 to 20. During the day, southeasterly wind prevailed and the wind speed
300 was higher. In the evening, the southeasterly wind was gradually replaced by a
301 southwesterly or northwesterly wind and the wind speed decreased (Fig. R1). The
302 cycle started again in the morning when the westerly wind was gradually replaced by
303 southeasterly wind. Such land-sea breeze effects can result in an effective
304 redistribution and accumulation of air pollutants within the PRD region (Lo et al.,
305 2006).

306

307 Table R1. Summary of concentrations of PM_{2.5}, OC, EC and the ratio of OC to EC
 308 (OC/EC) in the five clusters.

	Cluster				
	Coastal	Maritime		Continental	
	1	2	3	4	5
Origin (to the site)	NE	NE/E	NE	NW	NW
PM _{2.5} (μg m ⁻³)	58.5 ± 24.4	58.9 ± 30.9	47.5 ± 28.4	33.9 ± 15.9	33.8 ± 19.3
OC (μg m ⁻³)	10.8 ± 6.01	10.84 ± 7.22	10.13 ± 6.89	5.51 ± 3.3	7.32 ± 2.75
EC (μg m ⁻³)	4.38 ± 2.97	4.98 ± 4.21	3.43 ± 3.12	1.8 ± 0.98	2.46 ± 0.59
OC/EC	2.83 ± 1.05	2.62 ± 1.03	3.65 ± 1.6	3.18 ± 1.26	2.94 ± 0.73

309

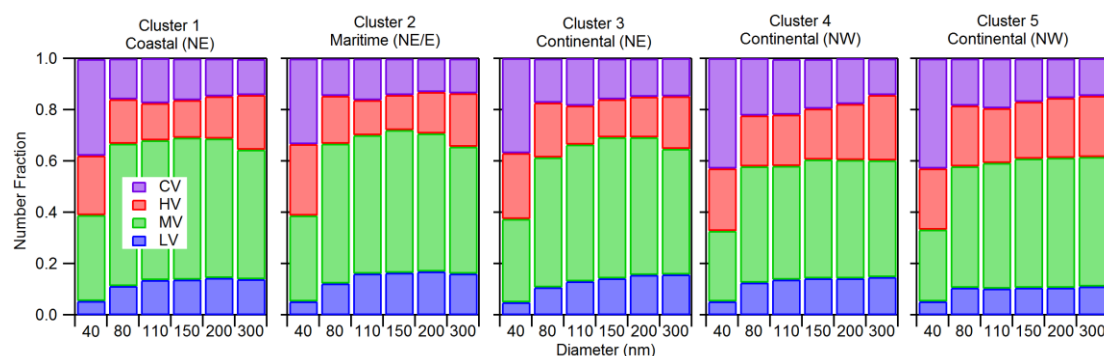
310 Furthermore, PM_{2.5} in the northeastern parts of China can exceed 200 μg m⁻³ due to
 311 both enhanced emissions from coal combustion for heating and poor dispersion during
 312 wintertime (Gu et al., 2014). Under the influence of the prevailing northerly or
 313 northeasterly wind in China, these pollutants were often transported to southern China
 314 and the East China Sea (Chen et al., 2012). Pollutants might also have accumulated
 315 when the maritime air masses spent about two days across Taiwan and the coast of
 316 south China. In contrast, continental air masses in cluster 5 moved slightly faster, and
 317 were often associated with the cold front period during which the local wind speed and
 318 pressure increased but the temperature decreased (Fig. R1). As the cold air masses
 319 passed through the city, dispersion and clearance of pollutants were promoted,
 320 resulting in lower PM_{2.5} concentrations (Tan et al., 2013a). Therefore, unlike in other
 321 coastal cities like Hong Kong (Lee et al., 2013), in Panyu maritime air masses could
 322 lead to more severe pollution than the continental ones in winter.

323

324 The five clusters were further analyzed to study the influence of air mass history on
 325 aerosol volatility. The number fractions of CV, HV, MV and LV of the six selected
 326 diameters in VTDMA measurements are regrouped based on the clusters as shown in
 327 Fig. R9. The total number fractions of the non-volatile residuals (sum of HV, MV and
 328 LV) were similar in all clusters. Maritime air masses (cluster 2) had a slightly higher
 329 fraction of LV particles while continental air masses originating from the northwest of
 330 the site (clusters 4 and 5) had a higher fraction of HV particles. Although the air masses
 331 in clusters 1 and 5 originated from farther away and traveled at relatively higher speeds

332 than those in clusters 2, 3 and 4, all clusters involved transport at low altitudes (below
 333 1500 m) for over 40 h, likely due to the generally lower mixing heights in winter.
 334 Therefore, aerosols in these air masses were all well-aged upon arrival (Wehner et al.,
 335 2009). This could be another reason for the lack of size dependence of the number,
 336 volume fractions and diurnal variation for particles larger than 80 nm. When the
 337 transported air masses mixed with local pollutants, the size dependence of the number
 338 fractions of different volatility groups as well as the aging of local emissions was
 339 further reduced.

340



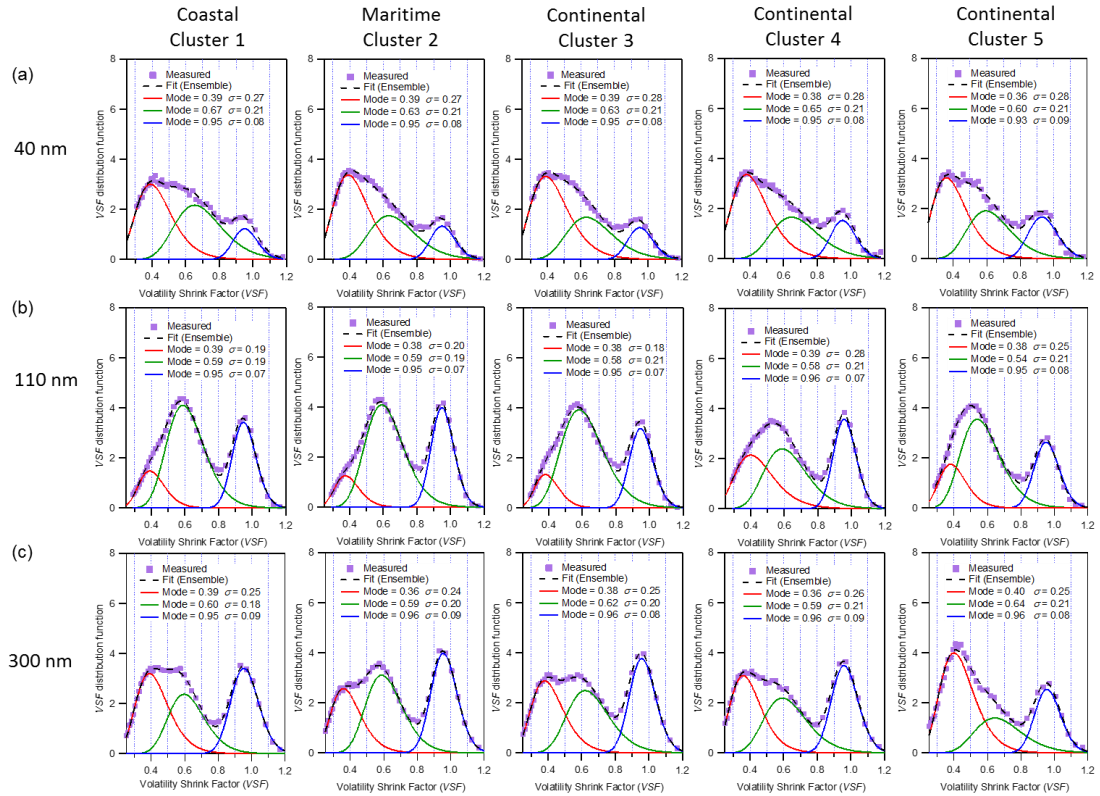
341

342 Fig. R9. Average number fractions of CV, HV, MV and LV particles in clusters 1 to 5
 343 at different selected diameters.

344

345 We also examine at the volatility shrinkage factor (*VSF*) distributions of 40 nm, 110
 346 nm and 300 nm particles upon heating at 300 °C (Fig. R10). Log-normal fittings with
 347 a three-peak solution were applied to the distributions. The average *VSF* modes of the
 348 peaks were located at 0.38 ± 0.021 (peak 1), 0.60 ± 0.066 (peak 2) and 0.95 ± 0.007
 349 (peak 3), respectively. The standard deviation of the corresponding normal distribution
 350 (σ) of peak 3 was the smallest among the three peaks ($\sigma < 0.1$). For the same particle
 351 size, the *VSF* distributions in the *VSF* range between 0.3 and 0.8 in cluster 5 was
 352 relatively more uni-modal than those of other clusters (Fig. R10b and R10c). This
 353 suggests that the composition in cluster 5 was more homogeneous. Cluster 1 also
 354 consisted of long-range transported air masses but they likely passed through areas that
 355 are more polluted and mixed with different types of pollutants. Note that the fractions
 356 of HV, MV and LV have been traditionally defined based on the values of *VSF*, i.e. HV
 357 < 0.4 ; $0.4 < MV < 0.9$; $LV > 0.9$ (Wehner et al., 2009). The *VSF* distributions above
 358 suggest that these definitions using *VSF* = 0.4 and 0.9 may need to be re-visited in the
 359 future.

360



361

362 Fig. R10. Volatility shrinkage factor (VSF) distribution function in different clusters.

363 Solid and dotted lines are the peaks fitted with log-normal function and the ensemble

364 distributions, respectively.

365

366

367 2. We have revised the introduction to include a discussion of the non-volatile organics
368 (see item 1.1.1).

369

370 3. The data analysis in this work focused on the measurements made after the aerosols
371 were heated at 300 °C. The methodology section is revised stating clearly that the
372 definitions of *VSF*, LV, MV, HV and all relevant quantities defined in this work refer
373 to results at 300 °C.

374

375 **3.1 Revised Methodology (Section 2.1.2, P25275 of the original manuscript, line 8**
376 **onwards):**

377 ...The *VSF* is also used to divide the particles into three groups, namely the low
378 volatility (LV), medium volatility (MV) and high volatility (HV) particles. [In this study,](#)
379 [we focus on the measurements made at 300 °C. The *VSF* ranges for LV, MV and HV](#)
380 [particles upon heating at 300 °C are above 0.9, between 0.4 and 0.9 and below 0.4,](#)
381 [respectively](#) (Fig. 2) (Wehner et al., 2004; Wehner et al., 2009).

382

383 4. We agree that the term low volatility in this manuscript refers to material that is
384 elsewhere referred to as extremely low volatile (e.g. Donahue et al., 2013, Murphy
385 et al., 2014). In this study, the terms “volatile” and “non-volatile” are defined based
386 on the heating temperature (i.e. 300 °C in this work) set in the VTDMA to
387 characterize carbonaceous compounds. They are therefore different from the
388 volatilities defined under ambient conditions (Donahue et al., 2009; Murphy et al.,
389 2014) or in other measurement techniques, which aim to characterize other
390 chemical components (Twomey, 1968; Pinnick et al., 1987; Huffman et al., 2009).
391 We have clarified this definition in the revised introduction (see item 1.1).

392

393 5. Unnecessary abbreviations for number and volume fractions in both the
394 methodology and results sections are avoided in the revised manuscript by using
395 the original terms such as “number fractions” or “volume fractions”.

396

397 6. Please refer to item 1.2 for the information and discussions added.

398

399 7. We agree that the residuals of the finest particles (with an initial diameter of 40 nm)
400 might go below the detection limit of the downstream DMA and CPC in the
401 VTDMA system, i.e. 10 nm, upon heating at 300 °C. The number concentrations
402 (and fractions) of HV and CV of the finest particles may therefore be
403 underestimated and overestimated, respectively. A note is added in the results
404 section of the revised manuscript.

405 **7.1 Revised Section 3.1 (Discussion on average number and volume fractions):**
406 ...Nevertheless, the detection limit of the downstream DMA and CPC in the VTDMA
407 system is 10 nm. It was assumed that the residuals having a diameter below 10 nm were
408 small enough to be considered as completely vaporized. However, such assumption
409 would lead to an overestimation of CV and an underestimation of the non-volatile
410 residuals for the finest particles selected (with an initial diameter of 40 nm).

411

412 **8.** The heating tube was a 1/2", 80 cm long stainless steel tube with an inner diameter
413 of 8 mm. With a sample flow rate of 1 L min⁻¹, the resulting residence time in the
414 heated section of the VTDMA was 2.4 s. The estimated aerosol velocity on the
415 center line was 0.33 m s⁻¹. After leaving the heating unit, particles entered a heat
416 exchanger measuring 30 cm in length to ensure sufficient cooling before entering
417 DMA₂. The relevant information is added to the methodology section.

418

419 **8.1 Revised Methodology (Section 2.1.2 VTDMA measurements, P25375 of the**
420 **original manuscript, line 5 onwards):**

421 Afterwards, the monodisperse aerosols were directed via path (b) to a heated tube for
422 volatility measurement (V-Mode) sequentially at 25, 100 and 300 °C. The heating tube
423 was a 1/2", 80 cm long stainless steel tube with an inner diameter of 8 mm. With a
424 sample flow rate of 1 L min⁻¹, the resulting residence time in the heated section of the
425 VTDMA was 2.4 s. The estimated aerosol velocity on the center line was 0.33 m s⁻¹.
426 Compared to the residence time of 0.3 s to 1 s in other VTDMA systems (e.g. Brooks
427 et al., 2002; Philippin et al., 2004; Villani et al., 2007), the residence time in our
428 VTDMA is assumed to be long enough for the volatile materials to be effectively
429 vaporized. After leaving the heating tube, the flow entered a heat exchanger measuring
430 30 cm in length to ensure sufficient cooling before entering DMA₂.

431

432 **9.** Please refer to item 1.2 for the information and discussions added.

433 **Minor comments:**

434 **1. P25271, abstract:** *Please explain how the medium and low-volatility aerosol*
435 *fractions are determined. Also it should be clear from the abstract that by low-*
436 *volatility fraction essentially “non-volatile” fraction is meant, i.e. LV aerosol*
437 *fraction consists of compounds that do not evaporate significantly even at 300 °C.*
438 *Also, it is somewhat confusing to say “nonvolatile materials ... contain... less*
439 *volatile OC”.*

440

441 **Response:**

442 The abstract is rewritten using clearer definitions.

443

444 **Revised:**

445 ... Low-volatility (LV) particles, with a volatility shrinkage factor (VSF) at 300 °C
446 exceeding 0.9, contribute to 5% of number concentrations of 40 nm particles and 11–
447 15% of 80–300 nm particles. They were non-volatile materials externally mixed with
448 the volatile ones and therefore did not evaporate significantly at 300 °C. Non-volatile
449 materials mixed internally with the volatile ones are referred to as the medium
450 volatility (MV, $0.4 < VSF < 0.9$) and high volatility (HV, $VSF < 0.4$) particles...

451

452 ...The closure analysis of the total mass of LV and MV residuals and the mass of EC
453 or the sum of EC and non-volatile OC also suggests that non-volatile OC, in addition
454 to EC, was one of the components of the non-volatile residuals measured by the
455 VTDMA in this study.

456

457

458 2. *P25271, abstract: OC contents are named from OC₁ to OC₄. It is not clear in the*
459 *abstract what is meant by OC₂-OC₄ compounds. Does it refer to the amount of*
460 *carbon in the compound? Please clarify.*

461

462 **Response:**

463 In the revised abstract, the term non-volatile OC, which evaporated at 475 °C or above,
464 is used instead of OC₂-OC₄.

465

466 **Revised:**

467 ... [Non-volatile OC evaporating at 475 °C or above](#), together with EC, contributed to
468 67% of the total carbon mass.

469

470

471

472 3. *P25271, l 24-26: check the references during recent years.*

473

474 **Response:**

475 Two references in recent years are added.

476

477 **Original:**

478 P25271, l 24-26

479 Carbonaceous aerosols comprising organic carbon (OC) and elemental carbon (EC) or
480 black carbon (BC) are one of the major light absorption constituents and are abundant
481 in particulate matter (PM) (Rosen et al. 1978; Hansen et al. 1984; Japar et al. 1986;
482 Chow et al. 1993; Horvath 1993; Lioussse et al. 1993; Fuller et al. 1999; Putaud et al.
483 2010).

484

485 **Revised:**

486 Carbonaceous aerosols comprising organic carbon (OC) and elemental carbon (EC) or
487 black carbon (BC) are major light absorption constituents and occur abundantly in
488 particulate matter (PM) (Rosen et al. 1978; Hansen et al. 1984; Japar et al. 1986; Chow
489 et al. 1993; Horvath 1993; Lioussse et al. 1993; Fuller et al. 1999; Putaud et al. 2010;
490 [Tao et al., 2014; Zhang et al., 2015](#)).

491

492 **4. P25272, l 4-6:** *were the data reported in 2007, or the measurements were*
493 *performed in 2007, please clarify it.*

494

495 **Response:**

496 The measurements were performed in 2007 but reported by Yu et al. (2010). However,
497 the mass of OC was incorrectly reported. It should be 13.4 to 22.5 $\mu\text{g m}^{-3}$. The sentence
498 is revised.

499

500 **Original:**

501 P25272, l 4-6

502 In 2007, the mass concentrations of EC and OC at an urban Guangzhou (GZ) site were
503 reported to be 6.8 to 9.4 and 6.6 to 22.5 $\mu\text{g m}^{-3}$ respectively (Yu et al., 2010).

504

505 **Revised:**

506 In 2007, the mass concentrations of EC and OC **measured** at an urban Guangzhou (GZ)
507 site ranged from 6.8 to 9.4 and **from 13.4** to 22.5 $\mu\text{g m}^{-3}$ respectively (Yu et al., 2010).

508

509

510

511 **5. P25273, l 1-4:** *Firstly, I think the definition is not clear. It should be particles with*
512 *LV, MV and HV fractions, but not LV, MV and HV particles according to Wehner et*
513 *al. (2009). Secondly, they performed the measurements at 300 °C. Please add the*
514 *temperature reference in the text. Thirdly, what do these completely vaporized*
515 *aerosols refer to ambient aerosols, from what you wrote in the discussion part, it*
516 *could be sulfate, ammonium nitrate?*

517

518 **Response:**

519 Sorry for the confusing definitions. The definitions are revised to show that they follow
520 the definitions by Wehner et al. (2004) and Rose et al. (2006): LV particles are particles
521 containing a less volatile fraction and do not evaporate significantly upon heating at
522 300 °C; MV and HV particles are particles with more volatile fractions.

523

524 The completely vaporized aerosols at 300 °C can be sulfate, nitrate and volatile organics.
525 Please refer to item 1.1 of the major comments for the revised content.

526 **6. P25273, line 13:** *Please write what AMS stands for.*

527

528 **Original:**

529 P25273, line 13

530 ...with the mass fraction of organics measured by an AMS.

531

532 **Revised:**

533 ... with the mass fraction of organics measured using an [aerosol mass spectrometer](#).

534

535

536

537 **7. P25273, line 15-21:** *“However, because of its higher volatility compared to EC,*
538 *they were often considered completely evaporated upon heating at temperatures*
539 *above 300 C in VTDMA studies” contradicts with “It is therefore possible, that a*
540 *significant amount of non-volatile OC can exist together with EC in ambient*
541 *aerosol, even after heating in a VTDMA.” Clarify what is meant by the former*
542 *sentence. Also, using “its” and “they” causes some confusion.*

543

544 **Response:**

545 We apologize for the contradicting sentence. The paragraphs in the introduction are
546 revised. Please refer to item 1.1 in the major comments for the revised content.

547

548

549

550 8. *P25274, section 2.1.2: The approach to determine the LV/MV/HV aerosol fractions*
551 *is explained in the end of the section. I suggest that it is explained whenever*
552 *LV/MV/HV are mentioned for the first time in this section.*

553

554 **Response:**

555 LV, MV and HV are now defined when the terms first appear. It is also assumed that
556 LV particles represent EC particles externally mixed with volatile materials while MV
557 and HV particles represent EC particles internally mixed with volatile materials.

558

559 **Original:**

560 Section 2.1.2, P25275 line 8 onwards

561 Upon heating at 100 °C and above, volatile components of particles such as sulfate,
562 nitrate and volatile organics would vaporize at different temperatures depending on
563 their volatilities.

564

565 **Revised:**

566 Upon heating at 100 °C and above, volatile components of particles such as sulfate,
567 nitrate and volatile organics would vaporize at different temperatures depending on
568 their volatilities. A volatility shrinkage factor, *VSF*, is defined as the ratio of particle
569 diameter after heating at temperature *T*, $D_{p,T}$, to that before heating, D_0 , to indicate the
570 size reduction of the ambient particles (Eq. (1)). The value of *VSF* is always smaller
571 than or equal to one, depending on the amount of volatile materials vaporized at the
572 heating temperature *T*.

$$573 \quad VSF(T) = \frac{D_{p,T}}{D_0} \quad (1)$$

574 The *VSF* is also used to divide the particles into three groups, namely the low volatility
575 (LV), medium volatility (MV) and high volatility (HV) particles. In this study, we focus
576 on the measurements made at 300 °C. The *VSF* ranges for LV, MV and HV particles
577 upon heating at 300 °C are above 0.9, between 0.4 and 0.9 and below 0.4, respectively
578 (Fig. 2) (Wehner et al., 2004; Wehner et al., 2009). The LV particles are assumed to
579 represent EC particles externally mixed with the volatile materials, while MV and HV
580 particles are assumed to represent EC particles internally mixed with volatile materials.
581 While the volatile materials in the MV and HV particles are referred to as VM, those
582 exist as external mixtures with the LV, MV and HV particles are referred to as
583 completely vaporized (CV) particles. The CV particles evaporate completely without
584 leaving behind any residuals at 300 °C.

585

586 9. *P25275, l 5-7: Please provide the residence time in your heating unit as well as the*
587 *time after the heating unit but before being sampling by the CPC as mentioned*
588 *above.*

589

590 **Response:**

591 Please refer to item 8 in the major comments.

592

593

594

595 10. *P25275, l 13-15: The complete run took around two hours, during which the*
596 *chemical composition of ambient aerosols might vary a lot, especially related to*
597 *traffic emissions. Can this be added into your discussion part?*

598

599 **Response:**

600 The chemical composition of ambient aerosols might vary a lot in two hours. However,
601 the campaign lasted for about two months, and clear diurnal patterns were observed.

602 The variations in aerosol compositions within a two-hour span are likely not affect any
603 of our conclusions.

604 Furthermore, although a complete run took around two hours, the sampling time at
605 each set temperature (25 °C, 100 °C and 300 °C) only took about half an hour. SMPS
606 scans were made between each temperature. A sentence is added for clarification.

607

608 **Original:**

609 P25275, l 13-15

610 Overall it took around one and a half to two hours to complete a cycle of measurements
611 which consisted of SMPS scans and V-Mode measurements at 25, 100 and 300 °C.

612

613 **Revised:**

614 Overall it took around one and a half to two hours to complete a cycle of measurements
615 which consisted of SMPS scans and V-Mode measurements at 25, 100 and 300 °C. *At*
616 *each temperature, the sampling time for the six selected diameters from DMA₁ (40 nm,*
617 *80 nm, 110 nm, 150 nm, 200 nm and 300 nm) took about half an hour and SMPS scans*
618 *were made in-between.*

619

620 *11. P25275, l 24-25: This is based on the assumptions that diffusion losses are*
621 *neglected.*

622

623 **Response:**

624 Yes. The sentence is modified with a mention of this assumption.

625

626 **Original:**

627 P25275, l 24-25

628 Evaporation of VM and CV does not change the number concentrations of LV, MV and
629 HV particles.

630

631 **Revised:**

632 **Excluding particle diffusional and thermophoretic losses, the** evaporation of VM and
633 CV does not change the number concentrations of LV, MV and HV particles.

634

635 **12. P25276, l 1-4:** *VSF is depending on chemical composition of your particles, but*
636 *also depending on which temperature you are using in your measurement. The*
637 *definition regarding to LV, MV and HV is not valid without giving the temperature*
638 *you are using for the number size distribution (Fig. 2) after heating. Also for Fig.*
639 *2, please explain VSF in the figure caption. Figure 2 is referred in the text prior to*
640 *introducing VSF.*

641

642 **Response:**

643 The description is revised to emphasize the fact that the analysis was performed on
644 data collected at 300 °C. The definition of *VSF* is moved to the earlier part of Section
645 2.1.2. It is now introduced before the reference to Figure 2 is made. Please refer to item
646 3.1 in the major comments and item 8 in minor comments for the revised methodology.
647

648 **Original:**

649 P25292, Fig. 2, Caption

650 Examples of particle size distributions of (left) ambient aerosols before entering DMA₁
651 and (right) residuals of the size-selected particles (D_0) after heating. The left and right
652 distributions correspond to (1) and (2) in Fig. 1 respectively. Residuals are divided into
653 several groups—LV (blue), MV (green) and HV (red)—based on their volatilities.

654

655 **Revised:**

656 Examples of particle size distributions of (a) ambient aerosols before entering DMA₁
657 and (b) residuals of the size-selected particles (D_0) after heating at 300 °C. The
658 distributions in Fig. 2a and 2b correspond to (1) and (2) in Fig. 1 respectively. The
659 residuals are divided into three groups—LV (blue), MV (green) and HV (red)—based
660 on their *VSF*.

661

662

663

664 *13. P25276, l 8-14: Should this part be moved to either introduction part or discussion*
665 *section? It is more relevant to general picture about volatility.*

666

667 **Response:**

668 In the revised introduction, the possible volatile and non-volatile materials at 300 °C
669 are discussed. This part is thus removed from the methodology section. Please refer to
670 item 1.1 in the major comments for the revised content.

671

672

673

674 *14. P25276, l 12: Provide references here please.*

675

676 **Response:**

677 The sentence is removed while it is revised in the introduction.

678

679

680

681 *15. P25276, l 21-22: Please add references here.*

682

683 **Response:**

684 The sentence is revised with more information added for a better description of OC₁ to
685 OC₄.

686

687 **Original:**

688 P 25276, line 19 – 22

689 “The OC/EC Analyzer adopts the ACE-Asia protocol (a NIOSH-derived protocol),
690 where OC evaporates at four set temperatures of 310, 475, 615 and 870 °C, and EC is
691 combusted at temperature above 550 °C (Schauer et al., 2003). Based on volatility and
692 refractoriness, the OC contents are named OC₁ to OC₄ with OC₁ being most volatile”

693

694 **Revised:**

695 The OC/EC analyzer adopts the ACE-Asia protocol (a NIOSH-derived protocol),
696 where OC evaporates at four set temperatures of 310, 475, 615 and 870 °C with pure
697 helium (He) as the carrier gas, and EC is combusted at temperatures between 550 °C
698 and 870 °C under He and 2% oxygen (O₂, Schauer et al., 2003, Wu et al., 2012). The
699 OC contents are named OC₁ to OC₄ based on the temperature protocol of the OC/EC
700 analyzer (Table R2). The mass of EC determined at different temperatures will be
701 grouped together for discussions.

702

703 Table R2. Temperature (T) and residence time (RT) protocol of the semi-continuous
704 Sunset OC/EC analyzer (Wu et al., 2012)

Carbon Fraction	Carrier Gas	T (°C)	RT (s)
OC ₁	He	310	80
OC ₂		475	60
OC ₃		615	60
OC ₄		870	90
EC ₁	He + 2% O ₂	550	45
EC ₂		625	45
EC ₃		700	45
EC ₄		775	45
EC ₅		850	45
EC ₆		870	45

705

706

707 *16. P25277, 14: Which section, please clarify.*

708

709 **Response:**

710 It should be Section 3.1 Overview. The average volume fraction of HV residuals only
711 contributed to less than 1% of the total volume (P25282 of the original manuscript,
712 lines 9-10). The sentence on P25277 is revised.

713

714 **Original:**

715 P25277, 14

716 We have ignored the HV residuals as their contributions are insignificant when
717 compared to LV and MV residuals (see later).

718

719 **Revised:**

720 We have ignored the HV residuals as their contributions [to the total volume of the](#)
721 [particles](#) are insignificant when compared to the contributions of the LV and MV
722 residuals ([Section 3.1](#)).

723

724

725 *17. P25277, l 8: I don't agree it is the number fraction of LV, MV and HV residuals, but*
726 *rather the number fraction of particles containing LV, MV and HV materials.*

727

728 **Response:**

729 The number fractions of LV, MV and HV residuals (after accounting for corrections
730 with CV particles and diffusional and thermophoretic losses) should be the same as the
731 number fractions of LV, MV and HV particles before heating. However, we understand
732 that in many studies number fraction is used for LV, MV and HV particles. In the
733 revised manuscript, we will only use “number fractions of LV, MV and HV residuals
734 ($\Phi'_{N,LV}$, $\Phi'_{N,MV}$ and $\Phi'_{N,HV}$, with their sum being equal to unity)” to represent the
735 measured values before any correction with CV particles and diffusional and
736 thermophoretic losses.

737

738 **Original:**

739 P25277, l 8 onwards:

740 The number fractions of LV, MV and HV residuals ($\Phi'_{N,LV}$, $\Phi'_{N,MV}$ and $\Phi'_{N,HV}$, with
741 their sum equals unity) in Stream 2 on Fig. 1 were obtained from $dN'/d\log D_p$ measured
742 by the CPC. However, these fractions are not the actual number fractions of LV, MV
743 and HV residuals ($\Phi_{N,LV}$, $\Phi_{N,MV}$ and $\Phi_{N,HV}$) of the selected particles before heating
744 because they have not taken into account the CV particles and particle diffusional and
745 thermophoretic losses.

746

747 **Revised:**

748 The number fractions of LV, MV and HV residuals ($\Phi'_{N,LV}$, $\Phi'_{N,MV}$ and $\Phi'_{N,HV}$, with
749 their sum being equal to unity) in Stream 2 in Fig. 1 were obtained from $dN'/d\log D_p$
750 measured with the CPC. However, these fractions **do not represent the actual number**
751 **fractions of LV, MV and HV particles ($\Phi_{N,LV}$, $\Phi_{N,MV}$ and $\Phi_{N,HV}$)** before heating because
752 they have not taken into account the CV particles and particle diffusional and
753 thermophoretic losses.

754

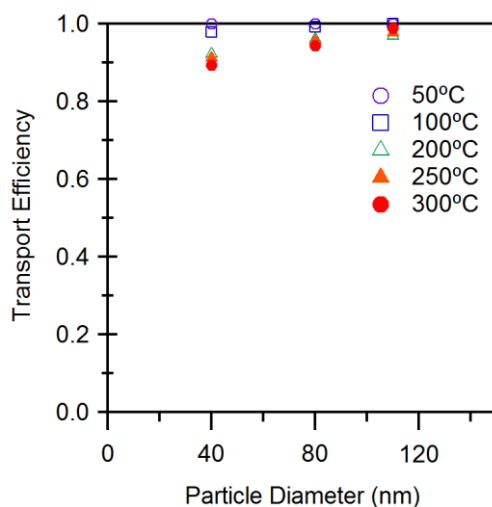
755 **18. P25277, l 20-23:** *it will be good to provide a calibration curve or transmission*
756 *curve from NaCl.*

757

758 **Response:**

759 A figure of the transport efficiency of NaCl in the VTDMA is added to the
760 supplementary information as Figure S2 (Fig. R11). A note is added in the
761 methodology section.

762



763

764 Fig. R11. Transport efficiency of NaCl in the VTDMA as a function of particle diameter
765 and heating temperature.

766

767 **Revised:**

768 P25277 l20-23

769 ...was determined by laboratory calibrations with sodium chloride (NaCl) particles,
770 which do not evaporate (i.e. $\Phi_{N,CV} = 0$) at the temperatures used in our experiments.

771 The transmission efficiency of NaCl of several selected diameters heated at
772 temperatures between 50 °C and 300 °C is provided in the supplemental information
773 (Fig. S2).

774

775 **19. P25279, I5:** We use VFR (volume fraction remaining) conventionally here to define
776 the ratio between the volume of the residuals and the host particles; please consider
777 changing it.

778

779 **Response:**

780 We have changed the term to VFR. Changes are made in both the methodology and
781 results sections.

782

783 **Original:**

784 P25279 I3-5:

785 Furthermore, we define the volume ratio of the residuals to their host particles for MV
786 and HV ($\Theta_{V,MV}$ and $\Theta_{V,HV}$) for our discussions later:

787
$$\Theta_{V,i} = \frac{N_i \times \frac{\pi}{6} D_{p,i}^3}{N_i \times \frac{\pi}{6} D_0^3} = \frac{D_{p,i}^3}{D_0^3} \quad (6)$$

788

789 **Revised:**

790 Furthermore, we also calculated the volume fraction remaining (VFR), defined as the
791 volume ratio of the residual to its host particle, to aid our discussions later:

792

793
$$VFR_i = \frac{N_i \times \frac{\pi}{6} D_{p,i}^3}{N_i \times \frac{\pi}{6} D_0^3} = \frac{D_{p,i}^3}{D_0^3} \quad (6)$$

794

795

796 **20. P25280, l 14-15:** *Could the reason be due to the detection limit of the CPC as*
797 *mentioned above?*

798

799 **Response:**

800 Yes it is a possibility. Please refer to item 7 in the major comments.

801

802

803

804 **21. P25280, l 20:** *What kind of atmospheric processes could be? Please clarify.*

805

806 **Response:**

807 The discussion on the lack of size dependence of number and volume fractions is
808 moved to section 3.2 diurnal variations of the revised manuscript. The diurnal
809 variations for particles larger than 80 nm were found much less obvious than those for
810 40 nm particles in this study and in others (Fig. R6) (Rose et al., 2011; Cheng et al.,
811 2012; Zhang et al., 2016). In winter, the atmosphere is more stable, resulting in a poorer
812 dilution of aged particles with the less polluted aerosols from higher up (Rose et al.,
813 2006). When the aged pollutants were trapped near the ground surface, the effect of
814 aging of fresh emissions weakened. The information is included in section 3.2 of the
815 revised manuscript.

816

817 On the other hand, most of the air masses arriving at the site traveled at low altitudes
818 (below 1500 m) for over 40 h (Fig. R8). The aerosols in these air masses contained
819 mainly MV and HV particles and were likely to be well-aged. When they mixed with
820 local pollutants, the size dependence of the number fractions of the volatility groups
821 was further reduced. Details are given in the trajectory analysis in item 1.2 of the major
822 comments.

823

824 **Original:**

825 P25280, l 20:

826 The lack of size dependence of number fractions for particles larger than 80 nm
827 suggests that they may be the result of similar atmospheric processes.

828

829 **Revised:**

830 Section 3.2 Diurnal variation of the revised manuscript:

831 The diurnal variations for particles larger than 80 nm were much less obvious than
832 those for 40 nm particles in this study and in others (Rose et al., 2011, Cheng et al.,
833 2012, Zhang et al., 2016). In winter, the atmosphere is more stable, resulting in a poorer
834 dilution of aged particles with the less polluted aerosols from higher up (Rose et al.,
835 2006). When the aged pollutants were trapped near the ground surface, the effect of
836 aging of fresh emissions weakened. Therefore, although a daily maximum and a daily
837 minimum were still observed for particles larger than 80 nm, the variation was mostly
838 within 15%.

839

840

841

842 *22. P25280, l 23: I don't agree with this, please rephrase the sentence.*

843

844 **Response:**

845 The whole sentence is rewritten for a proper explanation.

846

847 **Original:**

848 **P25280, l 20:**

849 The large fraction of CV in 40 nm particles is likely due to nucleation of fresh emissions
850 from more volatile primary sources or volatile secondary pollutants.

851

852 **Revised:**

853 As in Rose et al. (2006), fresh emissions like soot adsorbed or absorbed volatile
854 materials during atmospheric processing. Smaller particles grew to a greater extent
855 than the larger ones because of their higher ratios of surface area to volume. When they
856 were heated in the VTDMA at 300 °C, these smaller particles reduced more
857 substantially in size, as reflected in the higher CV and HV fractions and lower MV and
858 LV fractions.

859

860 *23. P25280, l 24-25: Please add appropriate references.*

861

862 **Response:**

863 The sentence here is combined with the sentence in the next comment and revised for
864 a more coherent discussion with references added.

865

866 **Original:**

867 P25280, l 24-25

868 Freshly emitted non-volatile primary sources such as EC and OC are in a larger size
869 range.

870

871 P25281, l 1-3

872 Yu et al. (2010) reported that the mass median aerodynamic diameter of urban EC in
873 the condensation mode in Guangzhou is about 380 nm.

874

875 **Revised:**

876 Yu et al. (2010) reported that the condensation and droplet modes of EC and OC in
877 urban sites of Guangzhou were approximately 400 nm and 900 nm, respectively. The
878 mode of fresh EC emitted from vehicles is also approximately 400 nm (Huang et al.,
879 2006).

880

881

882

883 *24. P25281, l 1-3: The sentence is not clearly written; please rephrase it.*

884

885 **Response:**

886 Please refer to the comment above (item 23).

887

888

889

890

891

892

893

894 **25. P25281, l 10-12:** *How do you define polluted days? Please clarify. Also, please add*
895 *references here.*

896

897 **Response:**

898 The whole description was rewritten for a proper explanation.

899

900 **Original:**

901 N_{MV} tracks reasonably well with $PM_{2.5}$ mass because of its dominance in the number
902 concentrations. Internally mixed soot particles, manifested as MV particles, play an
903 important role in Guangzhou, especially during polluted days.

904

905 **Revised:**

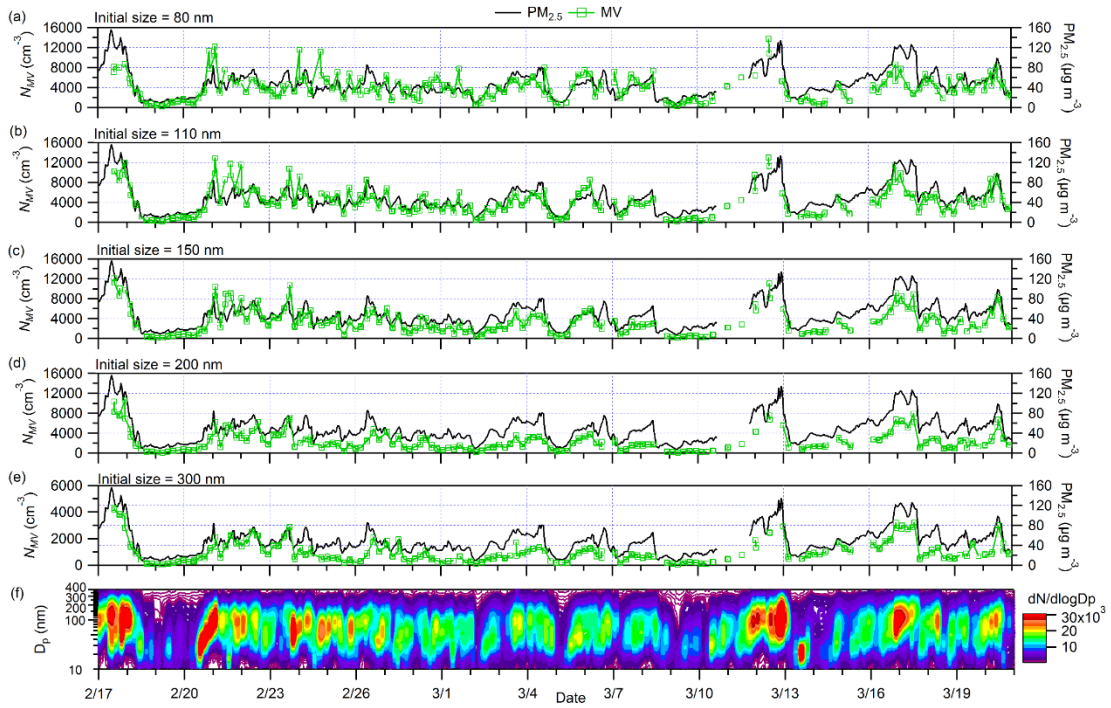
906 The temporal variation of the number concentration of MV particles having an initial
907 diameter of 80 nm or above tracked reasonably well with the accumulation of $PM_{2.5}$ as
908 particles aged and became more internally mixed. Furthermore, a size dependence was
909 observed for 80 nm to 300 nm MV particles. There were days, e.g., from Feb 24 to
910 Mar 10, when the number concentration of 300 nm MV particles did not track well
911 with $PM_{2.5}$. The mode of total particle number size distribution was below 100 nm and
912 the number concentrations of 300 nm particles were low (Fig. R12). $PM_{2.5}$ tracked
913 better with the number concentrations of 80 nm to 150 nm MV particles (Fig. R12a to
914 R12c) than those of 200 nm to 300 nm MV particles (Fig. R12d and R12e).

915

916

917

918



919

920 Fig. R12. (a–e) Time series of number concentrations of MV particles having initial
 921 diameters of 80 nm to 300 nm and (f) particle number size distributions during the
 922 campaign. Time series of $\text{PM}_{2.5}$ concentrations are plotted on the right axis in (a) to (e).

923

924 **26. P25282, l 1-3:** *The logics behind are not clear here; please rephrase the sentence.*

925

926 **Response:**

927 Please refer to item 21 for the revised content.

928

929

930

931 **27. P25282, l 10-13:** *Please consider rewriting it.*

932

933 **Response:**

934 The sentence is removed when the overall discussion of number and volume fractions

935 is rewritten for simplicity and clarity.

936

937

938

939 **28. P25282:** *Please add error bars in Fig. 5 and Fig. 7.*

940

941 **Response:**

942 The number and volume fractions of different groups are plotted separately after adding

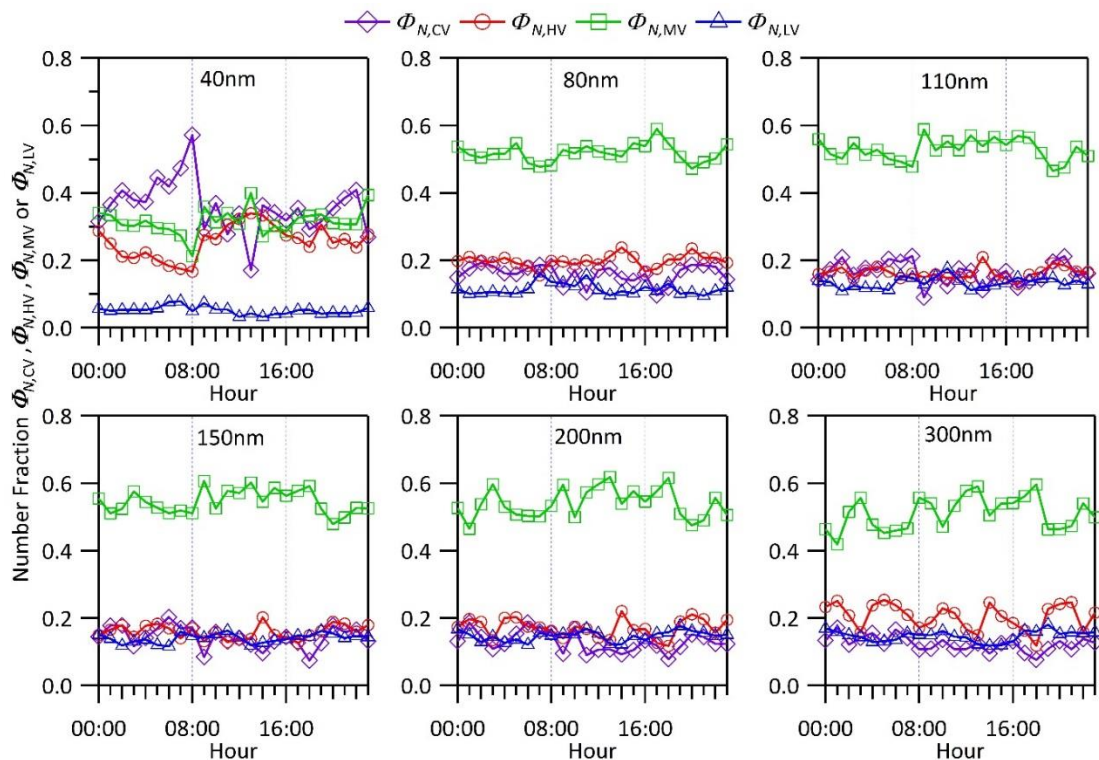
943 the error bars (Fig. R13 and R14). Since their diurnal patterns were similar, we only

944 add the diurnal patterns of volume fractions of 40 nm, 150 nm and 300 nm particles in

945 the revised manuscript (Fig. R6).

946

947 **Original:**



948

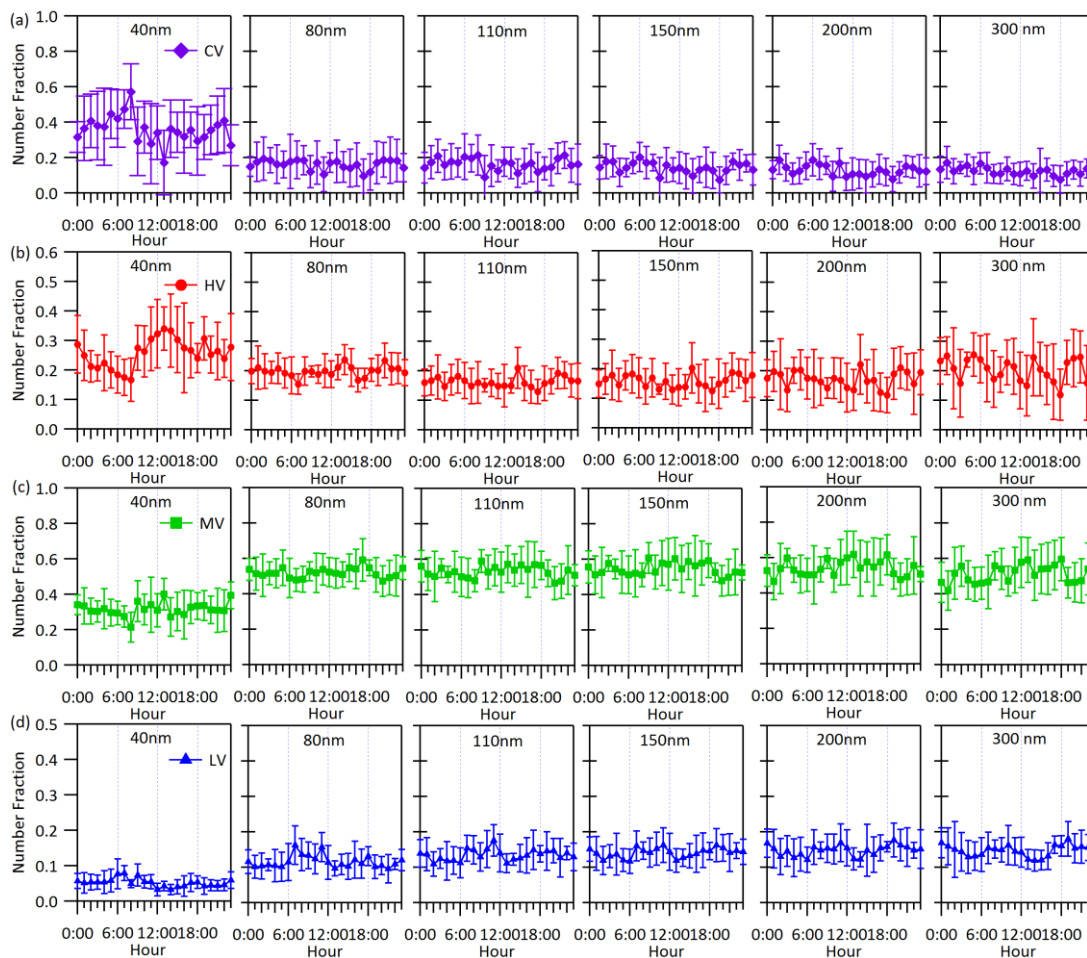
949 Fig. 5 (original manuscript). Diurnal variations in the number fractions of CV

950 (diamond (purple)), HV (circle (red)), MV (square (green)) and LV (triangle (blue))

951 particles that are 40 nm, 80 nm, 110 nm, 150 nm, 200 nm and 300 nm in dry size.

952

953



955

956 Fig. R13. (a–d) Diurnal variations in the number fractions of CV, HV, MV and LV
 957 particles having (from left to right) the six selected diameters ranging from 40 nm to
 958 300 nm. Error bars represent one standard deviation.

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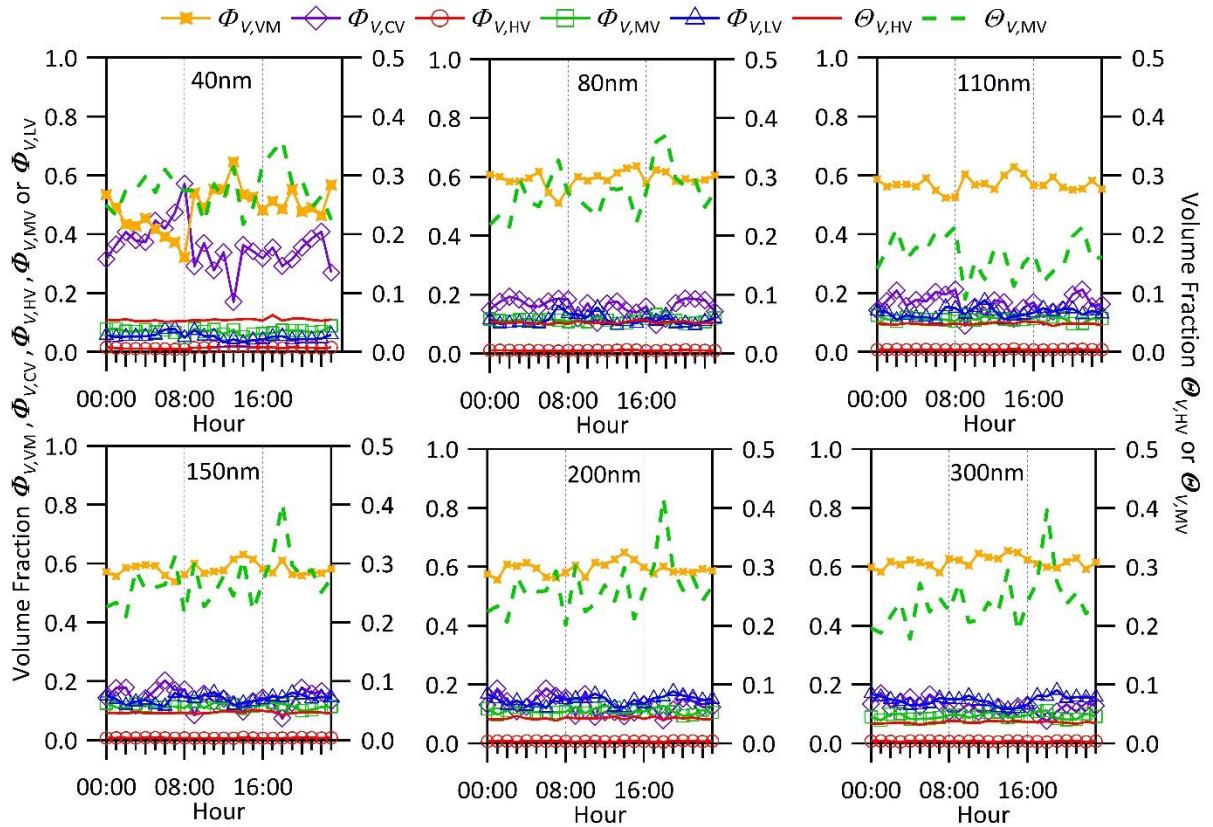
966

967

968

969

970 **Original:**



971

972 Fig. 7 (original manuscript). Diurnal variation in (left axis) $\Phi_{V,VM}$ (cross (orange)),
973 $\Phi_{V,CV}$ (diamond (purple)), $\Phi_{V,HV}$ (circle (red)), $\Phi_{V,MV}$ (square (green)), $\Phi_{V,LV}$ (triangle
974 (blue)), (right axis) $\Theta_{V,HV}$ (solid line (red)) and $\Theta_{V,MV}$ (dashed line (green)) particles
975 that are 40 nm, 80 nm, 110 nm, 150 nm, 200 nm and 300 nm in dry size.

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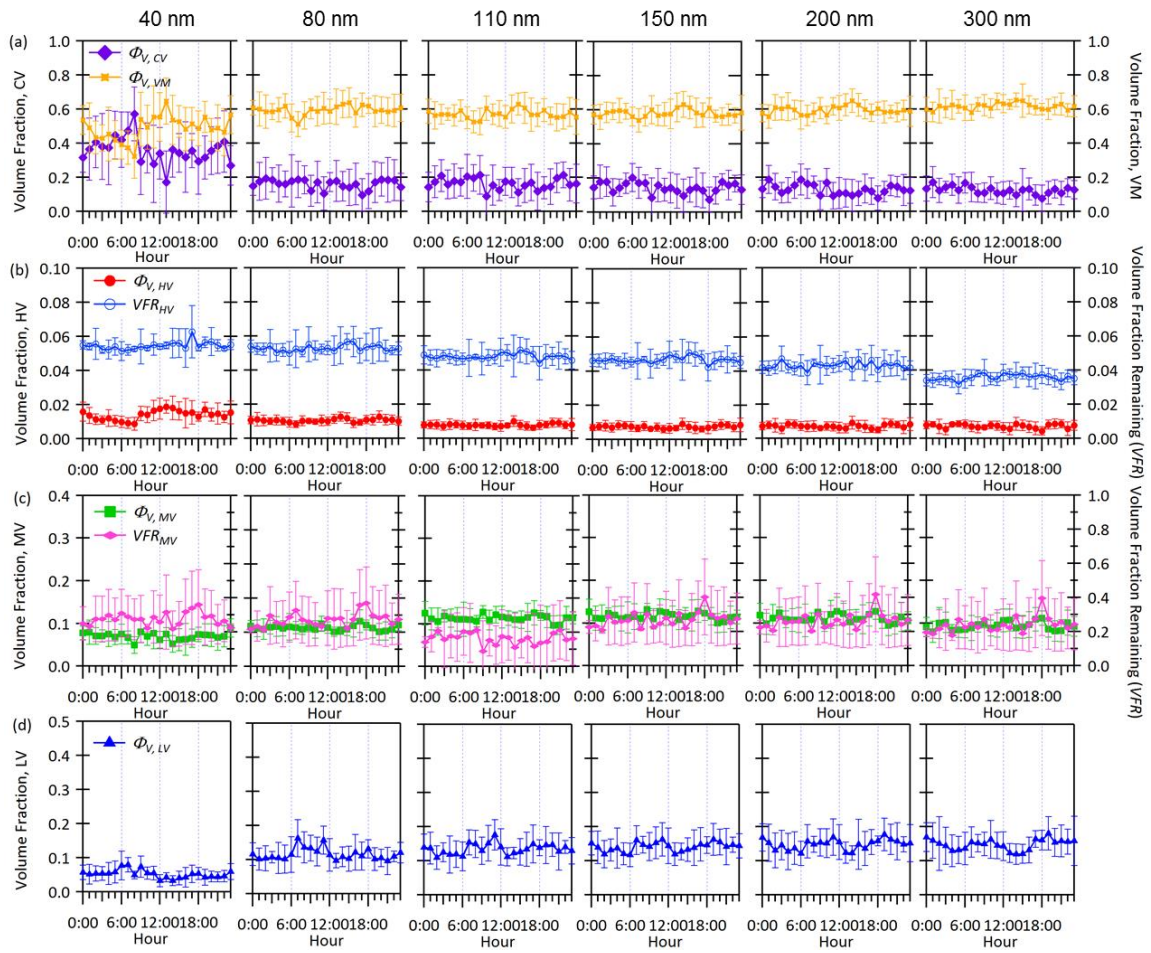
985

986

987

988

989 **Revised:**



990

991 Fig. R14. (a–d) Diurnal variations in the volume fractions of CV particles, VM, HV
992 residuals, MV residuals and LV residuals having the diameters of (from left to right)
993 the six selected diameters ranging from 40 nm to 300 nm. Diurnal variations in the
994 volume fraction remaining (*VFR*) of HV and MV are plotted on the right axis. Error
995 bars represent one standard deviation.

996

997 **29. P25282, l 19-21:** *What does the number concentration of MV+HV mean? Do you*
998 *mean number concentration of particles containing MV+HV materials or what you*
999 *wrote ‘MV+HV residuals’ at other part? Please rephrase the sentence. This kind of*
1000 *confusing statement is elsewhere along the text; please check the language before*
1001 *writing them into the text.*

1002

1003 **Response:**

1004 We mean the number concentration of MV and HV particles, i.e., particles containing
1005 a larger fraction of volatile materials. Similar notations in Section 3.3 such as “EC +
1006 OC₂₋₄” and “LV + MV” are all replaced by “the sum of EC, OC₂, OC₃ and OC₄” and
1007 “the total of LV and MV residuals”. We apologize for the mistake and the confusing
1008 statements.

1009

1010

1011

1012 **30. P25282, l 24-28:** *The sentence is too long; please try to make the statement clear*
1013 *in short sentences.*

1014

1015 **Response:**

1016 The sentence and the analysis are rewritten. We have also taken the reviewer's
1017 suggestion to use the more commonly used term "volume fraction remaining (*VFR*)"
1018 for the volume ratio of the residual to its host particle instead of $\Theta_{V,MV}$ and $\Theta_{V,HV}$.

1019

1020 **Original:**

1021 P25282, l 24-28

1022 There was no obvious diurnal variation of $\Theta_{V,MV}$ and $\Theta_{V,HV}$ for all sizes (except for a
1023 minor peak at about 06:00 p.m. for $\Theta_{V,MV}$, which may be related to traffic), even for 40
1024 nm particles where there is an obvious diurnal trend of $\Phi_{V,VM}$, which is the volume
1025 ratio of volatile materials internally mixed with non-volatile components to total
1026 volume before heating.

1027

1028

1029 **Revised:**

1030 We also used the diurnal variations in the volume fraction remaining (*VFR*), again
1031 defined as the volume ratio of the residual to its *host* particle (not to the total volume
1032 of all particles), to examine the size changes of the non-volatile residuals of HV and
1033 MV particles (Fig. R6). The *VFR* of HV did not exhibit any obvious diurnal variations
1034 but the *VFR* of MV peaked near 18:00. The *VFR* of 40nm MV particles increased after
1035 14:00 while those of 150 nm and 300 nm MV particles increased after 15:00.

1036

1037 **31. P25283**, section 3.3: *When you use extrapolation fitting the number size*
1038 *distribution of 300 nm particles to 5 μ m particles, you have to either assume the*
1039 *number size distribution is constant along the time or their mixing state is constant*
1040 *along different sizes. This did not reduce the uncertainties when comparing*
1041 *VTDMA results with OC/EC results. Please add appropriate discussions on the*
1042 *possible chemical composition within the size gap or refer to other studies.*

1043

1044 **Response:**

1045 When we conducted the extrapolation fitting, it was for the six diameters (from 40 nm
1046 to 300 nm) selected in each measurement cycle. We therefore only assumed that the
1047 mixing state or the size distributions of each of LV, MV or HV followed log-normal
1048 distributions.

1049

1050 Nevertheless, we agree with the reviewer that while the VTDMA measured the size
1051 distribution of particles between 10 and 400 nm in diameter, the OC/EC analyzer took
1052 into account particles up to 2.5 μ m in diameter. Yu et al. (2010) reported three EC and
1053 OC modes between 0.4 μ m and 10 μ m in ambient aerosols in Guangzhou: 0.4, 0.9 and
1054 5 μ m. The 0.4 μ m mode accounted for 44% to 49% of the measured EC but only 17%
1055 to 20% of the measured OC. A discussion is added to the manuscript.

1056

1057 **Original:**

1058 P25283 1 20 onwards:

1059 The extrapolated lognormal fitting of the size distribution of non-volatile particles can
1060 cause errors if the mode diameter of the fitting is beyond the range of measurements
1061 of the VTDMA.

1062

1063 **Revised:**

1064 The extrapolated lognormal fitting of the size distribution of non-volatile particles can
1065 also cause errors if the mode diameter of the fitting is beyond the VTDMA's range of
1066 measurements. While the VTDMA measured the size distribution of particles between
1067 10 and 400 nm in diameter, the OC/EC analyzer took into account particles up to 2.5
1068 μm in diameter. Yu et al. (2010) reported three EC and OC modes between 0.4 μm and
1069 10 μm in ambient aerosols in Guangzhou: 0.4, 0.9 and 5 μm . The 0.4 μm mode
1070 accounted for 44% to 49% of the measured EC but only 17% to 20% of the measured
1071 OC.

1072

1073

1074 **32. P25283, l 19:** *What kind of errors could be related to the measurements; please*
1075 *clarify.*

1076

1077 **Response:**

1078 The discussion of the presence of oxygen in the VTDMA on P25283, l 25-27 has been
1079 moved up to l 19 as a possible source of error in the measurement.

1080

1081 **Original:**

1082 P25283, l 19

1083 ...The presence of other refractory materials, as well as errors during the measurements,
1084 could also be a reason for the difference.

1085

1086 **Original:**

1087 P25283, l 25-27

1088 In the VTDMA, aerosols were heated in the presence of oxygen, while in the OC/EC
1089 Analyzer, samples were heated in the presence of helium for OC. In the presence of
1090 oxygen, it is possible that OC₂₋₄ in the aerosols may have evaporated in the VTDMA
1091 even at 300 °C.

1092

1093

1094 **Revised:**

1095 ...The presence of other refractory materials and the assumption made about the
1096 density of LV and MV are two other possible explanations.

1097 Other possible errors for the closure could be related to the different heating
1098 environments in the VTDMA and the OC/EC analyzer. In the OC/EC analyzer, OC
1099 was measured when the samples were heated in the presence of a non-oxidative carrier
1100 gas (He). In the VTDMA, aerosols were heated in air which contained O₂. Therefore,
1101 some “OC₂₋₄” that evaporated at 475 °C or above in the OC/EC analyzer may have been
1102 oxidized at 300 °C in the VTDMA. Charring of organic matter could also occur
1103 (Philippin et al., 2004).

1104

1105 **33. P25283, l 25-27:** *Do you mean oxidation might take place in the presence of oxygen?*

1106 *Please rephrase the sentence and add references there.*

1107

1108 **Response:**

1109 Yes. The content is revised with the comment above (item 32).

1110

1111

1112

1113 **34. P25283, l 13-15:** *What does ‘that LV and MV may contain non-volatile OC’ mean?*

1114 *Do you mean LV+MV residuals contain non-volatile OC?*

1115

1116 **Response:**

1117 We mean both LV and MV residuals contain non-volatile OC. In the VTDMA, all the
1118 residuals (HV, MV and LV residuals) were non-volatile upon heating at 300 °C. We
1119 cannot assume that non-volatile OC would only be present in MV residuals while EC
1120 is only present in LV residuals. All the terms using “LV+MV” are replaced by “the
1121 total mass of LV and MV” to avoid confusion. The sentence is also revised.

1122

1123 **Original:**

1124 P25283, L13-15

1125 Including non-volatile OC give better mass closure for LV+MV and this observation
1126 supports our initial postulation that LV and MV may contain non-volatile OC.

1127

1128 **Revised:**

1129 Including non-volatile OC (sum of OC₂ to OC₄) gives better mass closure with the total
1130 mass of LV and MV. This further supports our initial postulation that the non-volatile
1131 residuals which remained intact upon heating at 300 °C in the VTDMA may contain a
1132 significant amount of non-volatile OC.

1133

1134 **35. P25284, Section 4:** *I did not get a clear picture that what the authors want to*
1135 *conclude for the manuscript. Please consider revising it.*

1136

1137 **Response:**

1138 The section is rewritten.

1139

1140 **Revised:**

1141 This study presents the first VTDMA measurements in a suburban area of Guangzhou
1142 in the Pearl River Delta, China during wintertime. The LV fraction was assumed to be
1143 EC particles. These particles were externally mixed with volatile materials at 300 °C
1144 and contributed to less than 20% of the total particle number concentration at the
1145 sampling site. The diurnal variations in the number and volume fractions of LV, MV
1146 and HV were much less obvious in this study than in other studies, likely because of
1147 the more stable atmosphere and poorer dilution of aged aerosols in winter. Back
1148 trajectory analysis showed that the measured PM_{2.5}, EC and OC concentrations were
1149 higher when the sampling site came under the influence of maritime and coastal air
1150 masses originating from the east or northeast of the site. These observations are
1151 attributed to the high pressure system on the continent, the prevailing northerly wind
1152 and the enhanced pollution from north China in winter. Long-range transport
1153 continental trajectories were often associated with the cold front periods during which
1154 the dispersion of pollutants was promoted. The number fractions of LV, MV and HV
1155 particles did not show much variations among the clusters, likely because the air
1156 masses in all clusters were transported at low altitudes (below 1500 m) for over 40 h.
1157 They were therefore well-aged upon arrival at the site.

1158

1159 While previous studies have demonstrated soot as a major component of the non-
1160 volatile residuals at 300 °C measured by the VTDMA, this work identified non-volatile
1161 organics as another possible component. The diurnal variations in the LV fractions and
1162 the size of the MV residuals may be related to the variation in the abundance of both
1163 EC and non-volatile OC, which evaporated at 475 °C and above in the OC/EC analyzer.
1164 Analyses of the diurnal variations in the LV fractions and the VFR of MV particles, the
1165 latter of which reflects the change in size of the non-volatile materials in the MV
1166 particles, suggest that the increase in non-volatile fractions and size in the early

1167 afternoon may be related to the increase in non-volatile OC in addition to the effects
1168 of EC coagulation and condensation. The mass closure analysis of EC and non-volatile
1169 OC and the total mass of LV and MV residuals also suggest that non-volatile OC may
1170 have contributed to non-volatile residuals in our VTDMA measurements.
1171

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1289

1290 ***Anonymous Referee #2***

1291 ***Summary***

1292 *Cheung et al. conducted a set of ambient measurements from which they calculated*
1293 *size dependent volatility shrinkage factors (VSF) of aerosols in Guangzhou after*
1294 *heating to 300°C in a tandem differential mobility analyzer. Size-selected particles*
1295 *ranging from $D_m = 40$ to 300 nm were examined. Mass concentrations of OC and EC*
1296 *were also measured. Particles were classified as “completely volatile” (CV; $VSF \sim 0$),*
1297 *“high volatility” (HV; $VSF < 0.4$), “medium volatility” (MV; $0.4 < VSF < 0.9$) and “low*
1298 *volatility” (LV; $VSF > 0.9$). Three primary results are reported: (1) the number and*
1299 *volume fraction of CV particles decreases with increasing particle size, while the LV*
1300 *particle number and volume fractions increase with increasing diameter (2) size-*
1301 *resolved measurements combined with average diurnal patterns suggest that 40 nm*
1302 *CV and LV particles represent local, fresh emissions, whereas >80 nm HV and MV*
1303 *particles represent aged emissions. (3) A closure analysis of VHTDMA and OC/EC*
1304 *analyzer measurements suggests that organics comprise a significant fraction of the*
1305 *measured MV and LV. Overall, the results are interesting, but I suggest additional*
1306 *analysis of the data before I would support publication in ACP. In particular, I think it*
1307 *would be useful to present more of the OC/EC results to assist with, and expand on,*
1308 *the interpretation of the VHTDMA measurements.*

1309

1310 ***Main Comments***

1311

1312 1. *In my opinion, the closure analysis -- which currently focuses on a comparison of*
1313 *EC + OC2 + OC3 + OC4 versus LV + MV – is incomplete. The volatility resolved*
1314 *VHTMDA and OC/EC analyzer measurements should in principle allow for a more*
1315 *comprehensive closure/inter comparison study. Because the volatility fractions in*
1316 *both instruments are affected by the specific operation conditions, I think expanding*
1317 *on this subject in Section 3.3 would be interesting and possibly help with the*
1318 *interpretation of the VHTDMA measurements. I suggest that this subject be a major*
1319 *focus of a revised manuscript. For example:*

1320 a) *CV versus OC1*

1321 b) *HV versus OC1 and/or OC2*

1322 c) *MV and OC2 and/or OC3*

1323 2. *I think the authors should plot and discuss campaign-average mass fractions of OC1,*
1324 *OC2, OC3, OC4 and EC to accompany the volume fractions of VM, CV, HV, MV and*
1325 *LV that are presented in Figure 6 and related discussion.*

1326

1327 3. *Similarly, the authors could plot time series and diurnal patterns of OC1, OC2, OC3,*
1328 *OC4 and EC mass fractions as is done in Figure 7 and related discussion of the*
1329 *volume fractions of VM, CV, HV, MV and LV.*

1330

1331 **Response:**

1332 We thank the reviewer for the useful comments. Below please find our response to
1333 each of the points above. [Major changes to the manuscript are shown in blue.](#)

1334

1335 We have added the following new results in conjunction with the discussions of the
1336 VTDMA results:

- 1337 v) Time series and diurnal variations in OC and EC concentrations;
- 1338 vi) Meteorological conditions including wind speed, wind direction, temperature,
1339 and relative humidity;
- 1340 vii) Particle number size distribution from the SMPS; and
- 1341 viii) Back trajectory analysis

1342

1343 With the addition of the new materials, the subsections in the results and discussion
1344 section of the revised manuscript are re-organized:

- 1345 - 3.1 Overview
- 1346 - 3.2 Diurnal variations
- 1347 - 3.3 Back trajectory analyses
- 1348 - 3.4 New particle formation
- 1349 - 3.5 Closure analysis for LV and MV residuals at 300 °C, OC and EC

1350

1351 The response below will focus on the new discussions related to the OC and EC data
1352 in addition to the main comments raised by the reviewer. Detailed discussions about
1353 the meteorological conditions can be found in item 1.2 of the major comments for
1354 Reviewer 1 or the revised manuscript.

1355

1356 1. For suggested closure b) and c), we would like to point out that LV, MV, and HV
1357 particles differ in the relative abundance of the volatile fraction over the non-volatile
1358 fraction at 300°C but not the volatility of the evaporated materials. On the other hand,
1359 OC₁, OC₂, OC₃ and OC₄ represent OC of different volatilities, as measured at
1360 different evaporation temperatures. Since the differentiation of LV, MV and HV
1361 relies on a different set of principles than the differentiation of OC₁, OC₂, OC₃ and
1362 OC₄, we do not think it useful to conduct any closure analysis related to b) and c).

1363

1364 We agree that it would be useful to carry out the suggested closure a) of CV versus
1365 OC₁ as proposed by the reviewer. However, a closure analysis between VM or CV
1366 and OC₁ was not conducted because there is a large uncertainty in the calculation
1367 of the vaporized mass (VM and CV). The estimation of the mass of vaporized
1368 materials (VM and CV) requires subtracting the volumes of LV and MV particles
1369 from the total particle volume, which was estimated by SMPS. However, unlike LV,
1370 MV, and HV particles, which had volume distributions peaking at diameters below
1371 400 nm, the SMPS data suggest that the total volume almost always peaked at sizes
1372 above 400 nm. The calculation of VM and CV would involve large uncertainties
1373 due to the need to extrapolate the volume contributions of particles larger than 400
1374 nm in size. Hence, we are not confident that one can draw meaningful conclusions
1375 from such analysis.

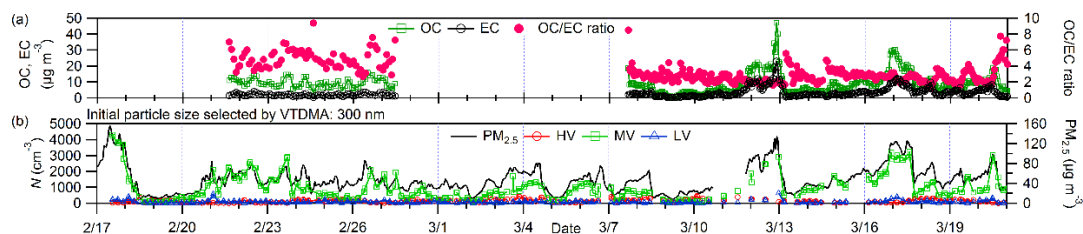
1376

1377 **2. New materials added**

1378 **2.1 Overview of OC/EC data**

1379 The time series of EC and OC concentrations and the OC/EC ratio during the campaign
1380 are shown in Fig. R1. OC concentrations ranged from 0.5 to 47.0 $\mu\text{g m}^{-3}$ with an
1381 average of $9.0 \pm 6.0 \mu\text{g m}^{-3}$, while EC concentrations ranged from 0.2 to 23.0 $\mu\text{g m}^{-3}$
1382 with an average of $3.4 \pm 3.0 \mu\text{g m}^{-3}$. OC₁, the most volatile group among OC₁ to OC₄
1383 in OC/EC analysis, accounted for one-third of the total carbon mass (Fig. R2). Similar
1384 to the number concentrations of MV particles (with an initial diameter of 80 nm and
1385 above) measured by the VTDMA at 300 °C, OC and EC mass correlated well with
1386 PM_{2.5}. The r^2 values of the correlations between OC and PM_{2.5} and between EC and
1387 PM_{2.5} are 0.8 and 0.7, respectively (Fig. R3).

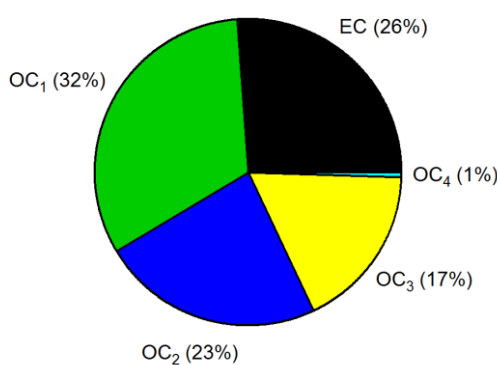
1388



1389

1390 Fig. R1. Time series of (a) OC and EC concentrations and the OC/EC ratio, (b) number
1391 concentrations of HV, MV and LV particles having an initial diameter of 300 nm upon
1392 heating at 300 °C (left axis) and concentration of PM_{2.5} (right axis).

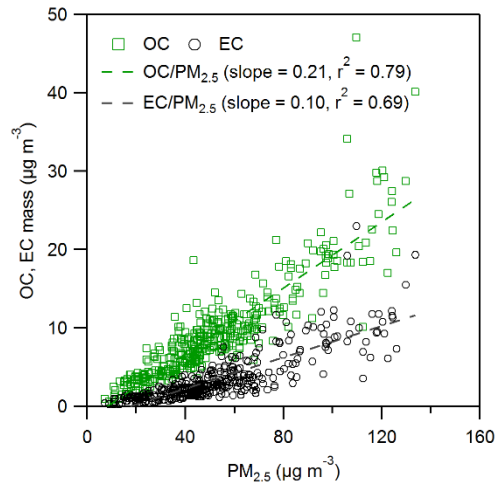
1393



1394

1395 Fig. R2. Average mass fractions of EC, OC₁, OC₂, OC₃ and OC₄ in PM_{2.5}.

1396



1397

1398 Fig. R3. Concentrations of OC and EC versus PM_{2.5}.

1399 **2.2 Comparison of the diurnal variations of OC/EC and VTDMA data**

1400 The diurnal variations in the mass fractions of OC and EC in PM_{2.5} are compared with
1401 the volume fractions of CV, HV residual, MV residual, LV residual and VM in
1402 particles of dry initial diameters of 40, 150 and 300 nm. The OC and EC data on Mar
1403 12 and 17 were excluded since they were more than two standard deviations higher
1404 than those on other days. Subtle morning peaks between 06:00 and 10:00 were
1405 observed for the volume fraction of LV residuals (Fig. R4). A similar peak was
1406 observed for the mass fraction of EC in PM_{2.5} in the morning (Fig. R5). This suggests
1407 that LV particles may be related to the EC from vehicle emissions in the morning. This
1408 EC was relatively less aged and externally mixed with other volatile materials. In the
1409 late afternoon, LV residuals showed another peak between 17:00 and 19:00 whereas
1410 the mass fraction of EC in PM_{2.5} exhibited a minimum at 15:00, after which it increased
1411 continuously. The continuous increase in EC at night is likely related to the increase
1412 of heavy-duty diesel vehicles (Zhang et al., 2015), which was restricted during daytime
1413 (Bradsher, 2007).

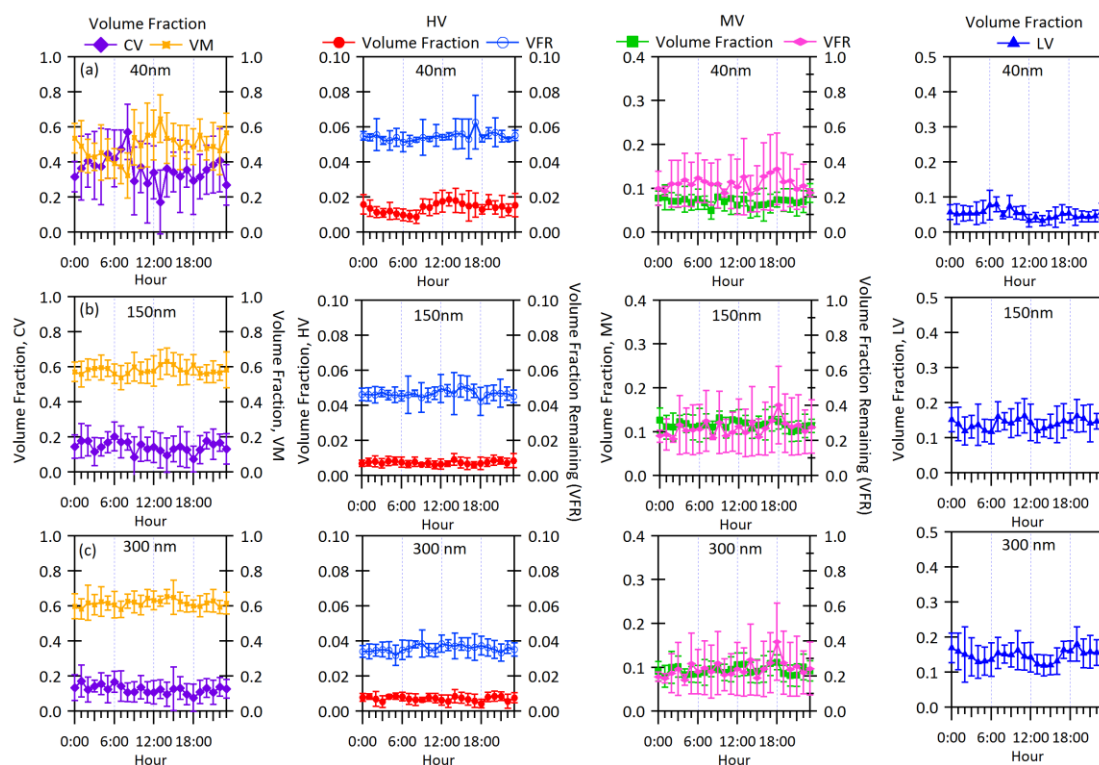
1414

1415 Although OC₁ contributed to about half of the total OC mass, the diurnal variation in
1416 the mass fraction of OC in PM_{2.5} was driven by the total mass of OC₂, OC₃ and OC₄
1417 (OC₂₋₄), which reached a minimum between 05:00 and 09:00 and increased until 19:00.
1418 OC can be attributed to both primary and secondary sources. The increased mass
1419 fraction of OC in PM_{2.5} and OC-to-EC ratio in the afternoon suggest that the sources
1420 of OC were less related to traffic but more to the aging and formation of secondary
1421 organic aerosols (Turpin et al., 1990; Chow et al., 1996). These OC₂, OC₃ and OC₄
1422 may be highly oxygenated species or oligomers that are less volatile than primary or
1423 less oxygenated organics (Kalberber et al., 2004; Huffman et al., 2009).

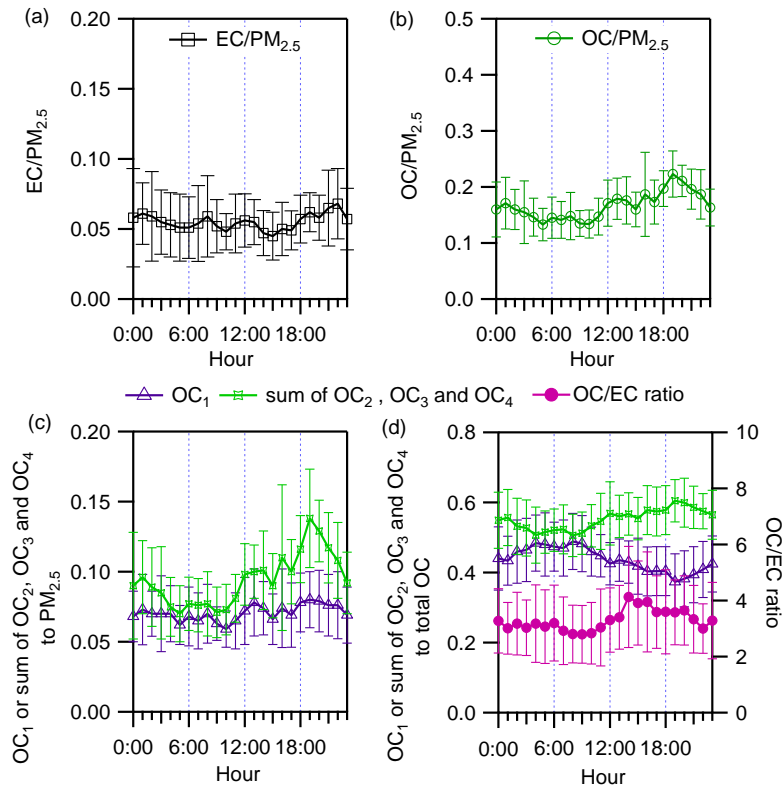
1424

1425 It is interesting to note that the volume fraction of LV residuals and the *VFR* of MV
1426 particles at different sizes showed a dip in the afternoon (Fig. R4, third column from
1427 the left). The *VFR* of 40 nm MV particles showed a dip at 14:00 while those in 150 nm
1428 and 300 nm particles showed a dip at 15:00. The volume fraction of LV residuals in
1429 150 nm and 300 nm particles reached a minimum at 13:00 and 15:00, respectively.
1430 Because EC decreased between 12:00 and 15:00, the increase in the volume fraction
1431 of LV residuals in 150 nm particles since 13:00 and the *VFR* of 40 nm MV particles

1432 since 14:00 may be related to the increased presence of aged organics as well as the
 1433 EC particles which aged via coagulation and condensation.
 1434



1435
 1436 Fig. R4. Diurnal variations in volume fractions of (columns from left to right) CV, VM,
 1437 HV residual, MV residual and LV residual in (a) 40 nm, (b) 150 nm and (c) 300 nm
 1438 particles. Diurnal variations in the volume fraction remaining (*VFR*) of HV and MV
 1439 particles are plotted on the right axis. Error bars represent one standard deviation.
 1440



1441

1442

1443

1444

1445

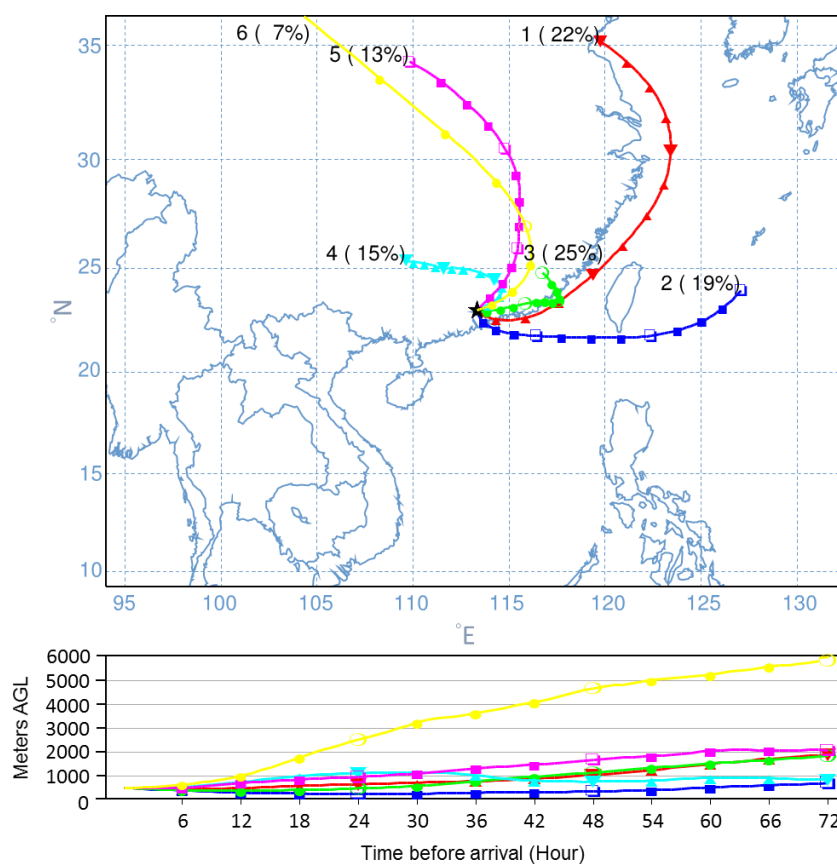
1446

Fig. R5. Diurnal variations in the mass fractions of EC, OC, OC₁ and the sum of OC₂, OC₃ and OC₄ in PM_{2.5}, the ratio of OC to EC, mass fractions of OC₁ and the sum of OC₂, OC₃ and OC₄ to total OC in February and March. Error bars represent one standard deviation.

1447 **2.3 Back Trajectory Analysis**

1448 We calculated the 72 h back trajectories of the air masses arriving at the sampling site
1449 (23°00 N, 113°25' E) at 4 h intervals (at 00:00, 04:00, 08:00, 12:00, 16:00 and 20:00
1450 local time, UTC +8) using the PC version of the HYSPLIT4 (Hybrid Single Particle
1451 Lagrangian Integrated Trajectory, version 4) model (Stein et al., 2015; Rolph, 2016).
1452 Archived meteorological data from the Global Data Assimilation System (GDAS) 1-
1453 deg was employed and the receptor height was set at 500 m above ground level (a.g.l.).
1454 The 191 back trajectories calculated were grouped into six clusters based on their
1455 spatial distribution (Fig. R6).

1456



1457

1458 Fig. R6. Mean back trajectories of the six types of air masses arriving at the sampling
1459 site.

1460

1461 Overall, the sampling site was mostly affected by northwesterly and northeasterly air
1462 masses. Cluster 1 and 3 are coastal and continental air masses, respectively, although
1463 both originated from the northeast. Clusters 4, 5 and 6 represent continental air masses
1464 originating from the northwest. Cluster 2 is a group of maritime air masses originating
1465 from the East China Sea northeast or east of Guangzhou. While air masses in cluster 6
1466 were transported at relatively high speeds and altitudes (over 3000 m a.g.l.), air masses
1467 in all the other clusters were transported at an altitude below 1500 m a.g.l. for over 40
1468 h before arriving at the site. Nevertheless, air masses in cluster 6 only persisted for less
1469 than three days. Since the corresponding VTDMA and OC/EC data were sometimes
1470 unavailable, cluster 6 will be excluded from the following discussion.

1471

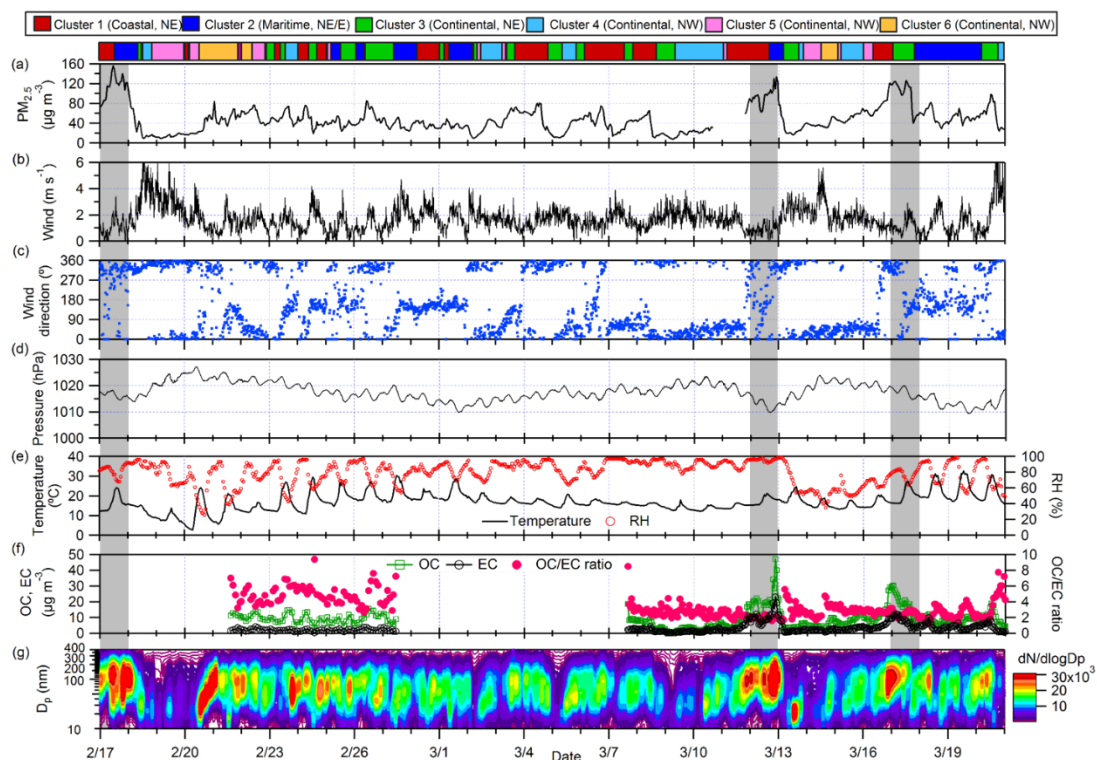
1472 The average PM_{2.5}, OC and EC concentrations associated with air masses from the
1473 northeast of Guangzhou (clusters 1, 2 and 3) were higher than those from the northwest
1474 (clusters 4 and 5, Table R1). Days associated with coastal and maritime air masses
1475 were more polluted than days associated with continental air masses for several
1476 reasons. First, south China as a region is often affected by the high pressure system
1477 moving eastward or southward from the continent out to sea in winter. When the
1478 maritime or coastal air streams entered from the southeast of the sampling site at Panyu,
1479 the atmosphere at the sampling site became more stable with low local wind speeds
1480 (e.g. the polluted days on Feb 17 and Mar 12, 16 and 17, Fig. R7 and R8). Local
1481 pollutants accumulated and the city was also affected by pollutants from the
1482 southeastern areas of the site (e.g. Shenzhen, Nansha and Dongguan). Second, land-
1483 sea breeze cycles were observed when the sampling site was under the influence of
1484 maritime air masses from Mar 18 to 20. During the day, southeasterly wind prevailed
1485 and the wind speed was higher. In the evening, the southeasterly wind was gradually
1486 replaced by a southwesterly or northwesterly wind and the wind speed decreased (Fig.
1487 R7). The cycle started again in the morning when the westerly wind was gradually
1488 replaced by southeasterly wind. Such land-sea breeze effects can result in an effective
1489 redistribution and accumulation of air pollutants within the PRD region (Lo et al.,
1490 2006).

1491

1492 Table R1. Summary of concentrations of PM_{2.5}, OC, EC and the ratio of OC to EC
 1493 (OC/EC) in the five clusters.

	Cluster				
	Coastal	Maritime	Continental		
	1	2	3	4	5
Origin (to the site)	NE	NE/E	NE	NW	NW
PM _{2.5} (µg m ⁻³)	58.5 ± 24.4	58.9 ± 30.9	47.5 ± 28.4	33.9 ± 15.9	33.8 ± 19.3
OC (µg m ⁻³)	10.8 ± 6.01	10.84 ± 7.22	10.13 ± 6.89	5.51 ± 3.3	7.32 ± 2.75
EC (µg m ⁻³)	4.38 ± 2.97	4.98 ± 4.21	3.43 ± 3.12	1.8 ± 0.98	2.46 ± 0.59
OC/EC	2.83 ± 1.05	2.62 ± 1.03	3.65 ± 1.6	3.18 ± 1.26	2.94 ± 0.73

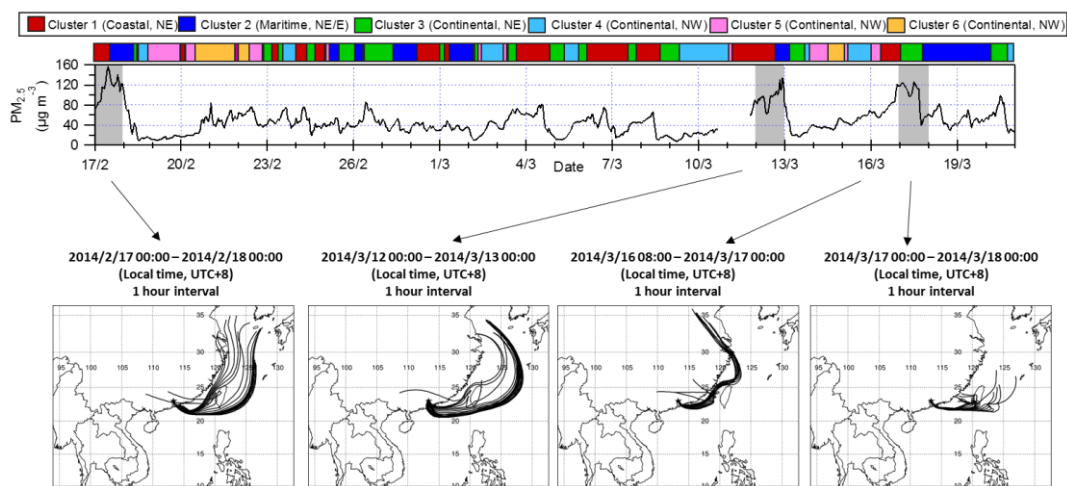
1494



1495

1496 Fig. R7. Overview of major meteorological parameters, PM_{2.5}, OC and EC
 1497 concentrations, OC/EC ratio and particle number size distributions in the campaign. Air
 1498 mass clusters are depicted at the top and the shaded areas indicate days with daily-
 1499 averaged PM_{2.5} concentrations exceeding 95 µg m⁻³.

1500



1501

1502 Fig. R8. Time series of $PM_{2.5}$ concentrations and 72 h back trajectories at hourly
 1503 intervals on Feb 17, and Mar 12, 16 and 17.

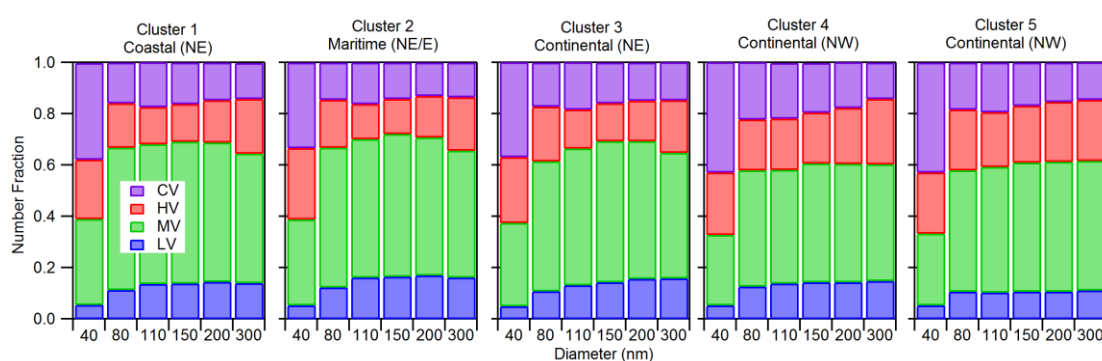
1504

1505 Furthermore, $PM_{2.5}$ in the northeastern parts of China can exceed $200 \mu\text{g m}^{-3}$ due to
 1506 both enhanced emissions from coal combustion for heating and poor dispersion during
 1507 wintertime (Gu et al., 2014). Under the influence of the prevailing northerly or
 1508 northeasterly wind in China, these pollutants were often transported to southern China
 1509 and the East China Sea (Chen et al., 2012). Pollutants might also have accumulated
 1510 when the maritime air masses spent about two days across Taiwan and the coast of
 1511 south China. In contrast, continental air masses in cluster 5 moved slightly faster, and
 1512 were often associated with the cold front period during which the local wind speed and
 1513 pressure increased but the temperature decreased (Fig. R7). As the cold air masses
 1514 passed through the city, dispersion and clearance of pollutants were promoted,
 1515 resulting in lower $PM_{2.5}$ concentrations (Tan et al., 2013a). Therefore, unlike in other
 1516 coastal cities like Hong Kong (Lee et al., 2013), in Panyu maritime air masses could
 1517 lead to more severe pollution than the continental ones in winter.

1518

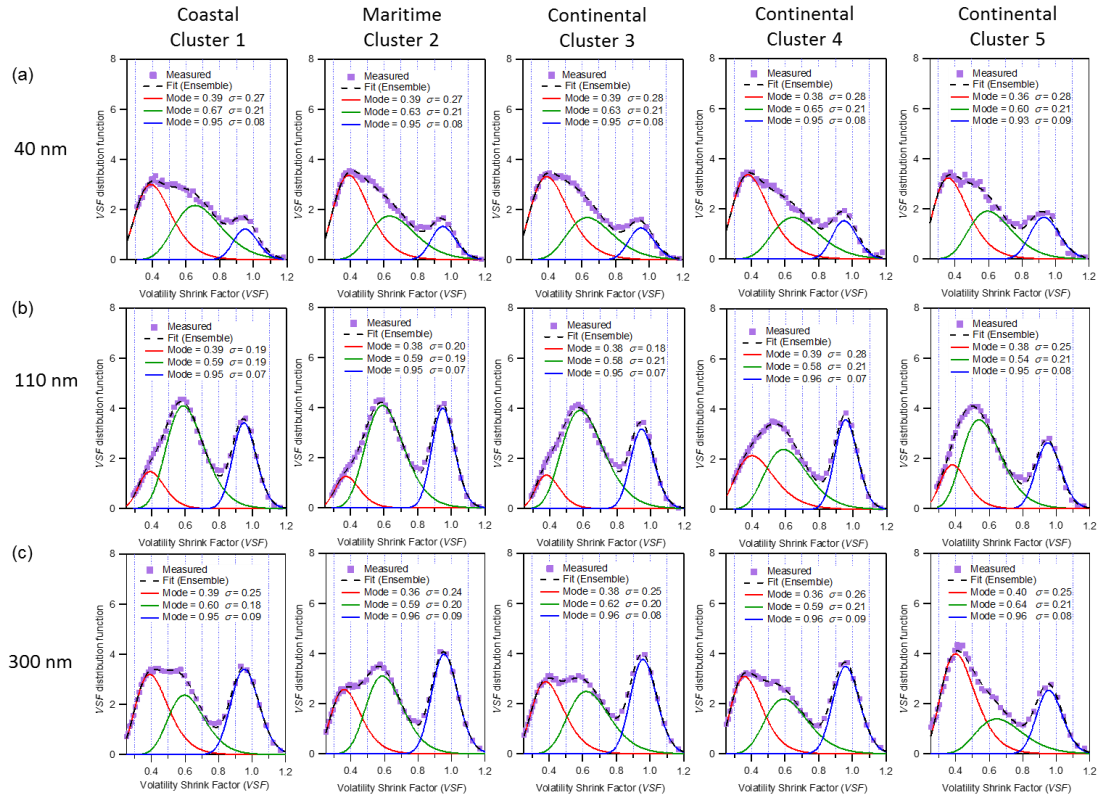
1519 The five clusters were further analyzed to study the influence of air mass history on
 1520 aerosol volatility. The number fractions of CV, HV, MV and LV of the six selected
 1521 diameters in VTDMA measurements are regrouped based on the clusters as shown in
 1522 Fig. R9. The total number fractions of the non-volatile residuals (sum of HV, MV and
 1523 LV) were similar in all clusters. Maritime air masses (cluster 2) had a slightly higher
 1524 fraction of LV particles while continental air masses originating from the northwest of
 1525 the site (clusters 4 and 5) had a higher fraction of HV particles. Although the air masses

1526 in clusters 1 and 5 originated from farther away and traveled at relatively higher speeds
 1527 than those in clusters 2, 3 and 4, all clusters involved transport at low altitudes (below
 1528 1500 m) for over 40 h, likely due to the generally lower mixing heights in winter.
 1529 Therefore, aerosols in these air masses were all well-aged upon arrival (Wehner et al.,
 1530 2009). This could be another reason for the lack of size dependence of the number,
 1531 volume fractions and diurnal variation for particles larger than 80 nm. When the
 1532 transported air masses mixed with local pollutants, the size dependence of the number
 1533 fractions of different volatility groups as well as the aging of local emissions was
 1534 further reduced.
 1535



1536
 1537 Fig. R9. Average number fractions of CV, HV, MV and LV particles in clusters 1 to 5
 1538 at different selected diameters.

1539
 1540 We also examine at the volatility shrinkage factor (*VSF*) distributions of 40 nm, 110
 1541 nm and 300 nm particles upon heating at 300 °C (Fig. R10). Log-normal fittings with
 1542 a three-peak solution were applied to the distributions. The average *VSF* modes of the
 1543 peaks were located at 0.38 ± 0.021 (peak 1), 0.60 ± 0.066 (peak 2) and 0.95 ± 0.007
 1544 (peak 3), respectively. The standard deviation of the corresponding normal distribution
 1545 (σ) of peak 3 was the smallest among the three peaks ($\sigma < 0.1$). For the same particle
 1546 size, the *VSF* distributions in the *VSF* range between 0.3 and 0.8 in cluster 5 was
 1547 relatively more uni-modal than those of other clusters (Fig. R10b and R10c). This
 1548 suggests that the composition in cluster 5 was more homogeneous. Cluster 1 also
 1549 consisted of long-range transported air masses but they likely passed through areas that
 1550 are more polluted and mixed with different types of pollutants. Note that the fractions
 1551 of HV, MV and LV have been traditionally defined based on the values of *VSF*, i.e.
 1552 $HV < 0.4$; $0.4 < MV < 0.9$; $LV > 0.9$ (Wehner et al., 2009). The *VSF* distributions
 1553 above suggest that these definitions using *VSF* = 0.4 and 0.9 may need to be re-visited
 1554 in the future.



1555

1556

Fig. R10. Volatility shrinkage factor (*VSF*) distribution function in different clusters.

1557

Solid and dotted lines are the peaks fitted with log-normal function and the ensemble distributions, respectively.

1558

1559

1560

1561

1562

3. Please refer to item 2.

1563

1564 *Minor/Technical Comments*

1565 **4.** *It is not clear to me how understand the difference between “Volatile Materials”*
1566 *(VM) are defined. I assumed that “VM” becomes “CV” after heating to 300°C, but*
1567 *this does not seem to be the case because separate volume fractions of “VM” and*
1568 *“CV” are presented in Figures 6 and 7. Please clarify the definition of VM.*

1569

1570 **Response:**

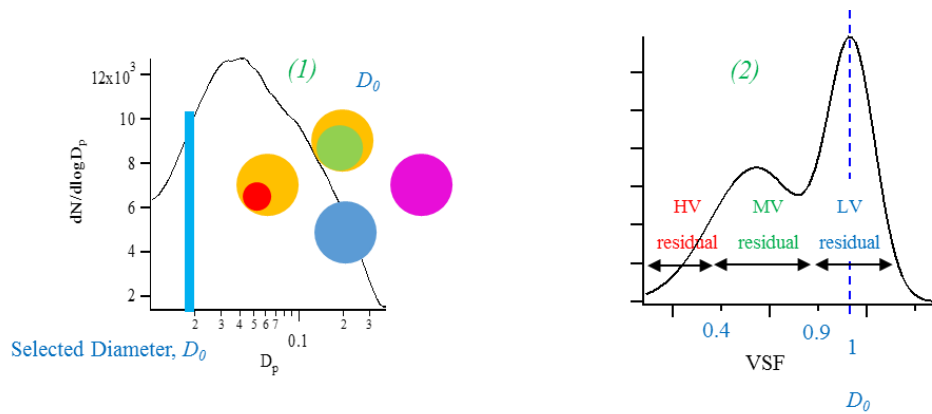
1571 VM and CV differ by how the evaporated materials mix with the non-volatile materials.
1572 VM refers to the volatile materials that are internally mixed with (or coated on) the
1573 non-volatile materials while CV refers to the volatile materials that are externally
1574 mixed with particles containing the non-volatile materials. Upon heating, VM
1575 evaporated, leaving behind HV, MV, or LV residuals. Evaporation of VM alone does
1576 not change the total number concentrations of particles. In contrast, CV particles
1577 evaporated completely without leaving any residuals behind. It reduced the total
1578 particle number concentrations.

1579

1580 On page 25275 of the original manuscript, Section 2.1.2, line 19 onwards, we
1581 mentioned:

1582 Figure 2 illustrates how thermal treatment in the VTDMA affects the size distributions
1583 of the ambient aerosols. At each selected diameter D_0 (and at each temperature) in
1584 DMA₁ in the VTDMA, the particles include CV particles (purple) and **LV, MV and**
1585 **HV particles that have VM (orange) internally mixed with the LV (blue), MV**
1586 **(green) and HV (red) residuals.** After heating, the remaining particles would form
1587 LV, MV and HV residuals without any CV or VM.

1588



1589

1590 Fig. 2. Examples of particle size distributions of (a) ambient aerosols before entering
 1591 DMA₁ and (b) residuals of the size-selected particles (D_0) after heating. The left and
 1592 right distributions correspond to (1) and (2) in Fig. 1 respectively. Residuals are
 1593 divided into three groups—LV (blue), MV (green) and HV (red)—based on their *VSF*.
 1594 CV (purple) and VM (orange) are completely vaporized and hence not measured as
 1595 residuals. VM appears as coating for illustration purposes only. It does not necessarily
 1596 reflect the morphology of the particles.

1597

1598

1599

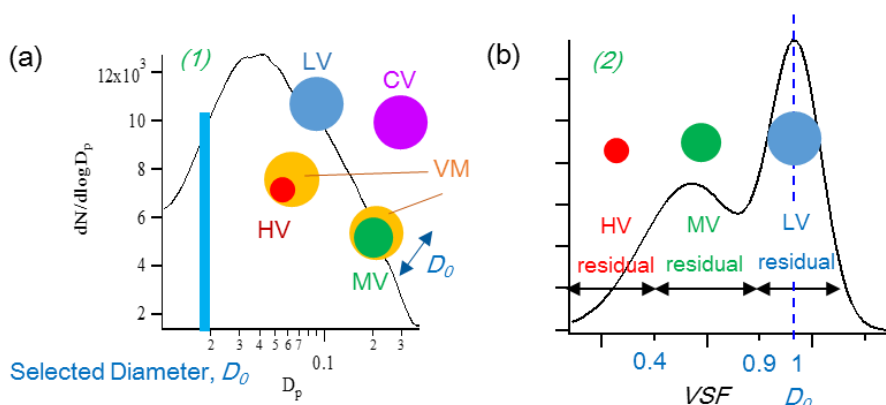
1600 In the revised manuscript, CV and VM are clearly defined in the methodology section
 1601 instead of the introduction section. VM refers to volatile materials internally mixed
 1602 with non-volatile ones while CV refers to volatile materials externally mixed with non-
 1603 volatile materials.

1604

1605 **Revised Methodology (Section 2.1.2):**

1606 ...The *VSF* is also used to divide the particles into three groups, namely the low
 1607 volatility (LV), medium volatility (MV) and high volatility (HV) particles. In this study,
 1608 we focus on the measurements made at 300 °C. The *VSF* ranges for LV, MV and HV
 1609 particles upon heating at 300 °C are above 0.9, between 0.4 and 0.9 and below 0.4,
 1610 respectively (Fig. 2) (Wehner et al., 2004; Wehner et al., 2009). The LV particles are
 1611 assumed to represent EC particles externally mixed with the volatile materials, while
 1612 the MV and HV particles are assumed to represent EC particles internally mixed with
 1613 volatile materials. While the volatile materials in the MV and HV particles are referred
 1614 to as VM, those exist as external mixtures with the LV, MV and HV particles are
 1615 referred to as completely vaporized (CV) particles. The CV particles evaporate
 1616 completely without leaving behind any residuals at 300 °C.

1617
 1618



1619
 1620 Fig. 2. Examples of particle size distributions of (a) ambient aerosols before entering
 1621 DMA₁ and (b) residuals of the size-selected particles (D_0) after heating. The left and
 1622 right distributions correspond to (1) and (2) in Fig. 1 respectively. Residuals are
 1623 divided into three groups—LV (blue), MV (green) and HV (red)—based on their *VSF*.
 1624 CV (purple) and VM (orange) are vaporized and hence not measured as residuals. VM
 1625 appears as coating for illustration purposes only. It does not necessarily reflect the
 1626 morphology of the particles.

1627
 1628

1629 **5. *OC₂, OC₃ and OC₄ are never defined in the manuscript.***

1630

1631 **Response:**

1632 On page 25276 of the original manuscript, line 19 – 22, we mentioned:

1633 “The OC/EC Analyzer adopts the ACE-Asia protocol (a NIOSH-derived protocol),
1634 where OC evaporates at four set temperatures of 310, 475, 615 and 870 °C, and EC is
1635 combusted at temperature above 550 °C (Schauer et al., 2003). Based on volatility and
1636 refractoriness, the OC contents are named OC₁ to OC₄ with OC₁ being most volatile”

1637

1638 We agree that the definitions did not explicitly link the terms and the heating
1639 temperatures. The revised description is shown below.

1640

1641 **Revised:**

1642 The OC/EC analyzer adopts the ACE-Asia protocol (a NIOSH-derived protocol),
1643 where OC evaporates at four set temperatures of 310 °C, 475 °C, 615 °C and 870 °C **with**
1644 **pure helium (He) as the carrier gas**, and EC is combusted at temperatures **between**
1645 **550 °C and 870 °C under He and 2% oxygen** (O₂, Schauer et al., 2003; Wu et al., 2012).

1646 The OC contents are named OC₁ to OC₄ **based on the temperature protocol of the**
1647 **OC/EC analyzer (Table R2). The mass of EC determined at different temperatures will**
1648 **be grouped together for discussions.**

1649

1650 Table R2. Temperature (T) and residence time (RT) protocol of the semi-continuous
1651 Sunset OC/EC analyzer (Wu et al., 2012)

Carbon Fraction	Carrier Gas	T (°C)	RT (s)
OC ₁	He	310	80
OC ₂		475	60
OC ₃		615	60
OC ₄		870	90
EC ₁	He + 2% O ₂	550	45
EC ₂		625	45
EC ₃		700	45
EC ₄		775	45
EC ₅		850	45
EC ₆		870	45

1652

1653

1654

1655 **6.** *What is the residence time in the heated section of the VTMDA, and how sensitive*
1656 *are the HV/MV/LV classifications to the residence time?*

1657

1658 **Response:**

1659 The heating tube was a 1/2", 80 cm long stainless steel tube with an inner diameter of
1660 8 mm. With a sample flow rate of 1 L min⁻¹, the resulting residence time in the heated
1661 section of the VTMDA was 2.4 s. The estimated aerosol velocity on the center line was
1662 0.33 m s⁻¹. Compared to the residence time of 0.3 s to 1 s in other VTMDA systems
1663 (e.g. Brooks et al., 2002; Philippin et al., 2004; Villani et al., 2007), the residence time
1664 in our VTMDA is assumed to be long enough for the volatile materials to be effectively
1665 vaporized. After leaving the heating tube, the flow entered a heat exchanger measuring
1666 30 cm in length to ensure sufficient cooling before entering DMA₂. The relevant
1667 information is added to the methodology section.

1668

1669 **Revised, Page 25275 of the original manuscript, line 5 onwards:**

1670 Afterwards, the monodisperse aerosols were directed via path (b) to a heated tube for
1671 volatility measurement (V-Mode) sequentially at 25, 100 and 300 °C. *The heating tube*
1672 *was a 1/2", 80 cm long stainless steel tube with an inner diameter of 8 mm. With a*
1673 *sample flow rate of 1 L min⁻¹, the resulting residence time in the heated section of the*
1674 *VTMDA was 2.4 s. The estimated aerosol velocity on the center line was 0.33 m s⁻¹.*
1675 *Compared to the residence time of 0.3 s to 1 s in other VTMDA systems (e.g. Brooks*
1676 *et al., 2002; Philippin et al., 2004; Villani et al., 2007), the residence time in our*
1677 *VTMDA is assumed to be long enough for the volatile materials to be effectively*
1678 *vaporized. After leaving the heating tube, the flow entered a heat exchanger measuring*
1679 *30 cm in length to ensure sufficient cooling before entering DMA₂.*

1680

1681 **7. P25275, L8-10:** *The authors state: “Upon heating at 100 °C and beyond, volatile*
 1682 *components of the particle such as sulfate, nitrate and volatile organics vaporize”.*
 1683 *Please plot VSF (at 300°C) of ammonium sulfate, perhaps as a supplemental figure,*
 1684 *over a few sizes ranging from 40 nm to 300 nm. I would not have thought that*
 1685 *ammonium sulfate completely vaporizes at only 300°C.*

1686

1687 **Response:**

1688 In a number of earlier studies, ammonium sulfate test aerosols were found to volatilize
 1689 at temperatures between 160 °C and 280 °C (Table R3). The volatilization temperature
 1690 of the tested aerosols varies with the initial diameter of the aerosols and their residence
 1691 time in the heated section. In this work, the residence time in the heated section was
 1692 2.4 s, hence we believe that ammonium sulfate would be completely vaporized upon
 1693 heating at 300 °C in the VTDMA. We did not mean to claim that ammonium sulfate
 1694 would be completely vaporized at 100 °C in the original sentence (“Upon heating at
 1695 100 °C and beyond...”). The sentence is revised to avoid confusion.

1696

1697 Table R3. Volatilization temperature of ammonium sulfate test aerosols in the VTDMA
 1698 (Villani et al., 2007)

	O'Dowd et al. (1992)	Philippin et al. (2004)	Burtscher et al. (2001)	Brooks et al. (2002)	Villani et al. (2007)
Volatilization temperature	280 °C	180 °C	180 °C	235 °C	160 to 180 °C

1699

1700 **Revised, Page 25275 of the original manuscript, line 8 – 10:**

1701 Upon heating at 100 °C and **above**, volatile components of the particle such as sulfate,
 1702 nitrate and volatile organics would vaporize **at different temperatures depending on**
 1703 **their volatilities.**

1704

1705 **References**

- 1706 Bradsher, K.: Trucks power China's economy, at a suffocating cost., The New York
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1849 **Measurements of non-volatile aerosols with a VTDMA and**
1850 **their correlations with carbonaceous aerosols in**
1851 **Guangzhou, China**

1852
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1866

1867 **Abstract**

1868 Simultaneous measurements of aerosols of varying volatilities and carbonaceous matters were
1869 conducted at an suburban site ~~of~~ in Guangzhou, China ~~were conducted~~ in February and March
1870 2014 using a volatility tandem differential mobility analyzer (VTDMA) and an organic carbon/
1871 elemental carbon (OC/EC) analyzer. Low-volatility (LV) particles, with a volatility shrinkage
1872 factor (VSF) at 300 °C exceeding 0.9, contributed to 5% of number concentrations of 40 nm
1873 particles and 11–15% of 80–300 nm particles. They were non-volatile materials externally
1874 mixed with the volatile ones and therefore did not evaporate significantly at 300 °C. Non-
1875 volatile materials mixed internally with the volatile ones are referred to as the medium volatility
1876 (MV, $0.4 < VSF < 0.9$) and high volatility (HV, $VSF < 0.4$) particles. These MV and HV particles
1877 contributed to 57–71% of number concentrations for particles between 40 nm and 300 nm in
1878 size. The average EC and OC concentrations measured by the OC/EC analyzer were 3.4 ± 3.0
1879 $\mu\text{g m}^{-3}$ and $9.0 \pm 6.0 \mu\text{g m}^{-3}$, respectively. Non-volatile OC evaporating at 475 °C or above,
1880 together with EC, contributed to 67% of the total carbon mass. The diurnal variations in the
1881 volume fraction of the volatile materials, HV, MV and LV residuals were less than 15% for
1882 most of the particles except for the 40 nm ones, although a daily maximum and a daily minimum
1883 were still observed. Back trajectory analysis also suggests that over 90% of the air masses
1884 influencing the sampling site were well-aged as they were transported at low altitudes (below
1885 1500 m) for over 40 h before arrival. Further comparison with the diurnal variations in the mass
1886 fractions of EC and non-volatile OC in PM_{2.5} suggests that the non-volatile residuals may be
1887 related to both EC and non-volatile OC in the afternoon, during which the concentration of aged
1888 organics increased. The closure analysis of the total mass of LV and MV residuals and the mass
1889 of EC or the sum of EC and non-volatile OC also suggests that non-volatile OC, in addition to
1890 EC, was one of the components of the non-volatile residuals measured by the VTDMA in this
1891 study.~~In VTDMA, selected aerosols of 40 to 300 nm in mobility diameter were heated at~~
1892 ~~elevated temperatures up to 300 °C and the size distributions of the residual particles were~~
1893 ~~measured. Size dependent distributions were observed for both non-volatile and volatile~~
1894 ~~materials (VM). The 40 nm particles were dominated by particles that completely vaporized~~
1895 ~~(CV) at 300 °C, with an average number fraction of about 0.4. Particles larger than 80 nm were~~
1896 ~~dominated by the medium and low volatility (MV and LV, respectively) fractions, with average~~
1897 ~~number fractions of 0.5 and 0.15 respectively. VM did not contribute separately to number~~
1898 ~~fraction but contributed to over 50% of the total volume fraction for all sizes. In both number~~
1899 ~~and volume fractions, diurnal variation was only observed for the high volatility (HV) group,~~

1900 ~~CV and VM in 40 nm particles, likely because these particles were related to fresh emissions.~~
1901 ~~The little diurnal variation of larger particles could be attributed to non-locally aged aerosols.~~
1902 ~~Closure analysis between the residual mass of LV+MV and mass of EC or EC+OC₂₋₄ (sum of~~
1903 ~~EC, OC₂, OC₃, and OC₄ of the OC/EC Analyzer) suggests that non-volatile materials measured~~
1904 ~~by the VTDMA likely contain less volatile OC.~~
1905

1906 1 Introduction

1907 Carbonaceous aerosols comprising organic carbon (OC) and elemental carbon (EC) or black
1908 carbon (BC) are one of the major light absorption constituents and are abundant in particulate
1909 matter (PM) (Rosen et al., 1978; Hansen et al., 1984; Japar et al., 1986; Chow et al., 1993;
1910 Horvath, 1993; Liousse et al., 1993; Fuller et al., 1999; Putaud et al., 2010; Tao et al., 2014;
1911 Zhang et al., 2015). In China, the worsening of visibility degradation associated with PM is of
1912 increasing concern in recent years. In particular, numerous studies on air pollution were carried
1913 out in different cities in China including the Pearl River Delta (PRD) region which is a fast-
1914 developing economic zone (Cheng et al., 2006; Wu et al., 2007; Andreae et al., 2008; Chan and
1915 Yao, 2008; Gnauk et al., 2008; Tan et al., 2013a). In 2007, the mass concentrations of EC and
1916 OC measured at an urban Guangzhou (GZ) site were reported to be from 6.8 to 9.4 $\mu\text{g m}^{-3}$ and
1917 from ~~6.6~~13.4 to 22.5 $\mu\text{g m}^{-3}$ respectively (Yu et al., 2010).

1918 Soot particles are often characterized in terms of EC and BC, depending on whether they are
1919 measured thermally or optically (Penner and Novakov, 1996; Lavanchy et al., 1999; Cheng et
1920 al., 2011 and references therein). Their optical properties are distinct when they are freshly
1921 produced (Novakov et al., 2003). After aging processes such as cloud processing, reaction with
1922 other species and coagulation, their structure, shape, size, mixing state and thus optical
1923 properties change (Horvath, 1993; Liousse et al., 1993; Ghazi and Olfert, 2012). EC is typically
1924 measured by thermal method such as the OC/EC analyzer (Chow et al., 2007), BC are
1925 optically measured using instruments such as aethalometer (Hansen et al., 1984), multi-angle
1926 absorption photometer (~~MAAP~~) (Petzold and Schönlinner, 2004) and particle soot absorption
1927 photometer (~~PSAP~~) (Virkkula et al., 2005). However, it is not possible to retrieve the mixing
1928 state of soot particles from above techniques. To determine the mixing state of soot particles,
1929 single particle soot photometer (~~SP2~~) (Stephens et al., 2003), soot particle aerosol mass
1930 spectrometer (~~SP-AMS~~) (Onasch et al., 2012) and Volatility Tandem Differential Mobility
1931 Analyzer (VTDMA) (Philippin et al., 2004) have been used.

1932 Ambient aerosols have varying volatility properties based on their chemical compositions.
1933 VTDMA was first introduced by Rader and McMurry (1986) to study the behavior of aerosols
1934 upon thermal treatment. Philippin et al. (2004) later developed a VTDMA which is capable of
1935 evaporating volatile materials in aerosols at temperatures up to 300 °C. Non-volatile materials
1936 at 300 °C, such as EC, non-volatile organics and sea salt, can internally mix with (or be coated
1937 with) volatile materials. ~~(VM) which evaporate during thermal treatment at elevated~~

1938 ~~temperatures. Based on the relative abundance of the non-volatile materials to VM, these~~
1939 ~~internally mixed ambient aerosols can be categorized into three groups, namely the low~~
1940 ~~volatility (LV), the medium volatility (MV) and the high volatility (HV) particles in VTDMA~~
1941 ~~measurements (Wehner et al., 2004). When volatile materials exist as external mixtures with~~
1942 ~~LV, MV and HV, they evaporate completely without leaving any residuals at elevated~~
1943 ~~temperatures. They are referred as CV (completely vaporized) particles. Note that the terms~~
1944 ~~“volatile” and “non-volatile” are defined at the heating temperature of 300°C in the VTDMA.~~
1945 ~~They are different from the volatilities defined under ambient conditions (Donahue et al., 2009;~~
1946 ~~Murphy et al., 2014) or in other measurement techniques (Twomey, 1968; Pinnick et al., 1987;~~
1947 ~~Huffman et al., 2009). The composition of these non-volatile residuals can vary spatially and~~
1948 ~~temporally in VTDMA measurements. Previous studies have demonstrated good agreement~~
1949 ~~between the mass of black carbon and the mass of particles with small volatile fractions, which~~
1950 ~~experienced size reductions of 5 to 10% upon heating at 300 °C in the VTDMA. Various studies~~
1951 ~~have also used an VTDMA to estimate the mixing states of soot particles. Particles with small~~
1952 ~~volatile fractions are often assumed to be soot particles externally mixed with particles with~~
1953 ~~volatile materials at 300 °C. Particles with larger volatile fractions, which experienced size~~
1954 ~~reductions of more than 10% upon heating at 300 °C in the VTDMA, were assumed to represent~~
1955 ~~soot particles internally mixed (coated) with the volatile materials.~~

1956 ~~An assumption often made in VTDMA measurements is that the majority of the non-volatile~~
1957 ~~materials are EC. In some studies, the non-volatile materials measured in VTDMA poorly~~
1958 ~~correlated with OC but gave better correlations with BC or light absorbing carbon (LAC)~~
1959 ~~(Philippin et al., 2004; Cheng et al., 2006; Frey et al., 2008; Wehner et al., 2009; Rose et al.,~~
1960 ~~2011; Levy et al., 2014; Zhang et al., 2016). On the other hand, Häkkinen et al. (2012) found~~
1961 ~~that the mass fraction remaining (MFR) of non-BC residuals, which is the difference between~~
1962 ~~the residual mass derived from a volatility differential mobility particle sizer (VDMPS) at~~
1963 ~~280 °C and black carbon mass derived from an aethalometer, is positively correlated with the~~
1964 ~~mass fraction of organics measured by an AMS.~~

1965 ~~Organics are also known as another contributor of also contribute to~~ light absorption by
1966 atmospheric particles (Bond, 2001; Kirchstetter et al., 2004; Chen and Bond, 2010). ~~However,~~
1967 ~~because of its higher volatility compared to EC, they were often considered completely~~
1968 ~~evaporated upon heating at temperatures above 300 °C in VTDMA studies. In recent years, it~~
1969 ~~has been widely accepted organic aerosol exhibit a wide range of volatilities (Donahue et al.,~~

1970 ~~2011; Donahue et al., 2012). It is therefore possible, that a significant amount of non-volatile~~
1971 ~~OC can exist together with EC in ambient aerosol, even after heating in a VTDMA. Laboratory~~
1972 ~~studies have shown that organic aerosols may form low volatility oligomers after aging for a~~
1973 ~~long time (e.g. Kalberer et al., 2004). Huffman et al. (2009) showed that highly oxygenated,~~
1974 ~~aged organic aerosols exhibited similar or lower volatility than the primary organic aerosols or~~
1975 ~~the less oxygenated ones. Recently,~~On the other hand, Häkkinen et al. (2012) found that the
1976 mass fraction remaining (MFR) of non-BC residuals, which is i.e. the difference between the
1977 residual mass derived from a volatility differential mobility particle sizer (VDMPS) at 280 °C
1978 and black carbon mass derived from an aethalometer, is positively correlated with the mass
1979 fraction of organics measured by an AMS.

1980 In this ~~paper study, we report~~ simultaneous measurements of aerosols ~~of varying~~ volatility and
1981 carbonaceous matter ~~were made~~ at a ~~suburban site of in~~ Guangzhou, China ~~during wintertime~~
1982 in February ~~to and~~ March 2014 using a VTDMA and a ~~semi-continuous~~ OC/EC analyzer,
1983 respectively. ~~Volatility measurements were made for ambient aerosols ranging from 40 nm to~~
1984 ~~300 nm in diameter. Residuals remaining after heating at 300 °C in the VTDMA are referred to~~
1985 ~~as non-volatile in this study. We report the average values, time series and diurnal variations in~~
1986 ~~the number and volume fractions of the volatile and non-volatile materials, as well as the OC~~
1987 ~~and EC concentrations. We examine the relationships of the non-volatile materials upon heating~~
1988 ~~at 300 °C to EC and to the non-volatile OC, based on analyses of the diurnal patterns and mass~~
1989 ~~closures of the OC/EC and VTDMA data. Finally, we discuss the influence of air mass origins~~
1990 ~~on the volatility of the sampled aerosols and concentrations of OC and EC based on back~~
1991 ~~trajectory analysis. The term “volatile” components refer to those that evaporate at elevated~~
1992 ~~temperatures and they may actually be semi-volatile under atmospheric conditions. We will~~
1993 ~~first present the average, temporal and diurnal trends of the number and volume fractions of~~
1994 ~~both non-volatile and volatile materials. We then conduct a closure analysis between the mass~~
1995 ~~of non-volatile materials derived by the VTDMA and EC and OC measured by the OC/EC~~
1996 ~~Analyzer to evaluate the significance of non-volatile OC in the VTDMA measurements.~~

1997

1998 **2 Methodology**

1999 **2.1 Experimental**

2000 **2.1.1 Measurement details**

2001 The campaign was taken place at the China Meteorological Administration (CMA)
2002 Atmospheric Watch Network (CAWNET) Station in Panyu, Guangzhou, China in summer from
2003 July to September 2013 and winter from 6 February to 21 March 2014, which is operated by
2004 the Institute of Tropical and Marine Meteorology (ITMM) of the CMA. The Panyu station is
2005 located at the center of the PRD region and on the top of Dazhengang Mountain (23°00' N,
2006 113°21' E) with an altitude of about 150 m (Figure S1 in Supplemental Information) (Tan et al.,
2007 2013a). It is about 120 m above the city average elevation and is surrounded by residential
2008 neighborhoods with no significant industrial pollution sources nearby. Measurements of
2009 particle number size distributions, volatility, mass concentrations of EC and OC were made in
2010 winter from 6 Feb to 21 Mar 2014. Some of the measurements were not made continuously due
2011 to maintenance work and hence only periods with both VTDMA and OC/EC measurements
2012 were analyzed.

2013 **2.1.2 VTDMA measurements**

2014 We used a custom-made VTDMA based on a Hygroscopic TDMA system developed in ITMM
2015 (Tan et al., 2013b), with the humidifier between the two DMAs replaced by a heated tube which
2016 effect evaporation of volatile materials. In our VTDMA system shown in Figure 1, ambient
2017 aerosols sampled by a PM_{2.5} inlet first passed through a dryer at relative humidity below 20%.
2018 The dry aerosols then passed through a neutralizer and entered the first differential mobility
2019 analyzer (DMA₁) (Stream 1) to produce mono-disperse aerosols of diameter between 40 nm
2020 and 300 nm, D_0 . The mono-disperse aerosols went either path (a) or (b) in [Figure-Fig. 1](#) after
2021 leaving DMA₁. In path (a), they (Stream 2) were directed to a condensation particle counter
2022 (CPC, TSI Model 3772) to obtain particle counts, N_{D0} . The particle number size distribution of
2023 the ambient aerosols, $dN/d\log D_p$, was also measured by varying the DMA₁ voltage (SMPS
2024 scan). Afterwards, the mono-disperse aerosols were directed via path (b) to a heated tube for
2025 volatility measurement (V-Mode) sequentially at 25 °C, 100 °C and 300 °C. The heating tube was
2026 a 1/2", 80 cm long stainless steel tube with an inner diameter of 8 mm. With a sample flow rate
2027 of 1 L min⁻¹, the resulting residence time in the heated section of the VTDMA was 2.4 s. The

2028 estimated aerosol velocity on the center line was 0.33 m s⁻¹. Compared to the residence time of
2029 0.3 s to 1 s in other VTDMA systems (e.g. Brooks et al., 2002; Philippin et al., 2004; Villani et
2030 al., 2007), the residence time in our VTDMA is assumed to be long enough for the volatile
2031 materials to be effectively vaporized. After leaving the heating tube, the flow entered a heat
2032 exchanger measuring 30 cm in length to ensure sufficient cooling before entering DMA₂.

2033 Upon heating at 100 °C and ~~beyond~~above, volatile components of particles such as sulfate,
2034 nitrate and volatile organics would vaporize at different temperatures depending on their
2035 volatilities. A volatility shrinkage factor, VSF, is defined as the ratio of particle diameter after
2036 heating at temperature T, D_{p,T}, to that before heating, D₀, to indicate the size reduction of the
2037 ambient particles (Eq. (1)). The value of VSF is always smaller than or equal to one, depending
2038 on the amount of volatile materials vaporized at the heating temperature T₃.

$$2039 \quad VSF(T) = \frac{D_{p,T}}{D_0} \quad (1)$$

2040 The VSF is also used to divide the particles into three groups, namely the low volatility (LV),
2041 medium volatility (MV) and high volatility (HV) particles. In this study, we focus on the
2042 measurements made at 300 °C. The VSF ranges for LV, MV and HV particles upon heating at
2043 300 °C are ~~larger than~~above 0.9, between 0.4 and 0.9 and ~~less than~~below 0.4, respectively
2044 (Figure 2b, 2) (Wehner et al., 2004; Wehner et al., 2009). The LV particles are assumed to
2045 represent EC particles externally mixed with the volatile materials, while MV and HV particles
2046 are assumed to represent EC particles internally mixed with volatile materials. While the
2047 volatile materials in the MV and HV particles are referred to as VM, those exist as external
2048 mixtures with the LV, MV and HV particles are referred to as completely vaporized (CV)
2049 particles. The CV particles evaporate completely without leaving behind any residuals at 300 °C.
2050 Excluding particle diffusional and thermophoretic losses, the evaporation of VM and CV does
2051 not change the number concentrations of LV, MV and HV particles.

2052 ~~, resulting in the shrinking of particles and a~~The new size distribution, dN'/dlogD_p of the
2053 remaining particles, i.e. the non-volatile materials in the LV/MV/HV aerosols (hereafter called
2054 the residuals). These size distributions of six selected diameters from DMA₁ (40 nm, 80 nm,
2055 100 nm, 150 nm, 200 nm and 300 nm) were measured by DMA₂ and CPC before they were
2056 heated at another temperature (Fig. 2b). Overall it took around one and a half to two hours to
2057 complete a cycle of measurements which consisted of SMPS scans and V-Mode measurements
2058 at 25 °C, 100 °C and 300 °C. At each temperature, the sampling time for six selected diameters

2059 from DMA₁ (40 nm, 80 nm, 110 nm, 150 nm, 200 nm and 300 nm) took about half an hour and
2060 SMPS scans were made in-between. Hereafter, notations with the superscript prime refer to the
2061 LV_′, MV_′ or HV_′ residuals measured by DMA₂ and CPC after heating, while the corresponding
2062 ones without the prime refer to the LV_′, MV_′ or HV_′ residuals in ambient aerosols prior to
2063 heating.

2064 ~~Figure 2 illustrates how thermal treatment in the VTDMA affects the size distributions of the~~
2065 ~~ambient aerosols. At each selected diameter D_0 (and at each temperature) in DMA₁ in the~~
2066 ~~VTDMA, the particles include CV particles (purple) and LV, MV and HV particles that have~~
2067 ~~VM (orange) internally mixed with the LV (blue), MV (green) and HV (red) residuals. After~~
2068 ~~heating, the remaining particles form LV, MV and HV residuals without any CV or VM.~~
2069 ~~Evaporation of VM and CV does not change the number concentrations of LV, MV and HV~~
2070 ~~particles.~~

2071 ~~A volatility shrinkage factor, VSF , is defined as the ratio of particle diameter after heating, D_p ,~~
2072 ~~to that before heating, D_0 , to indicate the size reduction of the ambient particles (Eq. (1)). The~~
2073 ~~value of VSF is always smaller than or equal to one, depending on the amount of volatile~~
2074 ~~materials vaporized,~~

$$2075 \quad VSF = \frac{D_p}{D_0} \quad (1)$$

2076 ~~The VSF range for LV, MV and HV are larger than 0.9, between 0.4 and 0.9 and less than 0.4,~~
2077 ~~respectively (Figure 2b) (Wehner et al., 2004; Wehner et al., 2009).~~

2078 ~~Residual particles are either freshly emitted soot particles or other non-volatile material such as~~
2079 ~~sea salt or crustal particles, which do not shrink significantly during heating (LV particles), or~~
2080 ~~particles that exhibit a larger size change due to evaporation of volatile materials (MV and HV~~
2081 ~~particles). Some volatile materials, such as sulfate and nitrate, are formed via chemical and/or~~
2082 ~~photochemical reactions. They mix internally with the non-volatile materials during~~
2083 ~~atmospheric aging process and evaporate at 300 °C in the VTDMA. Most of the organic species,~~
2084 ~~including primary and secondary, also evaporated at this temperature. In urban areas, the~~
2085 ~~majority of the non-volatile mass in submicron particles can be assumed to be soot (Kondo et~~
2086 ~~al., 2006; Kuwata et al., 2007).~~

2087 2.1.3 OC/EC measurements

2088 A semi-continuous Sunset OC/EC Analyzer (Model 4) was used to measure PM_{2.5} mass
2089 concentrations of organic carbon and elemental carbon, m_{OC} and m_{EC} respectively, on an hourly
2090 basis (Turpin et al., 1990; Birch and Cary, 1996; Wu et al., 2012). The OC/EC Analyzer adopts
2091 the ACE-Asia protocol (a NIOSH-derived protocol), where OC evaporates at four set
2092 temperatures of 310 °C, 475 °C, 615 °C and 870 °C with pure helium (He) as the carrier gas, and
2093 EC is combusted at temperatures between 550 °C and 870 °C under He and 2% oxygen
2094 (O₂) above 550 °C (Schauer et al., 2003; Wu et al., 2012). ~~Based on volatility and refractoriness,~~
2095 ~~†~~The OC contents are named OC₁ to OC₄ based on the temperature protocol of the OC/EC
2096 analyzer (Table 1). The mass of EC determined at different temperatures will be grouped
2097 together for discussions with OC₁ being most volatile. In the VTDMA measurements, there
2098 were volatile or semi-volatile OC which vaporize at 300 °C or below. These vaporized OC are
2099 assumed to be OC₁, which vaporizes at 310 °C, although this OC/EC set temperature is slightly
2100 higher than the set temperature of 300 °C in the VTDMA. With this assumption, the residuals
2101 of the VTDMA at 300 °C (LV and MV residuals) are postulated to consist of (1) OC₂ to OC₄,
2102 which vaporize at 475 °C and above, and (2) EC and other refractory PM components. We have
2103 ignored the HV residuals as their contributions to the total volume of the particles are
2104 insignificant when compared to LV and MV residuals (~~see later~~ Section 3.1). We will conduct a
2105 mass closure analysis based on the VTDMA and OC/EC measurements to examine this
2106 assumption.

2107 2.2 Data analysis

2108 2.2.1 Number fractions

2109 The number fractions of LV, MV and HV residuals ($\Phi'_{N,LV}$, $\Phi'_{N,MV}$ and $\Phi'_{N,HV}$, with their sum
2110 being equal to unity) in Stream 2 on Fig. 1 were obtained from $dN'/d\log D_p$ measured by the
2111 CPC. However, these fractions ~~are not do not represent~~ the actual number fractions of LV, MV
2112 and HV ~~residuals-particles~~ ($\Phi_{N,LV}$, $\Phi_{N,MV}$ and $\Phi_{N,HV}$) ~~of the selected particles~~ before heating
2113 because they have not taken into account the CV particles and particle diffusional and
2114 thermophoretic losses. The number fraction of CV ($\Phi_{N,CV}$) is first obtained by considering the
2115 number fractions due to the residuals ($1-\Phi_{N,CV}$) and the number concentrations at a selected
2116 diameter D_0 before heating (N_{D_0}) and after heating (N'):

$$2117 N_{D_0} \times \eta_{D_0} \times (1 - \Phi_{N,CV}) = N' \quad (2)$$

2118 where η_{D0} is the transport efficiency of particles.

2119 Equation (2) assumes that η is the same for LV, MV and HV particles. η accounts for particle
2120 loss between DMA₁ and DMA₂ due to diffusion and thermophoretic forces (Philippin et al.,
2121 2004), and it varies with particle size and heating temperature. η at each particle diameter and
2122 VTDMA temperature was determined by laboratory calibrations with sodium chloride (NaCl)
2123 particles, which do not evaporate (i.e., $\Phi_{N,CV} = 0$) at the ~~heating~~ temperatures used in our
2124 experiments. The transmission efficiency of NaCl of several selected diameters heated at
2125 temperatures between 50 °C and 300 °C is provided in the supplemental information (Fig. S2).
2126 From the known η and field measurements N_{D0} and N' , $\Phi_{N,CV}$ was obtained from Eq. (2).
2127 Afterwards, $\Phi_{N,LV}$, $\Phi_{N,MV}$ and $\Phi_{N,HV}$ were obtained by renormalizing $\Phi'_{N,LV}$, $\Phi'_{N,MV}$ and $\Phi'_{N,HV}$
2128 with $(1-\Phi_{N,CV})$ so that the sum of $\Phi_{N,LV}$, $\Phi_{N,MV}$, $\Phi_{N,HV}$ and $\Phi_{N,CV}$ equals to unity.

2129 2.2.2 Volume fractions

2130 The volume fractions of LV, MV, HV residuals and CV ($\Phi_{V,LV}$, $\Phi_{V,MV}$, $\Phi_{V,HV}$ and $\Phi_{V,CV}$) at each
2131 selected diameter D_0 are defined as the ratios of the volume of LV, MV, HV residuals and CV
2132 to the total volume of the mono-disperse particles before heating. By assuming that the residuals
2133 are in spherical shape, $\Phi_{V,LV}$, $\Phi_{V,MV}$ and $\Phi_{V,HV}$ can be calculated by:

$$2134 \Phi_{V,i} = \frac{N_i \times \frac{\pi}{6} D_{p,i}^3}{N_{D_0} \times \frac{\pi}{6} D_0^3} = \Phi_{N,i} \times \frac{D_{p,i}^3}{D_0^3} \quad (3)$$

2135 where N_i and $D_{p,i}$ are the number concentration and mean residual diameter of $i = LV, MV$ or
2136 HV residuals.

2137 For LV particles, it is assumed that D_0 and mean D_p are the same and hence $\Phi_{V,LV}$ is the same
2138 as $\Phi_{N,LV}$. For MV and HV particles, the mean D_p is smaller than D_0 due to the evaporation of
2139 volatile materials. The number weighted mean residual diameter (D_p) is calculated by:

$$2140 D_{p,i} = \frac{\sum_j D_{p,i} \times N_{i,j}}{N_i} \quad (4)$$

2141 where $D_{p,i}$ and $N_{i,j}$ are the residual diameter and number concentration of $i = MV$ or HV at the
2142 75 diameter bins (j) of *VSF*, respectively.

2143

2144 The volume fractions of the evaporated materials are calculated from the volume fractions of
2145 the residuals. The calculation for $\Phi_{V,CV}$ is similar to that for $\Phi_{V,LV}$. Since the particle has

2146 completely vaporized, the vaporized volume is equivalent to the volume of the original particle.
 2147 Hence, $\Phi_{V,CV}$ is the same as $\Phi_{N,CV}$:

$$2148 \quad \Phi_{V,CV} = \frac{N_{CV} \times \frac{\pi}{6} D_{p,CV}^3}{N_{D_0} \times \frac{\pi}{6} D_0^3} = \Phi_{N,CV} \quad (5)$$

2149 where $D_{p,CV} = D_0$. Since the sum of the total volume fraction of CV, VM and the residuals of
 2150 LV, MV, HV equals to unity, $\Phi_{V,VM}$ was obtained after the above volume fractions were
 2151 calculated. Furthermore, we also calculated the volume fraction remaining (VFR), defined as
 2152 the volume ratio of the residuals to their-its host particles, to aid for MV and HV ($\Phi_{V,MV}$ and
 2153 $\Phi_{V,HV}$) for our discussions later:

$$2154 \quad \Phi_{VFR_{V,i}} = \frac{N_i \times \frac{\pi}{6} D_{p,i}^3}{N_i \times \frac{\pi}{6} D_0^3} = \frac{D_{p,i}^3}{D_0^3} \quad (6)$$

2155 where N_i and $D_{p,i}$ are the number concentration and mean residual diameter of $i = MV$ or HV
 2156 after heating, respectively.

2157 **2.2.3 Particle size distributions of number, volume and mass concentrations of** 2158 **LV, MV and HV residuals**

2159 Due to the differences in the size cuts of the VTDMA and the OC/EC Analyzer, log-normal fits
 2160 extrapolated to 5 μm were applied to the particle number size distributions of the residuals of
 2161 LV, MV and HV ($dN/d\log D_{p,i}$, where $i = LV, MV$ or HV) to estimate the volume and then mass
 2162 concentrations (calculated later) of the ambient aerosols for comparison with $\text{PM}_{2.5}$ OC/EC
 2163 measurements. The volume size distributions ($dV/d\log D_{p,i}$) are calculated by:

$$2164 \quad \frac{dV}{d\log D_{p,i}} = \frac{dN}{d\log D_{p,i}} \times \frac{\pi}{6} D_{p,i}^3 \quad (7)$$

2165 where $D_{p,i}$ is the mean residual diameter as defined in Section 2.2.2.

2166 Volume (V) concentrations of LV, MV and HV residuals can then be calculated by integrating
 2167 the area under the fitted curves. As we only focus on LV and MV, densities of 1.0 g cm^{-3}
 2168 (Hitzenberger et al., 1999) and 1.5 g cm^{-3} are applied to V_{LV} and V_{MV} to obtain mass (m)
 2169 concentrations of LV and MV residuals, respectively. The choice of the densities is based on
 2170 the assumption that LV and MV residuals are dominated by soot and non-volatile OC,
 2171 respectively.

2172

2173 3 Results and Discussions

2174 3.1 Overview

2175 The time series of meteorological conditions, particle number size distribution, PM_{2.5}, OC and
2176 EC concentrations during the campaign are presented in Fig. 3. Overall, the campaign came
2177 under the influence of the prevailing northerly wind with an average wind speed and
2178 temperature (\pm one standard deviation) of $1.73 \pm 0.95 \text{ m s}^{-1}$ and $14.8 \pm 5.1 \text{ }^\circ\text{C}$, respectively. The
2179 average PM_{2.5} concentration was $48 \pm 26 \text{ } \mu\text{g m}^{-3}$. A few cold front periods were observed, during
2180 which the wind speed increased and the temperature decreased. In general, the low wind speed
2181 favored the accumulation of PM_{2.5}. OC concentrations ranged from 0.5 to $47.0 \text{ } \mu\text{g m}^{-3}$ with an
2182 average of $9.0 \pm 6.0 \text{ } \mu\text{g m}^{-3}$, while EC concentrations ranged from 0.2 to $23.0 \text{ } \mu\text{g m}^{-3}$ with an
2183 average of $3.4 \pm 3.0 \text{ } \mu\text{g m}^{-3}$. OC₁, the most volatile group among OC₁ to OC₄ in OC/EC analysis,
2184 accounted for one-third of the total carbon mass (Fig. 4).

2185 On Feb 17, and Mar 12 and 17, the daily-averaged PM_{2.5} concentrations exceeded $95 \text{ } \mu\text{g m}^{-3}$;
2186 they were nearly twice the daily-averaged values on other days (Fig. 3, shaded area in grey).
2187 Results of 72 h back trajectories (Stein et al., 2015; Rolph, 2016) showed that air masses
2188 arriving at the site on or before these three days mostly originated from the continental or
2189 oceanic area close to Eastern China (Fig. S3). The SMPS data also showed a mode near 100
2190 nm with a high particle number concentration (Fig. 3). ~~Figures 3 to 5 show the average values,~~
2191 ~~time series and diurnal variation of $\Phi_{N,LV}$, $\Phi_{N,MV}$, $\Phi_{N,HV}$ and $\Phi_{N,CV}$ during the campaign,~~
2192 ~~respectively. We will first discuss the trends of these number fractions and then the volume~~
2193 ~~fractions. Finally, we attempt to conduct closure analysis for the non-volatile species (LV and~~
2194 ~~MV residuals) with EC and OC₂₋₄. We focus only on the VTDMA data at 300 °C for comparison~~
2195 ~~with the OC/EC data.~~

2196 The temporal variation of the number concentration of MV particles having an initial diameter
2197 of 80 nm or above tracked reasonably well with the accumulation of PM_{2.5} as particles aged
2198 and became more internally mixed (Fig. 3 and S4). Furthermore, a size dependence was
2199 observed for 80 nm to 300 nm MV particles. There were days, e.g., from Feb 24 to Mar 10,
2200 when the number concentration of 300 nm MV particles did not track well with PM_{2.5}. The
2201 mode of total particle number size distribution was below 100 nm and the number
2202 concentrations of 300 nm particles were low (Fig. 3). PM_{2.5} tracked better with the number

concentrations of 80 nm to 150 nm MV particles (Fig. 4a to S4c) than those of 200 nm and 300 nm MV particles (Fig. S4d and S4e).

3.1.1 Number fractions

The average number fractions of CV and the residuals of LV, MV, and HV ($\Phi_{N,CV}$, $\Phi_{N,LV}$, $\Phi_{N,MV}$, and $\Phi_{N,HV}$) of 40 nm, 80 nm, 110 nm, 150 nm, 200 nm and 300 nm particles based on VTDMA measurements at 300 °C in Feb and Mar 2014 are shown in Figure 3. The average number and volume fractions of CV, HV, MV and LV in VTDMA measurements at 300 °C are summarized in Table 2. VM is internally mixed with (or coated on) MV and HV residuals, and hence it does not have a separate contribution to number concentrations. Overall, HV and MV particles, indicator for aged aerosols with internally mixed non-volatile and volatile materials, accounted for 57% to 71% of the total particle number concentration. Non-volatile materials (LV, MV and HV residuals) accounted for 15% to 26% of the total volume of selected particles before heating. While the CV and HV fractions were larger in the finest particles selected ($D_0 = 40$ nm), MV and LV were more abundant in larger particles ($D_0 > 80$ nm). As in Rose et al. (2006), fresh emissions like soot adsorbed or absorbed volatile materials during atmospheric processing. Smaller particles grew to a greater extent than the larger ones because of their higher ratios of surface area to volume. When they were heated in the VTDMA at 300 °C, these smaller particles reduced more substantially in size, as reflected in the higher CV and HV fractions and lower MV and LV fractions. The higher abundance of MV and LV in larger size particles could also be explained by the non-volatile primary particles. Larger particles ($D_0 > 80$ nm) have more LV particles, while smaller particles have significantly more CV particles. At 40 nm, the mean \pm standard deviation (SD) of $\Phi_{N,LV}$, $\Phi_{N,MV}$, $\Phi_{N,HV}$ and $\Phi_{N,CV}$ were 0.05 ± 0.026 , 0.31 ± 0.097 , 0.26 ± 0.097 and 0.38 ± 0.15 respectively. $\Phi_{N,CV}$ decreased while $\Phi_{N,HV}$, $\Phi_{N,MV}$ and $\Phi_{N,LV}$ increased as size increased from 40 nm to 80 nm and above. The lack of size dependence of number fractions for particles larger than 80 nm suggests that they may be the result of similar atmospheric processes. At 300 nm, the mean \pm SD of $\Phi_{N,LV}$, $\Phi_{N,MV}$, $\Phi_{N,HV}$ and $\Phi_{N,CV}$ were 0.15 ± 0.047 , 0.50 ± 0.125 , 0.21 ± 0.097 and 0.14 ± 0.065 respectively. The large fraction of CV in 40 nm particles is likely due to nucleation of fresh emissions from more volatile primary sources or volatile secondary pollutants. Freshly emitted non-volatile primary sources such as EC and OC are in a larger size range. Larger particles also likely contain more internally mixed aged aerosols (secondary pollutants) than the smaller ones and these aged aerosols are likely more affected by meteorology. Yu et al. (2010) reported that the mass median aerodynamic

2235 ~~diameter condensation and droplet modes of urban EC and OC in the condensation mode in~~
2236 ~~urban sites of~~ Guangzhou ~~were approximately~~ about 380 nm, 400 nm and 900 nm,
2237 respectively. The mode of fresh EC emitted from vehicles is also approximately 400 nm (Huang
2238 ~~et al., 2006~~). Larger particles also likely contain more internally mixed aged aerosols
2239 (secondary pollutants) than the smaller ones. ~~Nevertheless, the detection limit of the~~
2240 ~~downstream DMA and CPC in the VTDMA system is 10 nm. It was assumed that the residuals~~
2241 ~~having a diameter below 10 nm were small enough to be considered as completely vaporized.~~
2242 ~~However, such assumption would lead to an overestimation of CV and an underestimation of~~
2243 ~~the non-volatile residuals for the finest particles selected (with an initial diameter of 40 nm).~~
2244 ~~Figure 4 shows the time series data of N_{LV} , N_{MV} and N_{HV} , $\Phi_{N,LV}$, $\Phi_{N,MV}$ and $\Phi_{N,HV}$, together with~~
2245 ~~the mass concentration of $PM_{2.5}$. For 40 nm particles (Figure 4a and 4c), in both number~~
2246 ~~concentrations and fractions, HV and MV were comparable and LV was very low. There was~~
2247 ~~relatively little temporal variation of their concentrations and number fractions throughout the~~
2248 ~~whole period. CV had a large fraction, varying between 0.2 and 0.6. For 300 nm particles~~
2249 ~~(Figure 4b and 4d), CV, HV and LV fractions were small. N_{MV} tracks reasonably well with~~
2250 ~~$PM_{2.5}$ mass because of its dominance in the number concentrations. Internally mixed soot~~
2251 ~~particles, manifested as MV particles, play an important role in Guangzhou, especially during~~
2252 ~~polluted days. CV had a rather stable fraction of about 0.15, much smaller than that for 40 nm~~
2253 ~~particles.~~

2254 3.2 Diurnal variations

2255 Figure 5 shows the diurnal variation of the ~~fraction of CV, HV residual, MV residual, LV~~
2256 ~~residual and VM in the total volume of particles of dry initial diameters of 40, 150 and 300 nm.~~
2257 ~~number fractions. No obvious pattern of LV, MV, HV and CV was observed for particles larger~~
2258 ~~than 80 nm. For 40 nm particles, clear maximum and minimum of the fraction of CV fraction,~~
2259 ~~VM and HV residuals are observed at 08:00 a.m. and 01:00 p.m., respectively. The diurnal~~
2260 ~~variation of the HV and MV particles in 40 nm particles was clearer in terms of number fraction~~
2261 ~~(Fig. S5). Furthermore, the trend of CV is opposite to those of VM, HV and MV. For MV and~~
2262 ~~HV, the average number concentrations increased since 08:00 a.m. and reached their maxima~~
2263 ~~at 01:00 p.m. The increase of CV in 40 nm particles and to a lesser extent of LV in 150 nm and~~
2264 ~~300 nm larger particles in the morning (Figure 5) is consistent with traffic pattern, where freshly~~
2265 ~~emitted volatile and non-volatile materials, likely OC and EC, are externally mixed and~~
2266 ~~contributed to CV and LV, respectively. As time progresses in a day, the highly volatile species~~

2267 (CV) which were freshly emitted in the morning, may evaporate and react to form less volatile
2268 particles and become VM instead of CV (Robinson et al., 2007). Alternatively, these CV
2269 particles could also coagulate with smaller particles to form VM containing particles. Less fresh
2270 emissions with more CV particles turning into VM on MV and HV particles can explain the
2271 trend that the number ~~concentration~~ and volume fractions of CV decreased while those of MV
2272 and HV increased (Fig. 5 and Fig. S5). ~~VM does not contribute to number fraction and its~~
2273 ~~significance and diurnal variation will be discussed later in volume fraction. The lack of diurnal~~
2274 ~~trends for particles larger than 80 nm suggests that they are dominated by aged particles~~
2275 ~~accumulation likely due to low mixing height in the winter. Freshly emitted particles have little~~
2276 ~~contributions to the number fractions.~~

2277 **3.2 Volume fractions**

2278 ~~The average and diurnal variation of volume fractions of CV, the residuals of LV, MV, and HV,~~
2279 ~~and VM are shown in Figure 6 and 7. Overall, the volume fractions of CV and VM are about~~
2280 ~~0.15 and 0.6, respectively (Figure 6), indicating that most of the original volume of the ambient~~
2281 ~~particles has evaporated at 300 °C. For 40 nm particles, CV and VM altogether contribute to~~
2282 ~~almost 90% of the total volume. $\Phi_{V,LV}$, $\Phi_{V,MV}$ and $\Phi_{V,HV}$ are 0.15, 0.1 and less than 0.01,~~
2283 ~~respectively. Size dependence of $\Phi_{V,CV}$, $\Phi_{V,LV}$, $\Phi_{V,MV}$ and $\Phi_{V,HV}$ are similar to number fractions:~~
2284 ~~$\Phi_{V,CV}$ in 40 nm particles almost doubles and $\Phi_{V,LV}$ and $\Phi_{V,MV}$ are only half of those in 80 nm or~~
2285 ~~larger particles, and is more dominant in larger size. CV are mostly found and hence contributed~~
2286 ~~to $\Phi_{V,CV}$ in smaller particles while non-volatile materials contribute to $\Phi_{V,LV}$ in the larger~~
2287 ~~particles.—~~

2288 ~~The diurnal variation of $\Phi_{V,CV}$, $\Phi_{V,LV}$, $\Phi_{V,MV}$, $\Phi_{V,HV}$, $\Phi_{V,VM}$ and $\Theta_{V,MV}$ and $\Theta_{V,HV}$ (the volume~~
2289 ~~ratio of the residuals to their host particles for MV and HV, respectively) are shown in Figure~~
2290 ~~7. Similar to the diurnal trends of the number fractions in Figure 5, there was no significant~~
2291 ~~variation of $\Phi_{V,CV}$, $\Phi_{V,LV}$, $\Phi_{V,MV}$ and $\Phi_{V,HV}$ for all particle sizes except for 40 nm particles,~~
2292 ~~where $\Phi_{V,VM}$ shows a trend opposite to $\Phi_{V,CV}$. The opposite trends of VM and CV can be~~
2293 ~~explained by the trends of the number concentrations of MV+HV and CV. When there are more~~
2294 ~~MV and HV particles, volume fraction of VM increases. Based on $\Theta_{V,MV}$ and $\Theta_{V,HV}$, about 70~~
2295 ~~to 80% of $\Phi_{V,VM}$ is from MV and there is no size dependence.—~~

2296 ~~There was no obvious diurnal variation of $\Theta_{V,MV}$ and $\Theta_{V,HV}$ for all sizes (except for a minor peak~~
2297 ~~at about 06:00 p.m. for $\Theta_{V,MV}$, which may be related to traffic), even for 40 nm particles where~~

2298 ~~there is an obvious diurnal trend of $\Phi_{V,VM}$, which is the volume ratio of volatile materials~~
2299 ~~internally mixed with non-volatile components to total volume before heating. We also used~~
2300 ~~the diurnal variations in the volume fraction remaining (VFR), again defined as the volume ratio~~
2301 ~~of the residual to its *host* particle (not to the total volume of all particles), to examine the size~~
2302 ~~changes of the non-volatile residuals of HV and MV particles. The VFR of HV did not exhibit~~
2303 ~~any obvious diurnal variations but the VFR of MV peaked near 18:00. The VFR of 40 nm MV~~
2304 ~~particles increased after 14:00 while those of 150 nm and 300 nm MV particles increased after~~
2305 ~~15:00. Since the VFR of HV and MV were relatively constant during the day, the increase in~~
2306 ~~VM fraction $\Phi_{V,VM}$ after the morning rush hours is likely attributed to the increase in number~~
2307 ~~concentrations of HV and MV particles (N_{MV}) (Figure 5) instead of changes in the amount of~~
2308 ~~VM on the MV or HV residuals since $\Theta_{V,MV}$ and $\Theta_{V,HV}$ are relatively constant.~~

2309 ~~Together with the lack of size dependence and diurnal variation on the different volatility~~
2310 ~~components for particles of 80 nm or larger, the high volume contribution of VM and~~
2311 ~~association with MV particles suggest that aerosols sampled at the Panyu station are moderately~~
2312 ~~aged with a significant amount of volatile materials in this campaign.~~

2313 ~~The diurnal variations for particles larger than 80 nm were much less obvious than those for 40~~
2314 ~~nm particles in this study and in others (Rose et al., 2011; Cheng et al., 2012; Zhang et al.,~~
2315 ~~2016). In winter, the atmosphere is more stable, resulting in a poorer dilution of aged particles~~
2316 ~~with the less polluted aerosols from higher up (Rose et al., 2006). When the aged pollutants~~
2317 ~~were trapped near the ground surface, the effect of aging of fresh emissions weakened.~~
2318 ~~Therefore, although a daily maximum and a daily minimum were still observed for particles~~
2319 ~~larger than 80 nm, the variation was mostly within 15%.~~

2320 ~~The diurnal variations in the mass fractions of OC and EC in $PM_{2.5}$ provided further insights to~~
2321 ~~the observations above (Fig. 6). The OC and EC data on Mar 12 and 17 were excluded since~~
2322 ~~they were more than two standard deviations higher than those on other days. Subtle morning~~
2323 ~~peaks between 06:00 and 10:00 were observed for the volume fraction of LV residuals (Fig. 5).~~
2324 ~~A similar peak was observed for the mass fraction of EC in $PM_{2.5}$ in the morning (Fig. 6). This~~
2325 ~~suggests that LV particles may be related to the EC from vehicle emissions in the morning. This~~
2326 ~~EC was relatively less aged and externally mixed with other volatile materials. In the late~~
2327 ~~afternoon, LV residuals showed another peak between 17:00 and 19:00 whereas the mass~~
2328 ~~fraction of EC in $PM_{2.5}$ exhibited a minimum at 15:00, after which it increased continuously.~~

2329 The continuous increase in EC at night is likely related to the increase of heavy-duty diesel
2330 vehicles (Zhang et al., 2015), which was restricted during daytime (Bradsher, 2007).

2331 Although OC₁ contributed to about half of the total OC mass, the diurnal variation in the mass
2332 fraction of OC in PM_{2.5} was driven by the total mass of OC₂, OC₃ and OC₄ (OC₂₋₄), which
2333 reached a minimum between 05:00 and 09:00 and increased until 19:00. OC can be attributed
2334 to both primary and secondary sources. The increased mass fraction of OC in PM_{2.5} and OC-
2335 to-EC ratio in the afternoon suggest that the sources of OC were less related to traffic but more
2336 to the aging and formation of secondary organic aerosols (Turpin et al., 1990; Chow et al.,
2337 1996). These OC₂, OC₃ and OC₄ may be highly oxygenated species or oligomers that are less
2338 volatile than primary or less oxygenated organics (Kalberer et al., 2004; Huffman et al., 2009).

2339 It is interesting to note that the volume fraction of LV residuals and the VFR of MV particles at
2340 different sizes showed a dip in the afternoon (Fig. 5, third column from the left). The VFR of
2341 40 nm MV particles showed a dip at 14:00 while those in 150 nm and 300 nm particles showed
2342 a dip at 15:00. The volume fraction of LV residuals in 150 nm and 300 nm particles reached a
2343 minimum at 13:00 and 15:00, respectively. Because EC decreased between 12:00 and 15:00,
2344 the increase in the volume fraction of LV residuals in 150 nm particles since 13:00 and the VFR
2345 of 40 nm MV particles since 14:00 may be related to the increased presence of aged organics
2346 as well as the EC particles which aged via coagulation and condensation.

2347 **3.3 Back trajectory analyses**

2348 We calculated the 72 h back trajectories of the air masses arriving at the sampling site (23°00
2349 N, 113°25' E) at 4 h intervals (at 00:00, 04:00, 08:00, 12:00, 16:00 and 20:00 local time, UTC
2350 +8) using the PC version of the HYSPLIT4 (Hybrid Single Particle Lagrangian Integrated
2351 Trajectory, version 4) model (Stein et al., 2015; Rolph, 2016). Archived meteorological data
2352 from the Global Data Assimilation System (GDAS) 1-deg was employed and the receptor
2353 height was set at 500 m above ground level (a.g.l.). The 191 back trajectories calculated were
2354 grouped into six clusters based on their spatial distribution (Fig. 7).

2355 Overall, the sampling site was mostly affected by northwesterly and northeasterly air masses.
2356 Cluster 1 and 3 are coastal and continental air masses, respectively, although both originated
2357 from the northeast. Clusters 4, 5 and 6 represent continental air masses originating from the
2358 northwest. Cluster 2 is a group of maritime air masses originating from the East China Sea
2359 northeast or east of Guangzhou. While air masses in cluster 6 were transported at relatively

2360 high speeds and altitudes (over 3000 m a.g.l.), air masses in all the other clusters were
2361 transported at an altitude below 1500 m a.g.l. for over 40 h before arriving at the site.
2362 Nevertheless, air masses in cluster 6 only persisted for less than three days. Since the
2363 corresponding VTDMA and OC/EC data were sometimes unavailable, cluster 6 will be
2364 excluded from the following discussion.

2365 The average PM_{2.5}, OC and EC concentrations associated with air masses from the northeast of
2366 Guangzhou (clusters 1, 2 and 3) were higher than those from the northwest (clusters 4 and 5,
2367 Table 3). Days associated with coastal and maritime air masses were more polluted than days
2368 associated with continental air masses for several reasons. First, south China as a region is often
2369 affected by the high pressure system moving eastward or southward from the continent out to
2370 sea in winter. When the maritime or coastal air streams entered from the southeast of the
2371 sampling site at Panyu, the atmosphere at the sampling site became more stable with low local
2372 wind speeds (e.g. the polluted days on Feb 17 and Mar 12, 16 and 17, Fig. 3 and S3). Local
2373 pollutants accumulated and the city was also affected by pollutants from the southeastern areas
2374 of the site (e.g. Shenzhen, Nansha and Dongguan). Second, land-sea breeze cycles were
2375 observed when the sampling site was under the influence of maritime air masses from Mar 18
2376 to 20. During the day, southeasterly wind prevailed and the wind speed was higher. In the
2377 evening, the southeasterly wind was gradually replaced by a southwesterly or northwesterly
2378 wind and the wind speed decreased (Fig. 3). The cycle started again in the morning when the
2379 westerly wind was gradually replaced by southeasterly wind. Such land-sea breeze effects can
2380 result in an effective redistribution and accumulation of air pollutants within the PRD region
2381 (Lo et al., 2006).

2382 Furthermore, PM_{2.5} in the northeastern parts of China can exceed 200 µg m⁻³ due to both
2383 enhanced emissions from coal combustion for heating and poor dispersion during wintertime
2384 (Gu et al., 2014). Under the influence of the prevailing northerly or northeasterly wind in China,
2385 these pollutants were often transported to southern China and the East China Sea (Chen et al.,
2386 2012). Pollutants might also have accumulated when the maritime air masses spent about two
2387 days across Taiwan and the coast of south China. In contrast, continental air masses in cluster
2388 5 moved slightly faster, and were often associated with the cold front period during which the
2389 local wind speed and pressure increased but the temperature decreased (Fig. 3). As the cold air
2390 masses passed through the city, dispersion and clearance of pollutants were promoted, resulting
2391 in lower PM_{2.5} concentrations (Tan et al., 2013a). Therefore, unlike in other coastal cities like

2392 Hong Kong (Lee et al., 2013), in Panyu maritime air masses could lead to more severe pollution
2393 than the continental ones in winter.

2394 The five clusters were further analyzed to study the influence of air mass history on aerosol
2395 volatility. The number fractions of CV, HV, MV and LV of the six selected diameters in
2396 VTDMA measurements are regrouped based on the clusters as shown in Fig. 8. The total
2397 number fractions of the non-volatile residuals (sum of HV, MV and LV) were similar in all
2398 clusters. Maritime air masses (cluster 2) had a slightly higher fraction of LV particles while
2399 continental air masses originating from the northwest of the site (clusters 4 and 5) had a higher
2400 fraction of HV particles. Although the air masses in clusters 1 and 5 originated from farther
2401 away and traveled at relatively higher speeds than those in clusters 2, 3 and 4, all clusters
2402 involved transport at low altitudes (below 1500 m) for over 40 h, likely due to the generally
2403 lower mixing heights in winter. Therefore, aerosols in these air masses were all well-aged upon
2404 arrival (Wehner et al., 2009). This could be another reason for the lack of size dependence of
2405 the number, volume fractions and diurnal variation for particles larger than 80 nm. When the
2406 transported air masses mixed with local pollutants, the size dependence of the number fractions
2407 of different volatility groups as well as the aging of local emissions was further reduced.

2408 We also examine at the volatility shrinkage factor (*VSF*) distributions of 40 nm, 110 nm and
2409 300 nm particles upon heating at 300 °C (Fig. 9). Log-normal fittings with a three-peak solution
2410 were applied to the distributions. The average *VSF* modes of the peaks were located at $0.38 \pm$
2411 0.021 (peak 1), 0.60 ± 0.066 (peak 2) and 0.95 ± 0.007 (peak 3), respectively. The standard
2412 deviation of the corresponding normal distribution (σ) of peak 3 was the smallest among the
2413 three peaks ($\sigma < 0.1$). For the same particle size, the *VSF* distributions in the *VSF* range between
2414 0.3 and 0.8 in cluster 5 was relatively more uni-modal than those of other clusters (Fig. 9b and
2415 9c). This suggests that the composition in cluster 5 was more homogeneous. Cluster 1 also
2416 consisted of long-range transported air masses but they likely passed through areas that are
2417 more polluted and mixed with different types of pollutants. Note that the fractions of HV, MV
2418 and LV have been traditionally defined based on the values of *VSF*, i.e. $HV < 0.4$; $0.4 < MV <$
2419 0.9 ; $LV > 0.9$ (Wehner et al., 2009). The *VSF* distributions above suggest that these definitions
2420 using $VSF = 0.4$ and 0.9 may need to be re-visited in the future.

3.4 New particle formation

Two new particle formation (NPF) events were observed in the campaign on Feb 20 and Mar 13 (Fig. 3). Since VTDMA data were not available during the NPF event on Mar 13, we only focus on the NPF event on Feb 20 which happened after a cold front under a low $PM_{2.5}$ concentration. On Feb 20, a sub-20 nm particle mode was first observed at 12:00. This particle mode grew continuously until it reached 120 nm at 02:00 on Feb 21. In VTDMA measurements, a sharp increase in the number concentration of HV particles having an initial diameter of 40 nm was observed at 17:00 on Feb 20 (Fig. 10). This event is likely related to the growth of the newly formed particles when they mixed with the volatile materials via condensation or adsorption. As these particles aged further, they grew larger as reflected in the increase in number concentrations of larger MV particles and the increase in $PM_{2.5}$ mass (Fig. 10). The growth of the newly formed particles can also be observed from the number size distributions of HV, MV and LV particles at different times on Feb 20 and 21 (Fig. 11). The mode of HV particles increased from 40 nm at 17:00 to 80 nm at 21:00 on Feb 20 Feb. The mode stayed at 80 nm while the corresponding number concentration decreased at 02:00 on Feb 21 Feb. In contrast, the number concentrations of MV particles grew continuously. The HV and MV particle concentrations and diameter modes underwent much smaller changes on the non-event day of Feb 28 (Fig. 11).

3.3.5 Closure analysis for LV, and MV residuals at 300°C, and OC/EC at 300°C and EC

Closure analysis of EC or $EC+OC_{2-4}$ (the sum of EC, OC_2 , OC_3 , and OC_4) and the total mass of LV and MV residuals $LV+MV$ is conducted (Figure 8, 12). Good correlations ($R^2 > 0.9$) for both EC and $EC+OC_{2-4}$ the sum of EC, OC_2 , OC_3 , and OC_4 with the total mass of LV and MV residuals $LV+MV$ were obtained. Nonetheless, the slope for the total mass of LV and MV residuals to the mass of EC m_{LV+MV}/m_{EC} (2.94) is more than two times of that for the total mass of LV and MV residuals to the sum of EC, OC_2 , OC_3 , and OC_4 $m_{LV+MV}/m_{EC+OC_{2-4}}$ (1.22), indicating that EC alone cannot account for the total mass of LV and MV residuals mass of $LV+MV$. Including non-volatile OC (sum of OC_2 to OC_4) give better mass closure for with the total of LV and MV residuals. $LV+MV$ and $EC+OC_{2-4}$ This observation further supports our initial postulation that LV and MV the non-volatile residuals which remained intact upon heating at 300 °C in the VTDMA may contain a significant amount of non-volatile OC. However, mass of $EC+OC_{2-4}$ the total mass of EC, OC_2 , OC_3 , and OC_4 do not explain all the mass of $LV+MV$ LV

2453 and MV residuals. A possible explanation could be that the vaporizing temperatures of some
2454 OC₁ are close to the upper limit (310 °C), hence they were not completely vaporized in the
2455 heated tube and remained in non-volatile residuals LV+MV. The presence of other refractory
2456 materials and the assumption made about the density of LV and MV are two other possible
2457 explanations., as well as errors during the measurements, could also be a reason for the
2458 difference. The extrapolated lognormal fitting of the size distribution of nonvolatile particles
2459 can cause errors if the mode diameter of the fitting is beyond the range of measurements of the
2460 VTDMA.

2461 Other possible errors for the closure could be related to the different heating environments in
2462 the VTDMA and the OC/EC analyzer. In the OC/EC analyzer, OC was measured when the
2463 samples were heated in the presence of a non-oxidative carrier gas (He). It should be noted that
2464 the heating environment in a VTDMA is different from that of an OC/EC Analyzer. In the
2465 VTDMA, aerosols were heated in the presence of oxygen, while in the OC/EC Analyzer,
2466 samples were heated in the presence of helium for OC. In the presence of oxygen, it is possible
2467 that OC₂₋₄ in the aerosols may have evaporated in the VTDMA even at 300 °C. In the VTDMA,
2468 aerosols were heated in air which contained O₂. Therefore, some “OC₂₋₄” that evaporated at
2469 475 °C or above in the OC/EC analyzer may have been oxidized at 300 °C in the VTDMA.
2470 Charring of organic matter could also occur (Philippin et al., 2004). Further study is needed to
2471 quantify the effect of oxygen on the oxidation of OC in the VTDMA. The extrapolated
2472 lognormal fitting of the size distribution of non-volatile particles can also cause errors if the
2473 mode diameter of the fitting is beyond the VTDMA’s range of measurements of the VTDMA.
2474 While the VTDMA measured the size distribution of particles between 10 nm and 400 nm in
2475 diameter, the OC/EC analyzer took into account particles up to 2.5 µm in diameter. Yu et al.
2476 (2010) reported three EC and OC modes between 0.4 µm and 10 µm in ambient aerosols in
2477 Guangzhou: 0.4, 0.9 and 5 µm. The 0.4 µm mode accounted for 44% to 49% of the measured
2478 EC but only 17% to 20% of the measured OC.

2479

2480 **4 Conclusions**

2481 This study presents the first VTDMA measurements in a suburban area of Guangzhou in the
2482 Pearl River Delta, China during wintertime. The LV fraction was assumed to be EC particles.
2483 These particles were externally mixed with volatile materials at 300 °C and contributed to less
2484 than 20% of the total particle number concentration at the sampling site. The diurnal variations

2485 in the number and volume fractions of LV, MV and HV were much less obvious in this study
2486 than in other studies likely because of the more stable atmosphere and poorer dilution of aged
2487 aerosols in winter. Back trajectory analysis showed that the measured PM_{2.5}, EC and OC
2488 concentrations were higher when the sampling site came under the influence of maritime and
2489 coastal air masses originating from the east or northeast of the site. These observations are
2490 attributed to the high pressure system on the continent, the prevailing northerly wind and the
2491 enhanced pollution from north China in winter. Long-range transport continental trajectories
2492 were often associated with the cold front periods during which the dispersion of pollutants was
2493 promoted. The number fractions of LV, MV and HV particles did not show much variations
2494 among the clusters, likely because the air masses in all clusters were transported at low altitudes
2495 (below 1500 m) for over 40 h. They were therefore well-aged upon arrival at the site.

2496 While previous studies have demonstrated soot as a major component of the non-volatile
2497 residuals at 300 °C measured by the VTDMA, this work identified non-volatile organics as
2498 another possible component. The diurnal variations in the LV fractions and the size of the MV
2499 residuals may be related to the variation in the abundance of both EC and non-volatile OC,
2500 which evaporated at 475 °C and above in the OC/EC analyzer. Analyses of the diurnal variations
2501 in the LV fractions and the VFR of MV particles, the latter of which reflects the change in size
2502 of the non-volatile materials in the MV particles, suggest that the increase in non-volatile
2503 fractions and size in the early afternoon may be related to the increase in non-volatile OC in
2504 addition to the effects of EC coagulation and condensation. The mass closure analysis of EC
2505 and non-volatile OC and the total mass of LV and MV residuals also suggest that non-volatile
2506 OC may have contributed to non-volatile residuals in our VTDMA measurements.

2507 ~~This study presents the first VTDMA measurements in the PRD, China. The measured~~
2508 ~~volatility characteristics of ambient aerosols reflect the difference of the freshly emitted 40 nm~~
2509 ~~particles and the aged bigger ones (80 nm to 300 nm). The 40 nm particles had 50% of particles~~
2510 ~~that completely evaporated at 300 °C. Particles larger than 80 nm were more aged and contained~~
2511 ~~volatile components (VM) internally mixed with non-volatile residuals (MV) and VM~~
2512 ~~contributed to over 50% of the total volume fraction for all particles. From the mass closure~~
2513 ~~analysis of the VTDMA data and OC/EC data, it is likely that the non-volatile residuals at 300 °C~~
2514 ~~observed in VTDMA also contained some less volatile OC (OC₂₋₄).~~

2515 ~~Cheng et al. (2009) performed an aerosol optical closure to investigate the aerosol light~~
2516 ~~absorption coefficient and single scattering albedo using the soot mixing states determined by~~
2517 ~~a VTDMA in Yufa, Beijing. It is possible that some less volatile OCs (OC_{2,4}) also absorb light.~~
2518 ~~The mixing state is a key parameter for accurately assessing the climatic impacts of soot~~
2519 ~~partieles (Jacobson, 2001). In this study, we found that externally mixed soot partieles~~
2520 ~~contribute to about 10% for 40 nm particles and about 15% for 80 nm and larger particles in~~
2521 ~~number concentration. Such external mixing needs to be accounted for in assessing climatic~~
2522 ~~impacts of soot particles in the region.~~

2523

2524

2525

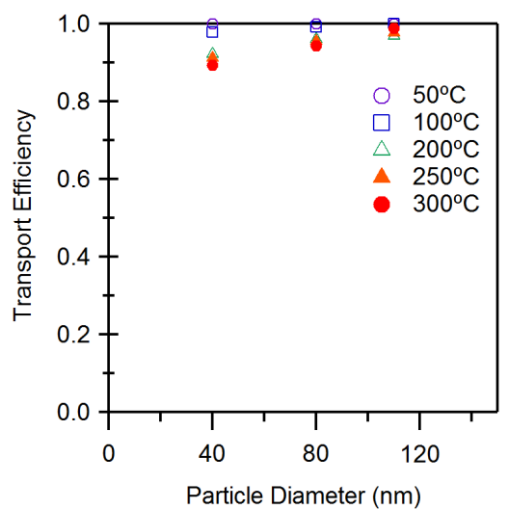
Supplemental Information:- Location of the measurement site



2526

2527 Fig. S1. Location of the measurement site.

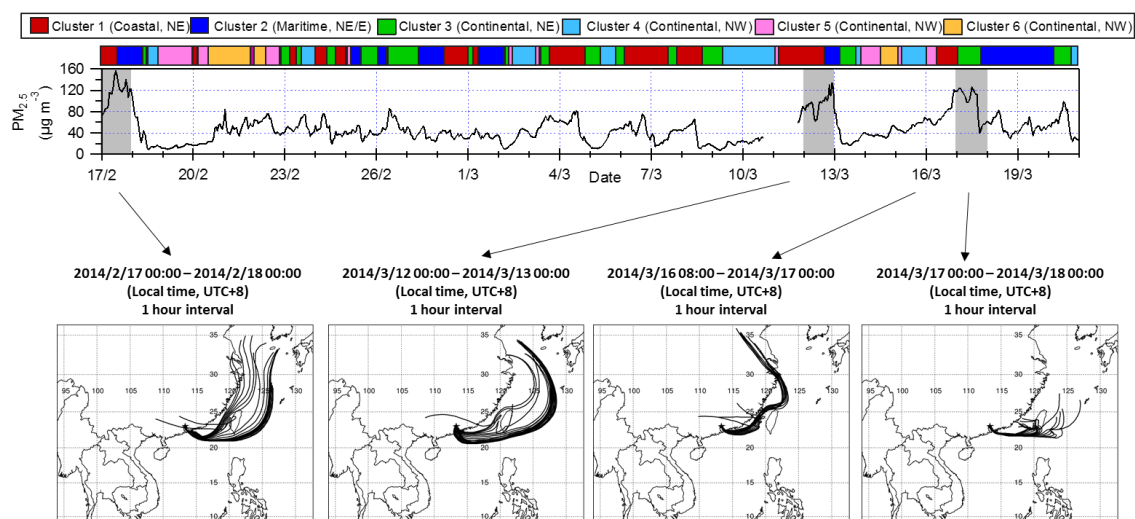
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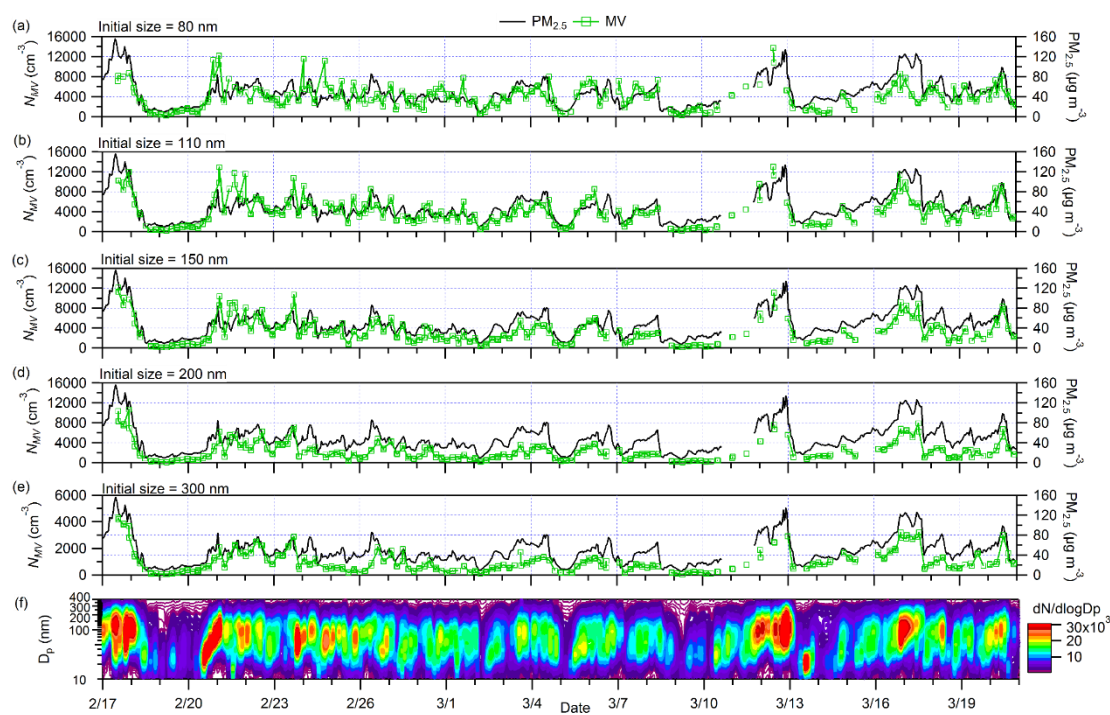
2529

2530 Fig. S2. Transport efficiency of NaCl in the VTDMA as a function of particle diameter and
2531 heating temperature.

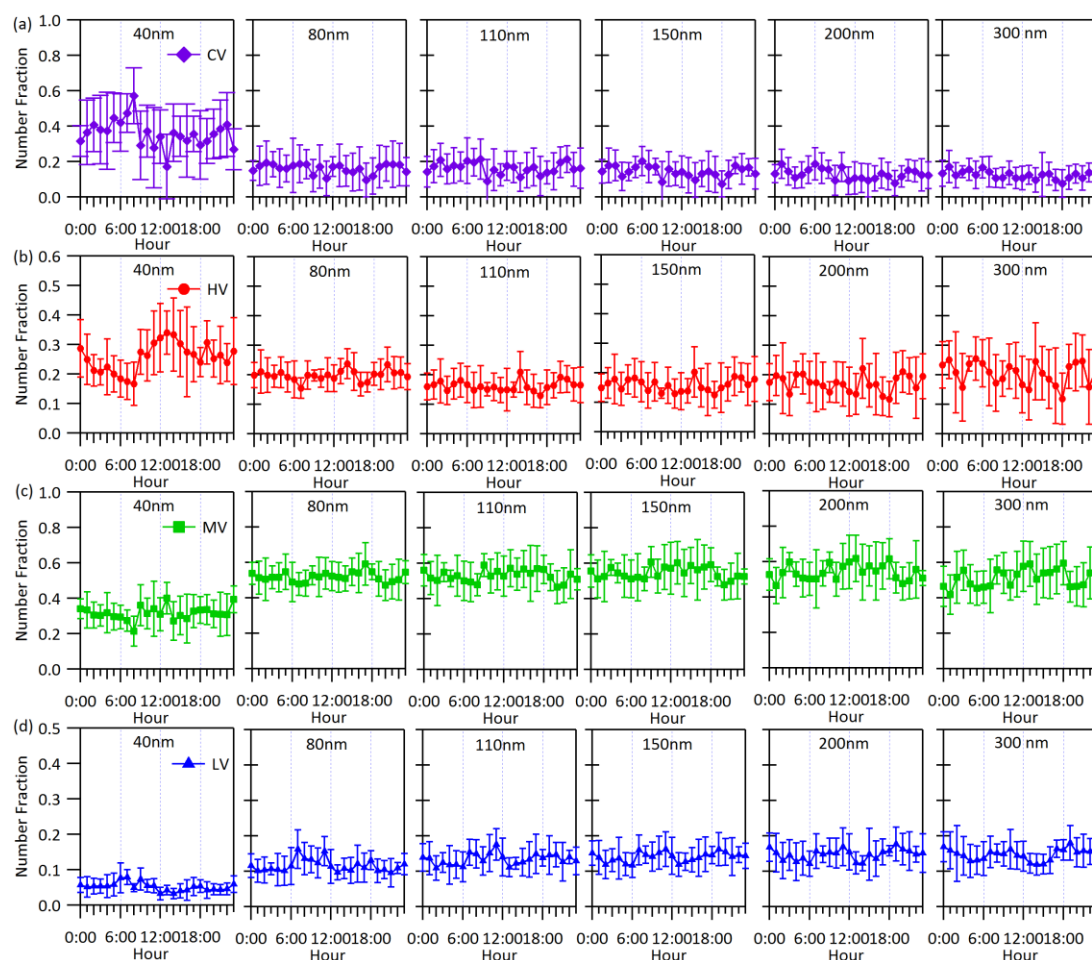
2532



2533
 2534 Fig. S3. Time series of PM_{2.5} concentrations and 72 h back trajectories at hourly intervals on
 2535 Feb 17, and Mar 12, 16 and 17.



2537
 2538 Fig. S4. (a–e) Time series of number concentrations of MV particles having initial diameters of
 2539 80 nm to 300 nm and (f) particle number size distributions during the campaign. Time series of
 2540 PM_{2.5} concentrations are plotted on the right axis in (a) to (e).



2542

2543 Fig. S5. (a–d) Diurnal variations in the number fractions of CV, HV, MV and LV particles having
 2544 (from left to right) the six selected diameters ranging from 40 nm to 300 nm. Error bars
 2545 represent one standard deviation.

2546

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2815 Table 1. Temperature (T) and residence time (RT) protocol of the semi-continuous Sunset
2816 OC/EC analyzer (Wu et al., 2012)

<u>Carbon Fraction</u>	<u>Carrier Gas</u>	<u>T (°C)</u>	<u>RT (s)</u>
<u>OC₁</u>	<u>He</u>	<u>310</u>	<u>80</u>
<u>OC₂</u>		<u>475</u>	<u>60</u>
<u>OC₃</u>		<u>615</u>	<u>60</u>
<u>OC₄</u>		<u>870</u>	<u>90</u>
<u>EC₁</u>	<u>He and 2% O₂</u>	<u>550</u>	<u>45</u>
<u>EC₂</u>		<u>625</u>	<u>45</u>
<u>EC₃</u>		<u>700</u>	<u>45</u>
<u>EC₄</u>		<u>775</u>	<u>45</u>
<u>EC₅</u>		<u>850</u>	<u>45</u>
<u>EC₆</u>		<u>870</u>	<u>45</u>

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Table 2. Summary of average number and volume fractions in VTDMA measurements at 300 °C.

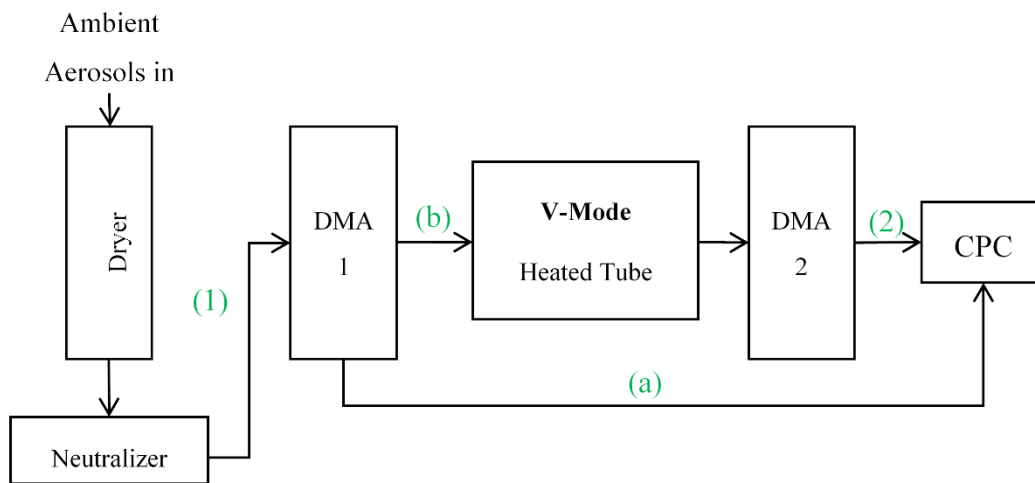
<u>Diameter (nm)</u>	<u>40</u>	<u>80</u>	<u>110</u>	<u>150</u>	<u>200</u>	<u>300</u>
<u>Number fraction</u>						
<u>CV</u>	<u>0.380 ± 0.153</u>	<u>0.174 ± 0.097</u>	<u>0.188 ± 0.081</u>	<u>0.167 ± 0.074</u>	<u>0.153 ± 0.070</u>	<u>0.141 ± 0.065</u>
<u>HV</u>	<u>0.255 ± 0.097</u>	<u>0.198 ± 0.052</u>	<u>0.165 ± 0.055</u>	<u>0.163 ± 0.064</u>	<u>0.178 ± 0.081</u>	<u>0.214 ± 0.097</u>
<u>MV</u>	<u>0.314 ± 0.097</u>	<u>0.513 ± 0.089</u>	<u>0.515 ± 0.098</u>	<u>0.530 ± 0.105</u>	<u>0.523 ± 0.116</u>	<u>0.497 ± 0.125</u>
<u>LV</u>	<u>0.051 ± 0.026</u>	<u>0.113 ± 0.040</u>	<u>0.132 ± 0.041</u>	<u>0.140 ± 0.041</u>	<u>0.146 ± 0.044</u>	<u>0.148 ± 0.047</u>
<u>Volume fraction</u>						
<u>VM</u>	<u>0.503 ± 0.131</u>	<u>0.600 ± 0.082</u>	<u>0.580 ± 0.073</u>	<u>0.590 ± 0.066</u>	<u>0.602 ± 0.064</u>	<u>0.627 ± 0.064</u>
<u>CV</u>	<u>0.361 ± 0.168</u>	<u>0.163 ± 0.105</u>	<u>0.166 ± 0.098</u>	<u>0.148 ± 0.086</u>	<u>0.134 ± 0.080</u>	<u>0.127 ± 0.073</u>
<u>HV</u>	<u>0.014 ± 0.005</u>	<u>0.011 ± 0.003</u>	<u>0.008 ± 0.002</u>	<u>0.007 ± 0.003</u>	<u>0.007 ± 0.003</u>	<u>0.007 ± 0.003</u>
<u>MV</u>	<u>0.070 ± 0.025</u>	<u>0.112 ± 0.024</u>	<u>0.112 ± 0.025</u>	<u>0.115 ± 0.026</u>	<u>0.109 ± 0.027</u>	<u>0.091 ± 0.025</u>
<u>LV</u>	<u>0.052 ± 0.026</u>	<u>0.114 ± 0.040</u>	<u>0.134 ± 0.044</u>	<u>0.140 ± 0.042</u>	<u>0.148 ± 0.048</u>	<u>0.148 ± 0.047</u>

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2821 Table 3. Summary of concentrations of PM_{2.5}, OC, EC and the ratio of OC to EC (OC/EC) in
 2822 the five clusters.

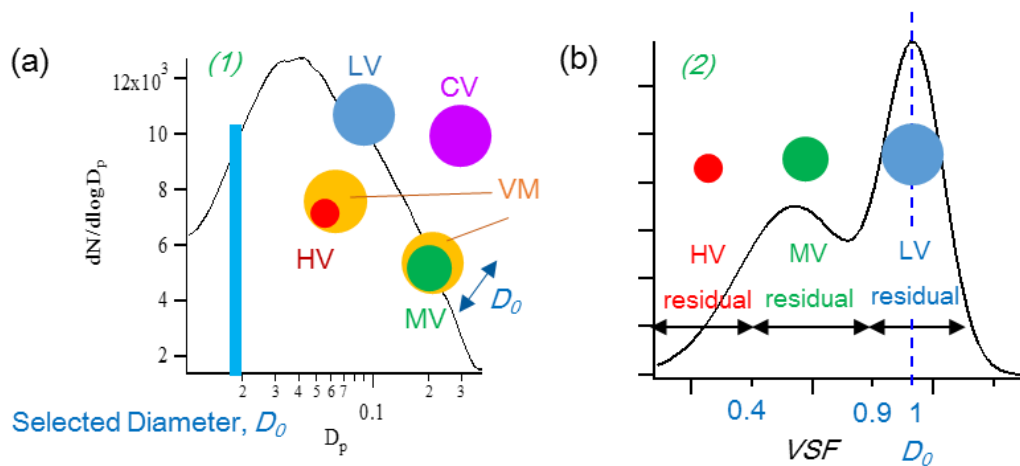
	<u>Cluster</u>				
	<u>Coastal</u>	<u>Maritime</u>		<u>Continental</u>	
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
<u>Origin (to the site)</u>	<u>NE</u>	<u>NE/E</u>	<u>NE</u>	<u>NW</u>	<u>NW</u>
<u>PM_{2.5} (µg m⁻³)</u>	<u>58.5 ± 24.4</u>	<u>58.9 ± 30.9</u>	<u>47.5 ± 28.4</u>	<u>33.9 ± 15.9</u>	<u>33.8 ± 19.3</u>
<u>OC (µg m⁻³)</u>	<u>10.8 ± 6.01</u>	<u>10.84 ± 7.22</u>	<u>10.13 ± 6.89</u>	<u>5.51 ± 3.3</u>	<u>7.32 ± 2.75</u>
<u>EC (µg m⁻³)</u>	<u>4.38 ± 2.97</u>	<u>4.98 ± 4.21</u>	<u>3.43 ± 3.12</u>	<u>1.8 ± 0.98</u>	<u>2.46 ± 0.59</u>
<u>OC/EC</u>	<u>2.83 ± 1.05</u>	<u>2.62 ± 1.03</u>	<u>3.65 ± 1.6</u>	<u>3.18 ± 1.26</u>	<u>2.94 ± 0.73</u>

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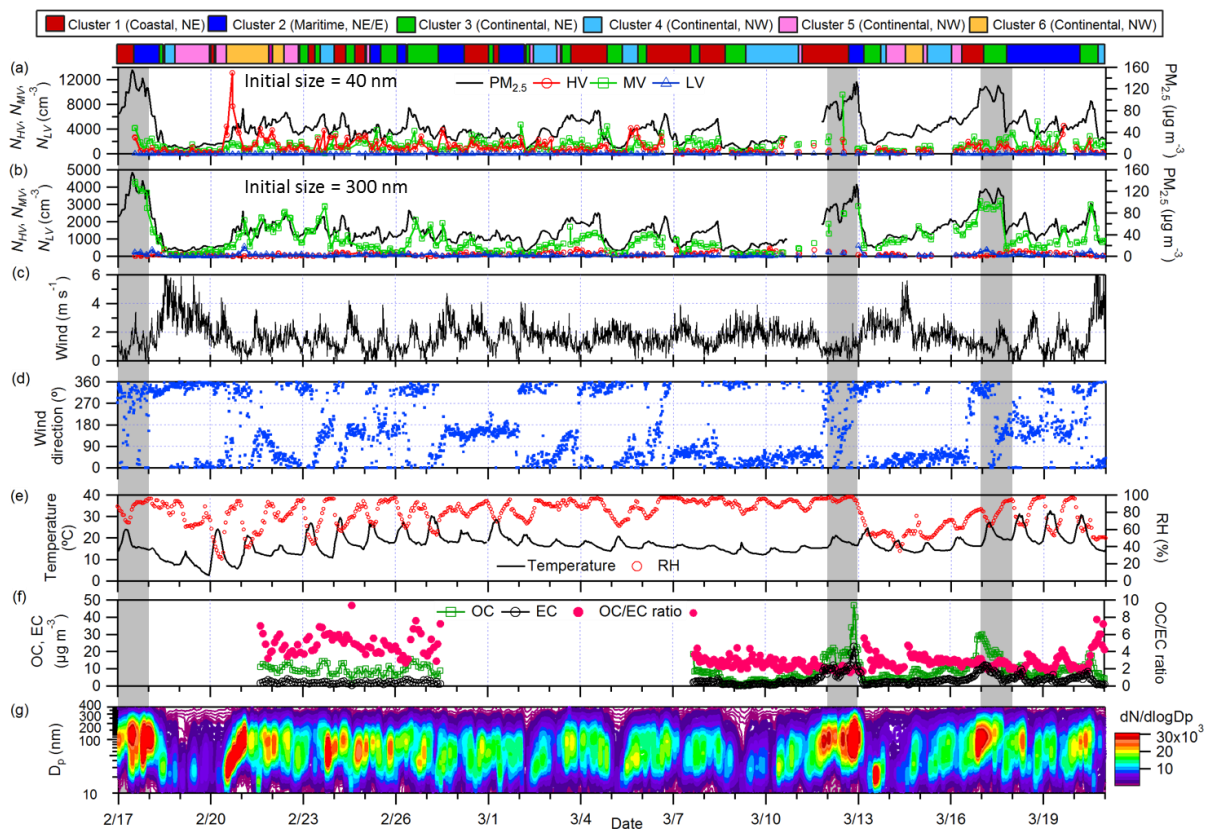
Fig. 1. Schematic diagram of the volatility tandem differential mobility analyzer (VTDMA).



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2829 Fig. 2. Examples of particle size distributions of ~~(left)-(a)~~ ambient aerosols before entering
 2830 DMA₁ and ~~(right)(b)~~ residuals of the size-selected particles (D_0) after heating. at 300 °C. The
 2831 distributions in Fig. 2a and 2b~~The left and right distributions~~ correspond to (1) and (2) in Figure
 2832 1 respectively. Residuals are divided into three groups—LV (blue), MV (green) and HV
 2833 (red)—based on their VSF~~volatilities~~. CV (purple) and VM (orange) are vaporized and hence
 2834 not measured as residuals. VM appears as coating for illustration purposes only. It does not
 2835 necessarily reflect the morphology of the particles.

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2837
 2838 Fig. 3. Temporal variation of number concentrations of HV, MV and LV in 40 nm and 300 nm
 2839 particles, PM_{2.5}, major meteorological parameters, OC and EC concentrations, OC-to-EC ratio
 2840 and particle number size distributions in the campaign. Air mass clusters are depicted at the
 2841 top and the shaded areas indicate days with daily-averaged PM_{2.5} concentrations exceeding 95
 2842 µg m⁻³.

2843
 2844 Figure 3. Average number fractions of CV (purple), HV (red), MV (green) and LV (blue)
 2845 particles of six selected particle dry diameters (40 nm, 80 nm, 110 nm, 150 nm, 200 nm and
 2846 300 nm) in Feb and Mar 2014.

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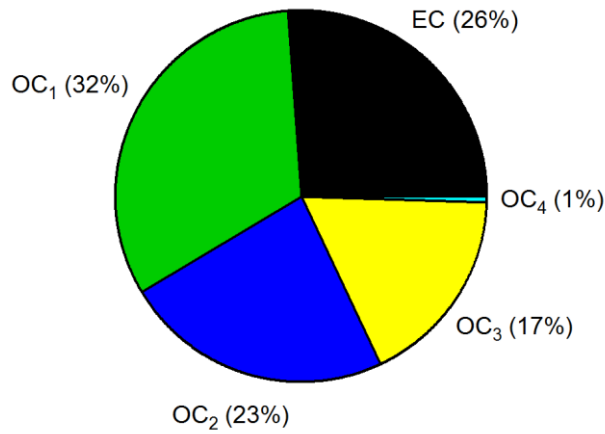
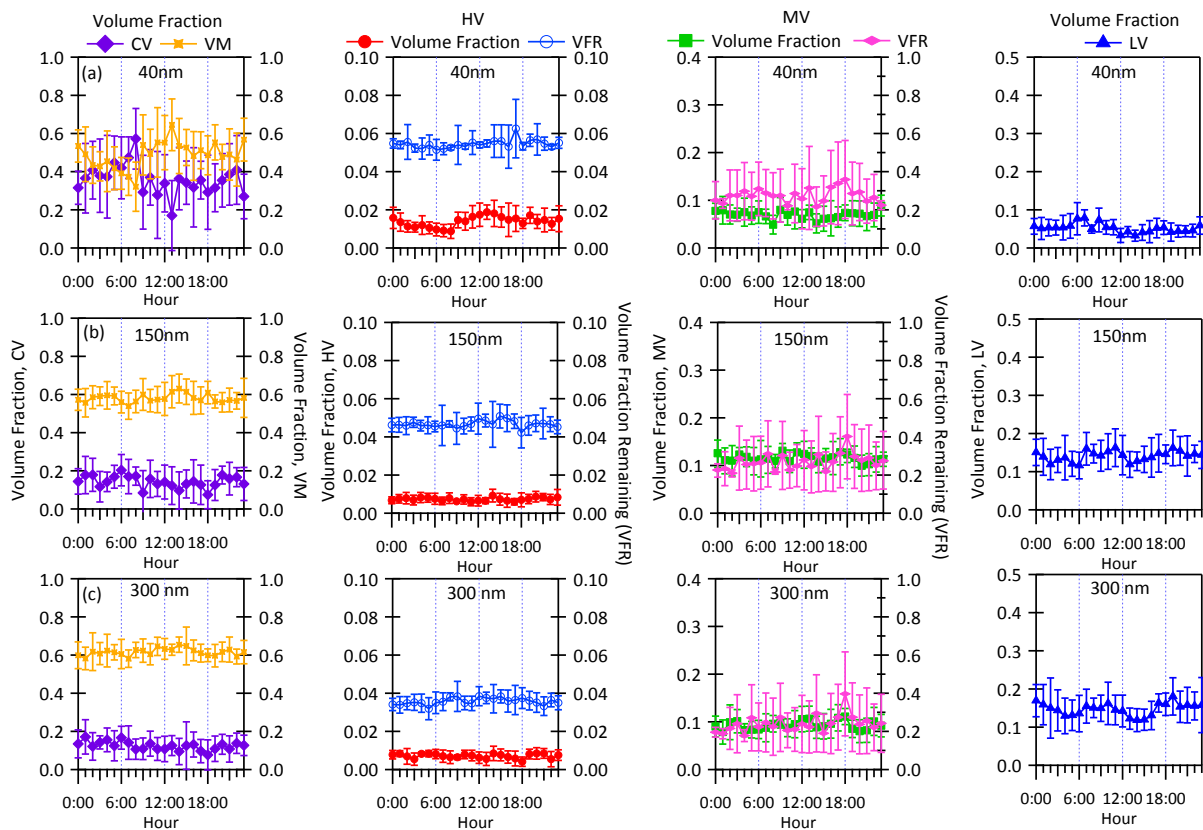


Fig. 4. Average mass fractions of EC, OC₁, OC₂, OC₃ and OC₄ in PM_{2.5}.

~~Figure 4. Time series of number concentrations of (a) 40 nm and (b) 300 nm HV (circle (red)), MV (square (green)), and LV (triangle (blue)) particles; number fractions of (c) 40 nm and (d) 300 nm CV (purple), HV (red), MV (green) and LV (blue) particles during the measurement period from 17 Feb to 20 Mar 2014. Time series of mass concentrations of PM_{2.5} (solid line (black)) are plotted on the right axis of each plot.~~



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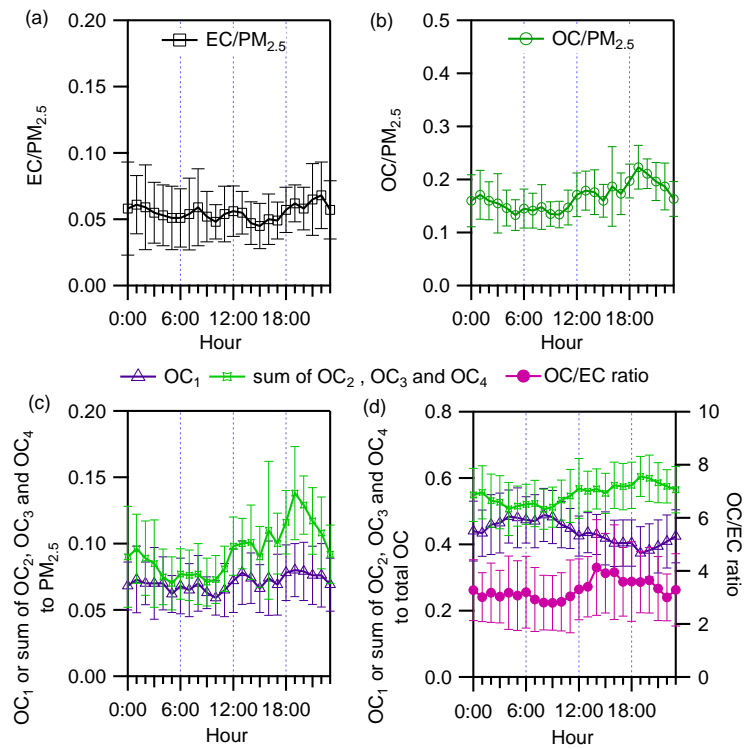
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Fig. 5. Diurnal variations in volume fractions of (columns from left to right) CV, VM, HV residuals, MV residuals and LV residuals in (a) 40 nm, (b) 150 nm and (c) 300 nm particles. Diurnal variations in the volume fraction remaining (VFR) of HV and MV particles are plotted on the right axis. Error bars represent one standard deviation.

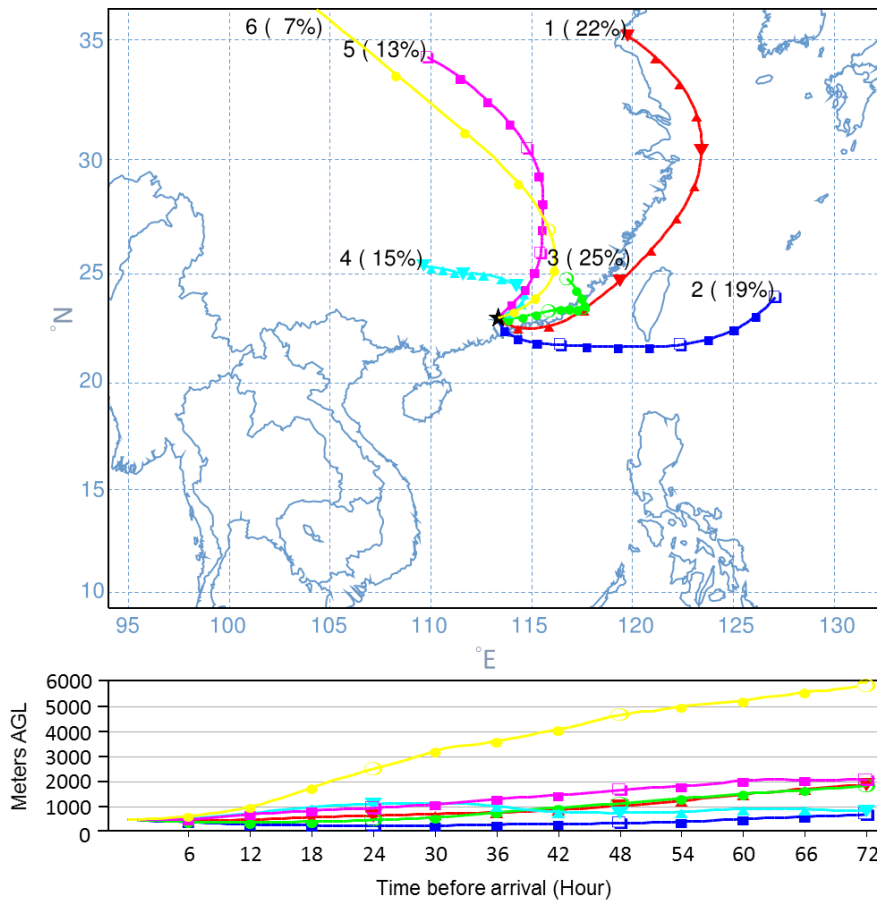
Figure 5. Diurnal variation in number fractions of CV (diamond (purple)), HV (circle (red)), MV (square (green)) and LV (triangle (blue)) particles that are 40 nm, 80 nm, 110 nm, 150 nm, 200 nm and 300 nm in dry size.



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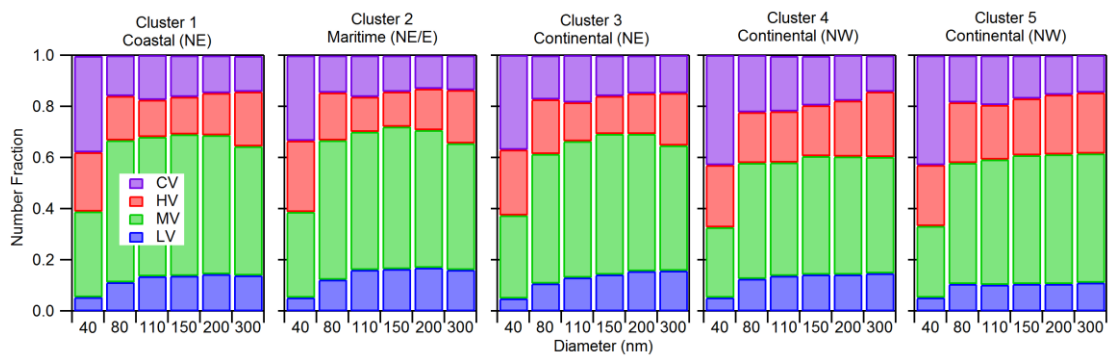
Fig. 6. Diurnal variations in the mass fractions of EC, OC, OC₁ and the sum of OC₂, OC₃ and OC₄ in PM_{2.5}, the ratio of OC to EC, mass fractions of OC₁ and the sum of OC₂, OC₃ and OC₄ to total OC in February and March. Error bars represent one standard deviation.

~~Figure 6. Overall average volume fractions of VM (orange), CV (purple), HV (red), MV (green), and LV (blue) particles as a function of particle diameter.~~



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2876 Fig. 7. Mean back trajectories of the six types of air masses arriving at the sampling site.

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2878 Figure 7. Diurnal variation in (left axis) $\Phi_{V,VM}$ (cross (orange)), $\Phi_{V,CV}$ (diamond (purple)),
2879 $\Phi_{V,HV}$ (circle (red)), $\Phi_{V,MV}$ (square (green)), $\Phi_{V,LV}$ (triangle (blue)), (right axis) $\Theta_{V,HV}$ (solid line
2880 (red)) and $\Theta_{V,MV}$ (dashed line (green)) particles that are 40 nm, 80 nm, 110 nm, 150 nm, 200
2881 nm and 300 nm in dry size.



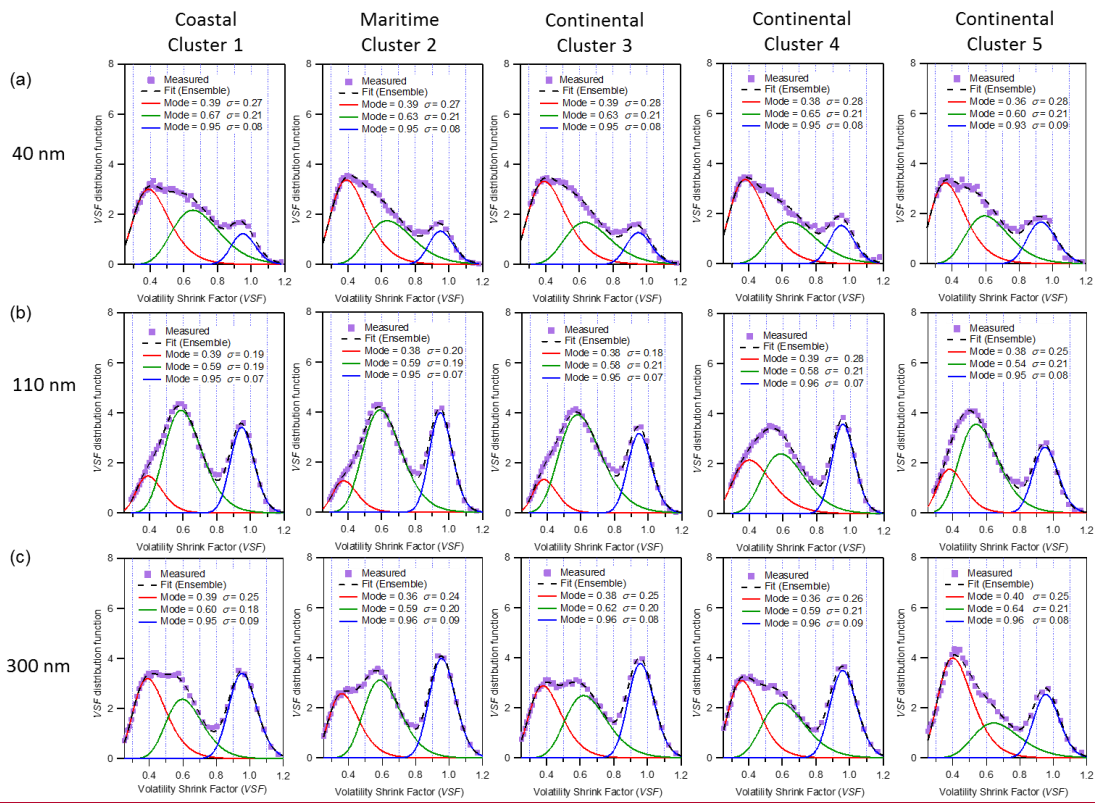
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Fig. 8. Average number fractions of CV, HV, MV and LV in clusters 1 to 5 at different selected diameters.



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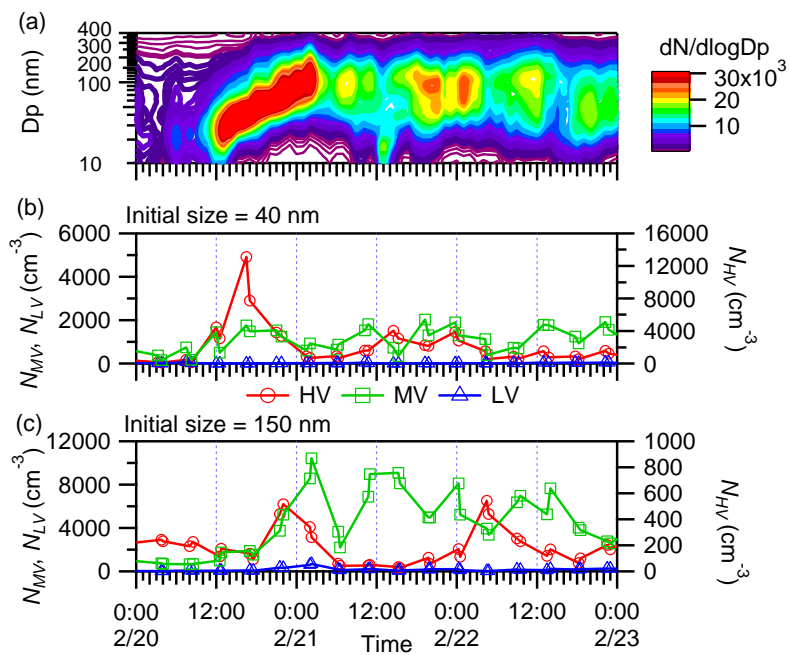
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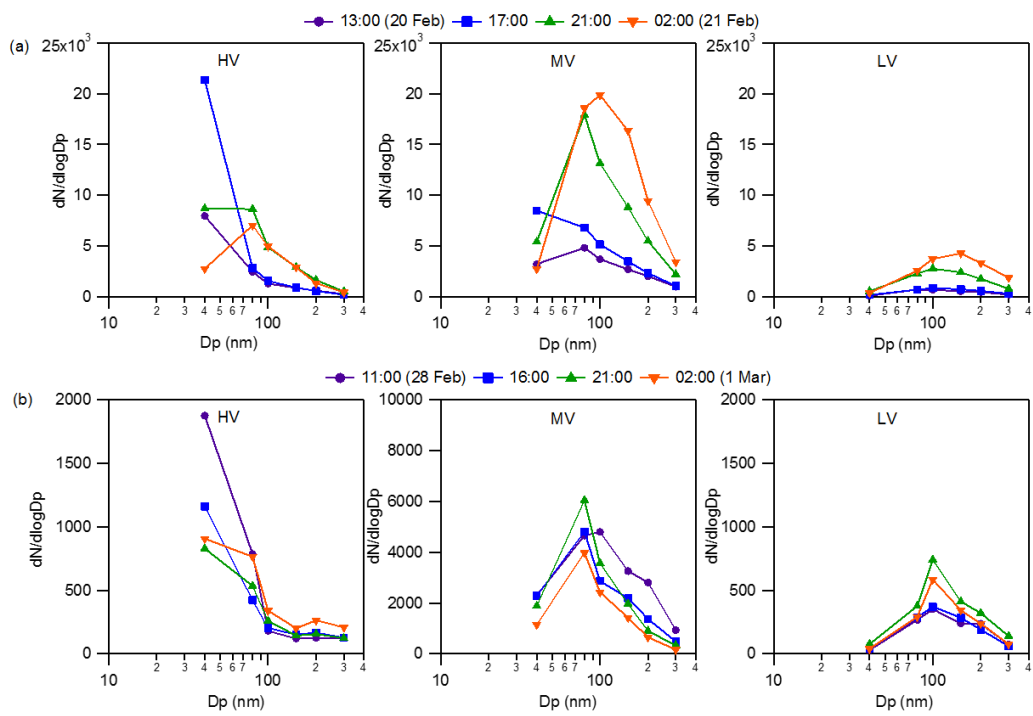
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Fig. 9. Volatility shrinkage factor (VSF) distribution function in different clusters. Solid and dotted lines are the peaks fitted with log-normal function and the ensemble distributions, respectively.



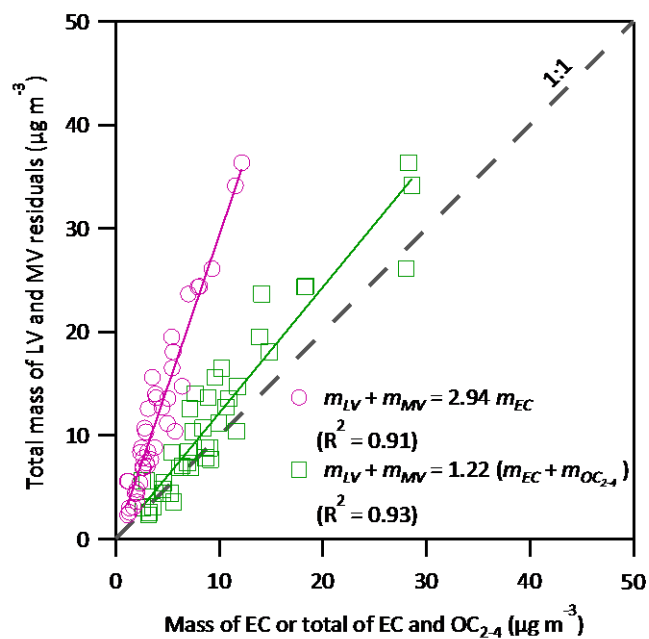
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Fig. 10. Time series of (a) particle number size distribution, (b) number concentrations of HV, MV and LV in 40 nm particles and (c) number concentrations of HV, MV and LV in 150 nm particles.



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 2898 Fig. 11. Particle number size distribution of (columns from left to right) HV, MV and LV
 2899 particles (a) at 13:00, 17:00, 21:00 on 20 Feb and 02:00 on 21 Feb and (b) at 11:00, 16:00,
 2900 21:00 on 28 Feb and 02:00 on 1 Mar.

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Fig. 812. Closure analysis of the total mass of LV and MV residuals (LV+MV) from VTDMA at 300 °C and measured mass of EC or total of EC and OC₂₋₄ from the OC/EC analyzer.