Impact of particle number and mass size distributions of major chemical components on particle mass scattering efficiency in urban Guangzhou of South China

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1 Abstract. To grasp the key factors affecting particle mass scattering efficiency (MSE), particle mass and number size distribution, PM_{2.5} and PM₁₀ and their major 2 3 chemical compositions, and particle scattering coefficient (b_{sp}) under dry condition were measured at an urban site in Guangzhou, south China during 2015-2016. On 4 annual average, 10±2%, 48±7% and 42±8% of PM₁₀ mass were in the condensation, 5 droplet and coarse modes, respectively, with mass mean aerodynamic diameters 6 7 (MMADs) of 0.78 ± 0.07 in the droplet mode and 4.57 ± 0.42 µm in the coarse mode. The identified chemical species mass concentrations can explain $79\pm3\%$, $82\pm6\%$ and $57\pm6\%$ 8 of the total particle mass in the condensation, droplet and coarse mode, respectively. 9 10 Organic matter (OM) and elemental carbon (EC) in the condensation mode, OM, 11 (NH₄)₂SO₄, NH₄NO₃ and crustal element oxides in the droplet mode, and crustal 12 element oxides, OM and CaSO₄ in the coarse mode were the dominant chemical species in their respective modes. The measured b_{sp} can be reconstructed to the level of 91±10% 13 using Mie theory with input of the estimated chemically-resolved number 14 15 concentrations of NaCl, NaNO3, Na2SO4, NH4NO3, (NH4)2SO4, K2SO4, CaSO4, Ca(NO₃)₂, OM, EC, crustal element oxides and unidentified fraction. MSEs of particle 16 17 and individual chemical species were underestimated by less than 13 % in any season based on the estimated b_{sp} and chemical species mass concentrations. Seasonal average 18 MSEs varied in the range of 3.5 ± 0.1 to 3.9 ± 0.2 m² g⁻¹ for fine particles (aerodynamic 19 diameter smaller than 2.1 µm), which was mainly caused by seasonal variations of the 20 mass fractions and MSEs of the dominant chemical species (OM, NH4NO3, 21 (NH₄)₂SO₄) in the droplet mode. MSEs of the dominant chemical species were 22 23 determined by their log-normal size distribution parameters including MMADs and 24 standard deviation (σ) in the droplet mode.

Keywords: particle size distribution, particle chemical composition, particle mass
 scattering efficiency

27 **1. Introduction**

Light extinct coefficient (bext) of atmospheric particles, which is the sum of their 28 29 scattering (b_{sp}) and absorption (b_{ap}) coefficients, is a key index of haze weather (Hand and Malm, 2007). In most cases, b_{sp} accounted for more than 90% of b_{ext} (Takemura et 30 31 al., 2002; Tao et al., 2017a). Numerous studies have demonstrated that haze is mainly caused by high concentrations of fine particles (PM_{2.5}, with aerodynamic diameter 32 smaller than 2.5 µm) (Hand and Malm, 2007; Huang et al., 2012; Malm et al., 1994; 33 34 Malm et al., 2000; Malm et al., 2003; Malm and Hand, 2007; Sisler and Latimer, 1993; 35 Sisler et al., 1996; Sisler and Malm, 2000; Wang et al., 2014; Zhao et al., 2013). Knowledge of the dominant chemical species in PM_{2.5} (e.g. (NH₄)₂SO₄, NH₄NO₃ and 36 OM) and their contributions to b_{sp} is crucial in making feasible policies for alleviating 37 38 haze (Watson, 2002).

Generally, b_{sp} can be estimated in reasonable accuracy using Mie theory when size 39 distributions of the dominant chemical species are known (Cheng et al., 2008; Cheng 40 41 et al., 2009; Gao et al., 2015; Malm et al., 2003; Watson et al., 2008). However, 42 routinely monitoring of the size distributions of all the dominant chemical components 43 is impractical. To evaluate haze in the national parks in U.S.A. under the Regional Haze Rule, the original and revised empirical formulas from the Interagency Monitoring of 44 Protected Visual Environments (IMPROVE) network were developed for 45 reconstructing b_{sp} based on the chemical species in PM_{2.5} and coarse particle mass 46 concentrations monitored in the IMPROVE network (Pitchford et al., 2007; Watson, 47 2002). MSEs of the chemical species are important parameters not only for building the 48

49	relationships between chemical species and b _{sp} (Hand and Malm, 2007), but also for
50	relating particle mass to its optical properties (Lin et al., 2015; Titos et al., 2012). The
51	recommended MSEs of (NH ₄) ₂ SO ₄ , NH ₄ NO ₃ , OM and fine soil (estimated from
52	crustal elements) in PM _{2.5} were 3.0, 3.0, 4.0 and $1.0 \text{ m}^2 \text{ g}^{-1}$, respectively, in the original
53	IMPROVE formula based on the assumed size distributions. However, MSE of any
54	particle species vary with its mass concentration and size distribution (Lowenthal and
55	Kumar, 2004; Malm et al., 2003; Malm and Hand, 2007; Malm and Pitchford, 1997).
56	Subsequently, MSEs and mass concentrations of (NH4)2SO4, NH4NO3 and OM in
57	PM _{2.5} were separated into small and large modes in the revised IMPROVE formula
58	(Hand and Malm, 2007).

59 China has been suffering from severe PM_{2.5} pollution and haze weather (Li et al., 60 2016; Ming et al., 2017; Wang et al., 2017; Zhang et al., 2013). To investigate the formation of haze, the original and revised IMPROVE formulas have been directly 61 applied in many cities in China (Hua et al., 2015; Shen et al., 2014; Tao et al., 2009; 62 Zhang et al., 2012a; Zou et al., 2018). The IMPROVE formulas have been proved to 63 over- or underestimate b_{sp} in urban cities in China (Cao et al., 2012; Cheng et al., 2015; 64 Han et al., 2014; Jung et al., 2009a; Jung et al., 2009b; Tao et al., 2012; Tao et al., 2014), 65 which were likely due to the significantly different size distributions of the major 66 chemical components and related mass fractions in PM2.5 between different countries 67 or even cities (Bian et al., 2014; Cabada et al., 2004; Chen et al., 2017; Guo et al., 2009; 68 Lan et al., 2011; Tian et al., 2014; Yao et al., 2003; Yu et al., 2010; Zhang et al., 2008; 69 Zhuang et al., 1999b). To reduce the uncertainties in the estimated b_{sp} using the original 70

and revised IMPROVE formulas, the average MSEs of the dominant chemical species were typically estimated by the multiple linear regression method (Hand and Malm, 2007). Although the estimated b_{sp} by the multiple linear regression model may be close to the measured b_{sp} , the rationality of the estimated MSEs of chemical species were unknown.

Variations in size distributions of the chemical components (e.g., MMADs and 76 mass fractions) are important factors for hindering the application of the IMPROVE 77 formulas and multiple linear regression models. Although many studies have focused 78 79 on size distributions and chemical compositions of fine particles in China, few studies have explored the relationship between the size distribution of major chemical species 80 81 and their MSEs (Cheng et al., 2008; Cheng et al., 2009; Gao et al., 2015). To fill this 82 knowledge gap, size-segregated particle mass, PM₁₀, PM_{2.5} and their major chemical components, and inline data including size distribution of particle number, b_{sp} under 83 dry condition and water-soluble inorganic ions were synchronously measured at an 84 85 urban site in Guangzhou covering four seasons in 2015-2016. Size distributions of 86 dominant chemical components were first characterized in section 3.1, followed by discussions on the closures of particle mass and number concentration and b_{sp} in 3.2. 87 Key factors controlling the variations of chemical species and their MSEs were then 88 discussed in section 3.3. Knowledge gained from the present study will improve the 89 assessments of air-quality and climate impact caused by atmospheric particles, 90 91 especially in urban areas.

92 **2. Methodology**

93 2.1 Site description

The observational site in urban Guangzhou is situated inside the South China Institute of Environmental Science (SCIES) (23°07′N, 113°21′E) (Fig. 1) with no obvious surrounding industrial activities. The instruments used in this study were installed on the roof of a building 50 m above ground (Tao et al., 2018). The working conditions of all the instruments were controlled under 26 degree in temperature and 40% in relative humidity (RH) by three air conditioners.

Insert Figure 1

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103 **2.2 Field sampling**

Size-segregated particle samples were collected using Anderson 8-stage air 104 samplers with the cut-off points of 0.43, 0.65, 1.1, 2.1, 3.3, 4.7, 5.8 and 9.0 µm 105 (Thermo-electronic Company, USA). Two sets of samplers were used alternatively due 106 to the need of daily clearance of the instruments. The samplers were operated at an 107 airflow rate of 28.3 L min⁻¹. The sampling flow rate was controlled by a flow meter 108 109 (Aalborg Inc., USA). Samples were collected on 81 mm quartz fiber filter (Whatman QM-A). Samples were collected during different seasons: 15 July- 6 August, 2015 110 (representative of summer), 15 October- 5 November, 2015 (autumn), 4-20 January, 111 2016 and 19-22 February, 2016 (winter), and 8-20 April, 2016 and 4-14 May, 2016 112 (spring). Sampling duration was 48 h in spring and 24 h in the other seasons, all starting 113 at 10:00 local time. 114

Bulk PM_{2.5} and PM₁₀ samples were collected using two Gravisol Sequential
Ambient Particulate Monitor (GSAPM) samplers (APM Inc., Korea) at a flow rate of

117 16.7 L min⁻¹. Samples were collected on 47 mm quartz fiber filter (Whatman QM-A). Sampling durations were the same as those for collecting size-segregated samples in 118 every season. The sampling information is summarized in Table 1. Moreover, 8 sets of 119 blank samples were also collected for each of the size-segregated particle, PM_{2.5} and 120 121 PM₁₀ samples during the whole sampling period. Two sets of blank filters in each category were put in the samplers without flow for 24 h when seasonal field campaigns 122 123 finished. The aerosol-loaded filter samples were stored in a freezer at -18 °C before analysis to prevent volatilization of particles. 124

- 125
- 126

Insert Table 1

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The blank water-soluble inorganic ions (WSII) (e.g. Na⁺, Ca²⁺) of quartz fiber filter were slightly high in general. Thus, 47mm and 81mm quartz fiber filters were first baked at 500 °C for 3 h to remove adsorbed organic vapors; they were then soaked in distilled-deionized water for 3 h for several times to remove WSII until the background values were less than 0.01 mg L⁻¹. Finally, the quartz fiber filters were dried through baking at 200 °C. All blank quartz fiber filters were stored in desiccators.

Particle number concentration for particles in the range of 14 nm - 615 nm in 134 mobility diameter (D_p) was measured using a scanning mobility particle sizer (SMPS; 135 136 TSI Model 3936, TSI, Inc., St. Paul, MN) combined with a long differential mobility analyzer (DMA; TSI Model 3080) and a condensation particle counter (CPC; TSI 137 Model 3010), and for particles in the range of 542 nm - 10 µm aerodynamic diameter 138 139 (D_a) using an Aerodynamics Particle Sizer (APS; TSI Model 3321), both at 5 min resolution. APS was calibrated using 5 sizes solid spheres (polystyrene latex 140 141 monodisperse). Dry b_{sp} was measured using a single wavelength integrating nephelometer (Ecotech Pty Ltd, Australia, Model Aurora1000G) at the wavelength of
520 nm at 5 min resolution. Zero calibration was performed every day with zero air,
and span check was done every 3 days using HFC-R134a gas.

To exclude the impact of particle hygroscopic growth on the measured size 145 distribution and b_{sp}, ambient air is forced to pass through three total suspended 146 particulate (TSP) cyclones, then stainless steel tubes and the Nafion driers prior to be 147 148 sampled by the SMPS, APS and nephelometer. According to the method described in Kulkarni et al. (2011), particle losses in different sizes from the tube are plotted in Fig. 149 150 S1. Generally, particle losses in the condensation (0.1-0.4 μ m), droplet (0.4-2.1 μ m) and coarse modes (2.1-10 µm) were less than 1.3%, 0.3% and 0.1%, respectively, 151 suggesting that the particle losses from the tube were minimal. Ambient RH and 152 153 temperature were measured by an automatic meteorological station (Vaisala Company, 154 Helsinki, Finland, model MAWS201) at the SCIES site, and the seasonal average of these two meteorological parameters were 53-75 % and 15-29 °C, respectively. RH of 155 156 aerosol samples was controlled to be lower than 30% by sweeping dry air from a compressed air pump. NO3⁻ was measured using an In-situ instrument of Gas and 157 Aerosol Composition (IGAC, Model S-611, Machine Shop, Fortelice International Co., 158 Ltd., Taiwan, China) at a resolution of 1-h (Tao et al., 2018). 159

160 **2.3 Lab chemical analysis and data quality assurance and control**

47 mm and 81 mm quartz fiber filters were measured gravimetrically for particle mass concentration using a Sartorius ME 5-F electronic microbalance with a sensitivity of $\pm 1 \ \mu g$ (Sartorius, Göttingen, Germany) after 24 h equilibration at temperature of 23 $\pm 1 \ ^{\circ}$ C and RH of 40 $\pm 5\%$. Microbalance was calibrated by 5 mg, 200 mg and 5000 mg weights before weighting. Each filter was weighed at least three times before and after sampling. Differences among replicate weights were mostly less than 20 μg for 167 each sample. Net mass was obtained by subtracting pre-weight from post-weight.

Three pieces of 0.526 cm^2 punches from each 47 mm quartz filter samples and 168 169 one-fourth of each 81 mm quartz filter samples were used to determine water-soluble inorganic ions. The extraction of water-soluble species from each filter was put into a 170 separate 4 mL bottle, followed by 4 mL distilled-deionized water (with a resistivity 171 172 of >18 M Ω), and then subjected to ultrasonic agitation for 1 h for complete extraction of the ionic compounds. The extract solutions were filtered (0.25 µm, PTFE, Whatman, 173 USA) and stored at 4 °C in pre-cleaned tubes until analysis. Cation (Na⁺, NH₄⁺, K⁺, 174 Mg²⁺ and Ca²⁺) concentrations were determined by ion chromatography (Dionex ICS-175 1600) using a CS12A column with 20 mM Methanesulfonic Acid eluent. Anions (SO4²⁻ 176 , NO₃⁻, Cl⁻, and F⁻) were separated on an AS19 column in ion chromatography (Dionex 177 ICS-2100), using 20 mM KOH as the eluent. A calibration was performed for each 178 analytical sequence. Procedural blank values were subtracted from sample 179 concentrations. Method detection limits (MDL) of ions were within the range of 0.001 180 to $0.002 \text{ mg } \text{L}^{-1}$. 181

OC and EC were analyzed using a DRI model 2001 carbon analyzer (Atmoslytic, Inc., Calabasas, CA, USA). An area of 0.526 cm² punched from each 47mm quartz filter and 1-4 dots punched from each 81mm quartz filter were analyzed for four OC fractions (OC1, OC2, OC3, and OC4 at 140 °C, 280 °C, 480 °C, and 580 °C, respectively, in a helium [He] atmosphere); OP (a pyrolyzed carbon fraction determined when transmitted laser light attained its original intensity after oxygen [O₂] was added to the analyzed atmosphere); and three EC fractions (EC1, EC2, and EC3 at 580 °C,

740 °C, and 840 °C, respectively, in a 2% O₂/98% He atmosphere). Here, OC is 189 operationally defined as OC1 + OC2 + OC3 + OC4 + OP and EC is defined as EC1 + 190 191 EC2 + EC3 – OP for 47mm samples. However, OC is operationally defined as OC1 + OC2 + OC3 + OC4 and EC is defined as EC1 + EC2 + EC3 for 81mm samples due to 192 193 extremely low OP level. Average field blanks were subtracted from each sample filter. MDLs of OC and EC were $0.41\pm0.2 \ \mu gC \ cm^{-2}$ and $0.03\pm0.2 \ \mu gC \ cm^{-2}$, respectively. 194 To obtain high quality data of the size distributions of major chemical components, 195 bulk PM_{2.5} and PM₁₀ samples were synchronously collected and the same chemical 196 components were analyzed. Generally, good correlations (R^2 >0.90) were found in the 197 198 mass concentrations of the total particle and major chemical components (including total carbon (TC), NO_3^- and SO_4^{2-}) between the size-segregated samples (PM₁₀ and 199 $PM_{2.1}$) and the GSAPM samplers (PM_{10} and $PM_{2.5}$). The regression slopes were in the 200 range of 0.91-1.05, suggesting good and acceptable data quality of the size distributions 201 of the major chemical components (Fig.S2). 202

203 2.4 Data analysis methods

The ISORROPIA II model was run at the reserved mode (Fountoukis and Nenes, 204 2007) with input data of K⁺, Ca²⁺, Mg²⁺, NH₄⁺, Na⁺, SO₄²⁻, NO₃⁻, Cl⁻, RH (40%), and 205 206 temperature (25°C), to estimate the size-resolved mass concentrations of NaCl, NaNO₃, Na2SO4, NaHSO4, NH4Cl, NH4NO3, (NH4)2SO4, NH4HSO4, K2SO4, KHSO4, KNO3, 207 KCl, MgSO₄, Mg(NO₃)₂, MgCl₂, CaSO₄, Ca(NO₃)₂, CaCl₂ and H₂O. Several of these 208 chemical species had extremely low mass concentrations and were thus excluded from 209 the calculation of b_{sp}. Generally, only NaCl, NaNO₃, Na₂SO₄, NH₄NO₃, (NH₄)₂SO₄, 210 K₂SO₄, Ca(NO₃)₂, CaSO₄ and H₂O were used to estimate b_{sp} in this study. 211 212 In this work, the cut-off point of 2.1 µm was chosen to separate the fine and coarse

213 mode particles for investigating the impact of aerosol size distribution on their

respective MSEs. Moreover, the cut-off sizes of $<0.43 \ \mu m$ and $0.43 - 2.1 \ \mu m$ were used to separate the condensation mode and droplet mode, respectively. Particle MSE was estimated by the sum of b_{sp} from individual chemical species divided by sum of particle mass concentration according to:

218
$$MSE = \frac{\int_{0}^{D_{i,j}^{max}} b_{sp} \, dD_{i,j}}{\int_{0}^{D_{i,j}^{max}} c \, dD_{i,j}}$$

219 (1)

220 Where i is chemical species, j is chemical species size, D_{i,j} is the chemical species 221 diameter, and C is chemical species mass concentration.

b_{sp} was estimated by the Mie model as follows:

223
$$b_{sp} = \int_0^{D_{i,j}^{max}} \frac{\pi}{4} D_{i,j}^2 Q_{sp}(m_{i,j}, D_{i,j}, \lambda) N_{i,j} dD_{ij}$$
(2)

224 Where Q_{sp} is single-particle scattering efficiency of chemical species (Fig. S3), 225 m_{i,j} is refractive index of chemical species (Table S1), λ is 550 nm, and N_{i,j} is number 226 concentration of chemical species calculated by the formula (3).

$$N = \frac{6C}{\pi\rho D^3}$$
(3)

228 Where N is chemical species number concentration, C is chemical species mass 229 concentrations, ρ is density of chemical species (Table S1), and D is geometric diameter 230 (D_g) of chemical species.

The particle number concentration in aerodynamic diameter (D_a) was converted to the particle number concentration in D_g (similar to D_p) according to:

233
$$D_{a}=D_{g}/(\rho)^{0.5}$$
234 (4)
235
$$\rho = \frac{\sum_{chemical \ species} m_{i}}{\sum_{chemical \ species} \frac{m_{i}}{\rho_{i}}}$$
(5)

236 Where ρ represents the daily average density of particle, i is chemical species, m_i

is chemical species mass concentration in a bin, and ρ_i is chemical species density. The seasonal average densities of particle are shown in Fig. S4.

239 Continuous size-distribution profiles of major chemical species are needed in order to accurately calculate b_{sp} using Mie theory. To improve the resolution of b_{sp}, 401 240 bins were used for chemical species ranging from 10 nm to 100 µm, with a constant 241 ratio between the adjacent size bins, defined as $log_{10}(D_{a2}/D_{a1})=0.01$. Further increasing 242 243 the number of size bins does not have any significant impact on the results, e.g., the changes in b_{sp} are smaller than 1% even if the above ratio of 0.01 is replaced with 0.001. 244 245 Continuous size-distribution profiles of major chemical species are obtained from the inversion of the measured mass concentration distribution in the size bins of the 246 Anderson 8-stage air samplers, using the technique described in Dong et al. (2004). The 247 key formulas to calculate the normal distribution of density function (f (D, μ , σ)) were 248 summarized as follows: 249

250
$$f(D,\mu,\sigma) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\left(\frac{(D-\mu)^2}{2\sigma^2}\right)}$$
(6)

$$\mu = \bar{y} - \mu \bar{x} \tag{7}$$

252
$$\sigma = \frac{n \sum xy - \sum x \times \sum y}{n \sum x^2 - (\sum x)^2}$$
(8)

Where D is log (D_a), and μ and σ are the mean and standard deviation, respectively, of the log (D_a) in the different modes. x is the inverse function value of the cumulative probability of a standard normal distribution in each bin, y is logarithm of D_a lower limit (e.g. 0.43, 0.65, 1.1, 2.1, 3.3, 4.7, 5.8 and 9.0 μ m) in each bin. An example of the calculation process was demonstrated in supplementary.

However, this approach is not applicable for the condensation mode because there is only one size bin in this mode. To obtain the number concentrations of all the concerned chemical species in the condensation mode, MMADs (= 10^{μ}) of this mode are calculated according to:

262 MMADs =
$$(D_{a1} \times D_{a2})^{0.5}$$

Where D_{a1} and D_{a2} represent the lower (0.10 μm, limits of detection of Anderson
8-stage air sampler) and upper (0.43 μm) boundaries of this size bin, respectively.

265 3. Results and Discussion

3.1 Size distributions of total particle mass and major chemical components

267 **3.1.1 Total particle mass**

268 Generally, any particle size distribution can be fitted into a combination of condensation, droplet and coarse modes (John et al., 1990). Continuous log-normal size 269 270 distributions of particle mass including the condensation, droplet and coarse modes 271 were calculated using the method described in section 2.4 and are summarized in Table 2. On annual average, 10±2%, 48±7% and 42±8% of total mass in the size-segregated 272 273 samples were in the condensation, droplet and coarse modes, respectively, with the 274 average MMADs being 0.78±0.07 µm in the droplet mode and 4.57±0.42 µm in the coarse mode. These values were comparable to those observed by the Micro-Orifice 275 276 Uniform Deposit Impactor (MOUDI) in the other cities (e.g. Shenzhen and Hong Kong) of the Pearl River Delta (PRD) region (Bian et al., 2014; Lan et al., 2011; Yu et al., 277 2010). 278

The estimated annual PM2.5 concentration based on the continuous log-normal 279 size distribution was $36.4\pm13.2 \,\mu g \, m^{-3}$, which was close to the synchronously measured 280 PM_{2.5} (36.8 \pm 15.3 µg m⁻³), although slightly higher than the sum of the mass 281 concentrations $(34.9\pm13.8 \ \mu g \ m^{-3})$ in the condensation and droplet modes. Thus, the 282 fine (sum of condensation and droplet) mode particles can reasonably represent PM_{2.5}. 283 284 Seasonal average particle mass concentrations were evidently lower in summer than in the other seasons for the condensation and droplet modes, and were similar during 285 spring, autumn and winter for all the three modes. These results agree with the seasonal 286

variations of PM_{2.5} observed at the same site in 2009-2010 (Tao et al., 2014). *Insert Table 2* **3.1.2 Water-soluble inorganic ions**

Generally, SO_4^{2-} , NO_3^{-} and NH_4^{+} are the dominant WSIIs, especially in the 292 condensation and droplet modes. They are mainly formed through aqueous-phase 293 reactions in moisture conditions in the PRD region (Lan et al., 2011; Yu et al., 2010). 294 As expected, 77±6% SO4²⁻, 46±16% NO3⁻ and 89±7% of NH4⁺ mass concentrations 295 were in the droplet mode on annual average due to their aqueous-phase formations 296 (Table 2). Much lower fractions for NO_3^- than SO_4^{2-} and NH_4^+ in the droplet mode 297 were mostly due to the high volatility of NH4NO3 (Zhang et al., 2008). The MMADs 298 299 of the three ions in the droplet mode were in the range of 0.70-0.94 µm, comparable with MOUDI measurements (0.78-1.03 µm) conducted in the PRD region (Bian et al., 300 301 2014; Lan et al., 2011; Yu et al., 2010).

Small fractions of SO_4^{2-} , NO_3^{-} and NH_4^+ masses were distributed in the condensation mode, e.g., $12\pm4\%$, $10\pm4\%$ and $6\pm5\%$, respectively, on annual average. The mass fractions of SO_4^{2-} in the condensation mode shown above were much lower than those (24-29%) observed in urban Guangzhou in 2006-2007 (Yu et al., 2010), suggesting gas-phase chemical reactions of SO_2 has become less important in the formation of SO_4^{2-} , likely due to the dramatic reduction of SO_2 emissions in urban or suburban Guangzhou in the recent decade (Zheng et al., 2009; Zheng et al., 2018).

309 $11\pm5\%$ SO₄²⁻, $44\pm18\%$ NO₃⁻ and $5\pm4\%$ of NH₄⁺ mass concentrations were 310 distributed in the coarse mode. In general, NO₃⁻ mainly exists in the form of NH₄NO₃ 311 in the condensation and droplet modes and associates with base cations in the coarse

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312 mode (e.g., Ca(NO₃)₂ and NaNO₃) (Zhang et al., 2015a). More than 50% NO₃⁻ mass concentrations were distributed in the coarse mode in summer and autumn when 313 ambient temperatures were high. The MMADs of NO₃⁻ in the coarse mode were 314 4.15±0.52 and 4.36±0.31 µm in summer and autumn, respectively, slightly lower than 315 those of Ca^{2+} (4.10±0.42 and 4.72±0.47 µm in the same seasons), but evidently higher 316 than those of Na⁺ (3.60 ± 0.19 and 3.64 ± 0.27 µm) (Table 2). This suggests that NH₄NO₃ 317 318 was prone to dissociate to HNO_{3(g)} in summer and autumn due to the high ambient temperatures with released HNO_{3(g)} further reacting with mineral dust and to a less 319 extent with sea salt particles. In comparison, the MMADs of SO₄²⁻ in the coarse mode 320 were in between of those of Ca^{2+} and Na^{+} , likely due to uptake of $H_2SO_{4(g)}$ by both 321 mineral dust and sea salt particles (Zhang et al., 2015a). In contrast, the MMAD of 322 NH_4^+ in the coarse mode was $3.25\pm0.69 \mu m$, much smaller than those of SO_4^{2-} and 323 NO_3^- , suggesting that NH_4^+ in the coarse mode was likely from hygroscopic growth of 324 NH_4^+ in the droplet mode (Tian et al., 2014). 325

326 It is also worth mentioning that most of Cl⁻ was distributed in the coarse mode and its MMAD ($3.77\pm0.35 \mu m$) was very close to that of Na⁺ ($3.75\pm0.38 \mu m$), especially in 327 summer when air masses were originated from the China South Sea (Tao et al., 2017b; 328 Xia et al., 2017). The mole ratios of Cl⁻/Na⁺ were less than 1.0 in all the seasons but 329 spring due to the reactions between sea salt and acid gasses (HNO_{3(g)} and H₂SO_{4(g)}) 330 331 (Zhuang et al., 1999a). The excess Cl⁻ in the coarse mode in spring was likely due to the aged biomass burning particles from the southeast Asian (Zhang et al., 2015c). In 332 fact, the concentration of the typical biomass burning tracer K⁺ in the coarse mode was 333 334 higher in spring than in the other seasons (Fig. S5). In any case, sea salt was mainly distributed in the coarse mode rather than the droplet mode in urban Guangzhou. 335

336 **3.1.3 OC and EC**

OC and EC in fine particles can be produced from both primary emissions of 337 338 vehicle exhaust, coal combustion, biomass burning and secondary formation (Chow et al., 2011; Gentner et al., 2012; Gentner et al., 2017; Hallquist et al., 2009; Zheng et al., 339 2006). In general, fresh OC and EC particles emitted from vehicle exhaust, coal 340 combustion and biomass burning should be distributed in the condensation mode 341 342 (Schwarz et al., 2008; Zhang et al., 2012b). Only 13±4% of OC and 31±7% of EC mass concentrations were distributed in the condensation mode in the present study (Table 343 344 2). OC/EC ratios were in the range of 0.9-1.6 in the condensation mode, suggesting that vehicle exhaust was the dominant source of OC and EC in this particle size range 345 (Huang et al., 2006a; Schwarz et al., 2008; Shiraiwa et al., 2007; Watson et al., 2001; 346 Wu et al., 2017). 62±9% of OC and 55±7% of EC mass concentrations were distributed 347 in the droplet mode (Table 2), similar to that of SO_4^{2-} . These numbers were similar to 348 those observed in the other cities of the PRD region, and was previously identified to 349 350 be mainly caused by in-cloud aerosol processing (Huang et al., 2006b). Cloud processing indeed plays important roles in forming droplet mode aerosols in urban 351 Guangzhou (Tao et al., 2018). OC/EC ratios were in the range of 2.2-3.2 in the droplet 352 mode, much higher than those in the condensation mode, suggesting that OC in the 353 droplet mode was mainly aged or secondary particles (Day et al., 2015; Huang et al., 354 355 2006a; Wu and Yu, 2016).

The MMADs of OC and EC in the droplet mode were $0.76\pm0.07 \ \mu m$ and 0.66±0.08 μm , respectively, which were slightly lower than those (0.7-1.0 μm for OC and 0.8-1.0 μm for EC) found in earlier studies in the PRD region (e.g. Guangzhou, Hong Kong and Shenzhen) (Lan et al., 2011; Yu et al., 2010). Noticeably, the MMADs of OC and EC in the droplet mode were very close to those (0.73 μm for OC and 0.77

16

 μ m for EC) measured in summer at a suburban site of Hong Kong, where the loadings of the dominant chemical components (e.g. OC, EC and SO₄²⁻) were low (Yu et al., 2010).

Road dust and biogenic aerosols were generally considered as the major sources 364 of OC and EC in the coarse mode (Ho et al., 2003; Zhang et al., 2015b). Significant 365 fractions of OC ($25\pm8\%$) and EC ($14\pm7\%$) mass concentrations were distributed in the 366 367 coarse mode. These numbers were comparable with those (13-38% for OC and 4-16% for EC) measured at suburban sites of Guangzhou, Shenzhen and Hong Kong (Lan et 368 369 al., 2011; Yu et al., 2010), but were lower than those (51-57% for OC and 17-21% for EC) measured in urban Guangzhou in 2006-2007. The MMADs of OC (3.73±0.58 µm) 370 and EC ($3.69\pm0.65 \,\mu$ m) in the coarse mode were close to those ($3.8-4.3 \,\mu$ m for OC and 371 372 3.7-4.1 µm for EC) measured in suburban of Hong Kong, although smaller than those (4.8-5.2 µm for OC and 5.0-5.2 µm for EC) measured in suburban of Shenzhen and 373 urban of Guangzhou (Lan et al., 2011; Yu et al., 2010). These results suggested that the 374 375 MMADs of OC and EC might decrease with their decreasing coarse mode mass fractions. Annual average PM₁₀ concentrations (46 μ g m⁻³) in 2015-2016 in the PRD 376 region were about 40% lower than that (76 µg m⁻³) in 2006-2007, which further 377 supported the above hypothesis. 378

379 **3.2 Closure of particle mass, number concentration, and b**_{sp}

380 **3.2.1 Closure of particle mass concentration**

To investigate the impact of chemical species in different size modes on b_{sp} , particle mass concentrations in the different modes were first reconstructed based on mass concentrations of individual known chemical components. The dominant watersoluble inorganic species including NaCl, NaNO₃, Na₂SO₄, NH₄NO₃, (NH₄)₂SO₄, K₂SO₄, CaSO₄ and Ca(NO₃)₂ were determined using the ISORROPIA II

17

thermodynamic equilibrium model as mentioned in section 2.4. A ratio of OM to OC 386 of 1.4, 1.6 and 1.6 would be appropriate for the condensation, droplet and coarse mode, 387 respectively, which was based on the findings of a previous study that suggested an 388 average OM/OC ratio of 1.57 and a range of 1.4-1.8 in an urban environment of the 389 PRD region (He et al., 2011). In our previous study (Tao et al., 2017b), mass 390 concentration of crustal element oxides in PM2.5 was estimated from the measurements 391 392 of five crustal elements (Al, Si, Ca, Fe and Ti) in urban Guangzhou. This approach cannot be used in the present study due to the lack of crustal elements measurements. 393 Alternatively, crustal element oxides mass concentration was estimated from Ca²⁺ mass 394 concentration because of their good correlations (slope=0.053, R^2 =0.79) as was found 395 in a previous study (Fig. S6) (Tao et al., 2017b). It was suggested that Ca²⁺ accounted 396 397 for 5.3% of crustal element oxides in PM_{2.5} in urban Guangzhou, a value that is close to the content of Ca^{2+} (5.0%) in soil dust source profiles (representing crustal element 398 oxides) in PM_{2.5} in cities of southern China (Sun et al., 2019). Because CaSO₄ and 399 400 $Ca(NO_3)_2$ were mainly from the reactions between calcium oxide and acids (e.g. H₂SO₄ and HNO₃), the estimated mass concentration of crustal element oxides needs 401 to deduct those of CaSO₄ and Ca(NO₃)₂. On annual average, the estimated crustal 402 element oxides accounted for $8\pm 2\%$, $10\pm 4\%$ and $29\pm 5\%$ of the total particle mass 403 404 concentrations in the condensation, droplet and coarse mode, respectively. The 405 reconstructed mass concentrations accounted for 79±3%, 82±6% and 57±6% of the total in the condensation, droplet and coarse mode, respectively. 406

407 As shown in Fig. 2, OM, EC, (NH₄)₂SO₄, NH₄NO₃ and crustal element oxides 408 dominated in different modes in four seasons. For example, OM and EC accounted for 409 31-39% and 14-19%, respectively, of particle mass in the condensation mode, OM, 410 (NH₄)₂SO₄, crustal element oxides and NH₄NO₃ accounted for 19-34%, 18-22%, 6-

411	15% and 4-11%, respectively, in the droplet mode, and crustal element oxides, OM and
412	CaSO ₄ accounted for 22-34%, 12-17% and 4-5%, respectively, in the coarse mode. In
413	addition, the total of the other identified chemical species only accounted for less than
414	10% of the total particle mass in every mode. For example, Na ₂ SO ₄ and K ₂ SO ₄ mainly
415	distributed in the droplet mode and together they accounted for only 2-5% of the
416	particle mass in this mode. NaCl, NaNO3 and Ca(NO3)2 mainly distributed in the
417	coarse mode and each of these species accounted for less than 2% of the total particle
418	mass in this mode.

- 419
- 420

Insert Figure 2

421

422 **3.2.2** Closure of particle number concentration

423 To estimate the contribution of individual chemical species on b_{sp} using Mie theory, number size distributions of the dominant chemical species were needed and were 424 calculated according to the method described in section 2.4. As shown in Fig. 3, most 425 426 chemical species (except (NH₄)₂SO₄ in summer) had much higher number 427 concentrations in the condensation than droplet or coarse mode. The estimated number 428 mean aerodynamic diameters (NMADs) of the number concentrations of individual chemical species mainly distributed in the range of 100-120 nm. The estimated NMADs 429 of particle number concentrations (sum of individual chemical species number 430 431 concentrations in the same size bin) were close to about 100 nm in the four seasons, which was larger than the NMADs (30-70 nm) of the simultaneously measured particle 432 433 number concentrations by the SMPS and APS (Fig. 4). This was because SMPS and APS collected dried particles while the size-segregated sampler collected ambient 434 particles. D_p of particles measured by SMPS can be converted to D_a using the average 435

particle density calculated from the synchronously measured size-segregated individual
chemical species mass concentrations and densities according to the method described
in section 2.4. In any case, the NMADs of particle number concentrations were less
than 100 nm regardless of using SMPS and APS measurements or the estimated sizesegregated chemical species mass concentrations.

As shown in Fig. 3 and Fig. 4, most of particle numbers were in the range of 10 -400 nm either observed by the SMPS or estimated from the size-segregated chemical species mass concentrations. Total particle number concentration in the range of 10 nm-10 μ m measured by the SMPS and APS were 7038±2250 cm⁻³, 9774±1471 cm⁻³, 5694±1942 cm⁻³ and 10801±2986 cm⁻³ in spring, summer, autumn and winter, respectively, which were 1.09±0.24, 2.66±0.48, 1.05±0.20 and 2.33±0.67 times of those estimated by the size-segregated chemical species mass concentrations.

448 NMADs estimated from the size-segregated chemical species mass concentrations were close to those measured by the SMPS and APS in spring and autumn, resulting in 449 450 the close estimation of particle number concentrations to the measured ones. In contrast, the estimated particle number concentrations from the the size-segregated chemical 451 species mass concentrations were evidently lower than those measured by the SMPS 452 and APS in summer and winter, due to the much higher NMADs (100 nm) estimated 453 454 from the size-segregated chemical species mass concentrations than those (about 30 or 455 40 nm) measured by the SMPS and APS.

To exclude the large uncertainties in the estimated particle number concentration caused by condensation mode particles (which were due to the design flaws of sizesegregated sampler), particles smaller than 430 nm were not included in the calculation below. On annual average, the estimated particle number concentrations in the range of 430 nm-10 µm based on the size-segregated chemical species mass concentrations were

20

461	33±42% higher than those measured by the SMPS and APS. This was likely because
462	particles in the droplet mode may shift to the smaller sizes (<430 nm) during the dry
463	process by Nafion tube. Correlation coefficients between the estimated and measured
464	particle number concentrations in the range of 430 nm-10 μ m were significantly
465	improved when the intercepts in the linear regression equations were retained. To some
466	extent, the intercepts represent the measurement errors of SMPS and APS and
467	estimation errors of the inversion technique and ISORROPIA II models. In any case,
468	good correlations (R^2 >0.81) between the estimated daily particle number concentrations
469	and the measured ones were found and the slopes ranged from 0.79 to 1.03 in the four
470	seasons (Fig. 5). These results suggested that the estimated particle number
471	concentrations were acceptable in the range of 430 nm-10 μ m, noting that particles in
472	this size range dominate particle scattering efficiency.
473	

474	Insert Figure 3
475	Insert Figure 4

Insert Figure 5 476

- 477
- 478

3.2.3 Closure between the measured and estimated b_{sp} 479

Daily b_{sp} was estimated using Mie model (in section 2.4) with input parameters 480 including refractive indices, densities and number concentrations in 401 bins of 481 chemical species (NaCl, NaNO3, Na2SO4, (NH4)2SO4, NH4NO3, K2SO4, CaSO4, 482 Ca(NO₃)₂, H₂O, OM, EC, crustal element oxides and unidentified fraction). The 483 484 refractive indices and densities of above chemical species are summarized in Table S1. Although the number concentrations in the condensation mode were underestimated, 485

good correlations ($R^2 > 0.92$) were found between the measured and estimated b_{sp} with 486 the slopes being 0.87, 0.87, 0.85 and 0.89 in spring, summer, autumn and winter, 487 488 respectively (Fig. 6). On annual arithmetic average, the estimated b_{sp} can explain 91±10% of the measured b_{sp}. The residual fractions were likely related to the chosen convert 489 factor between OM and OC, measurements and sampling errors of chemical species 490 (especially NO₃⁻), errors from the models (ISORROPIA II model, Mie model, and the 491 492 inversion technique method), and measurement errors caused by the size-segregated sampler (Vaughan, 1989). Magnitudes of the uncertainties caused by these sources are 493 494 discussed below.

495 Although the convert factor of 1.6 between OM and OC was reasonable in urban environment, a value of as high as 1.8 was found in literature (He et al., 2011). In 496 addition, OC mass concentrations were likely underestimated due to the OC/EC 497 protocol for size-segregated samples. Nevertheless, the estimated b_{sp} can only be 498 increased by less than 3% if increasing the convert factor to 1.8 in the droplet mode. 499 500 Note that a previous study at the Fresno Supersite increased the estimated b_{sp} by about 10% when increasing the convert factor from 1.4 to 1.8, likely due to the high mass 501 fraction of OC in fine particle at this site (Watson et al., 2008). 502

Different from the other chemical species, NH4NO3 can dissociate into HNO3(g) 503 and NH_{3(g)} during the filter gravimetric weighing process under dry condition. To 504 505 evaluate the evaporative loss of NH₄NO₃, synchronous inline data of NO₃⁻ were also measured by an In-situ Gas and Aerosol Composition monitoring system at hourly 506 temporal resolution (Fig. S7). Seasonal average NO₃⁻ concentrations were 42% (PM_{2.5}), 507 508 39% (PM₁₀), 42% (PM_{2.5}) and 19% (PM_{2.5}) less from filter measurements than inline measurements in spring, summer, autumn and winter, respectively. Adjusting the filter 509 NO_3^- data using the above ratios can increase the estimated b_{sp} by 7%, 2%, 4% and 2% 510

512

513 514

Insert Figure 6

Meanwhile, the measured b_{sp} could also be underestimated due to the 515 dissociation of NH₄NO₃ during the dry processes of ambient particles through the 516 517 Nafion dryer. A previous study indicated the measured b_{sp} being decreased by less than 10% due to the dissociation of NH4NO3 in a heated nephelometer (Bergin et al., 518 519 1997). In the present study, the chamber temperatures of nephelometer were less than 520 300 K and the particle residence time in both the Nafion dryer and the nephelometer chamber was about 7 seconds. Thus, the bias in the measured b_{sp} should be less than 521 2% in any season according to the relationship among the loss of b_{sp}, residence time 522 and the temperature in chamber in a previous study (Bergin et al., 1997). Combining 523 524 all of the above-mentioned factors, the adjusted estimated b_{sp} would increase to the level of 92%, 87%, 87% and 89% of the measured b_{sp} in spring, summer, autumn and 525 526 winter, respectively. This means the above methods for estimating b_{sp} were reasonable with the adjusted estimated values explaining 87-92% of the measured 527 values after the filter-based NO3⁻ concentrations were adjusted based on the inline 528 data. Thus, the errors from the models and size-segregated samplers may account for 529 the remaining 8-13% of the measured b_{sp}. Moreover, the size distributions would be 530 different under dry and ambient conditions due to the particle hygroscopic properties. 531 In fact, the NMADs of particle measured by SMPS and APS under dry condition 532 were less than those measured by the size-segregated sampler under ambient 533 condition according to section 3.2.2. Thus, the estimated b_{sp} based on size 534 distributions of chemical species would be systematically higher to some extent than 535

536 the measured b_{sp} under dry condition.

Generally, the estimated seasonal average b_{sp} were 146±40 Mm⁻¹, 99±33 Mm⁻¹, 537 169±54 Mm⁻¹ and 151±71 Mm⁻¹ in spring, summer, autumn and winter, respectively 538 (Fig. 7). The particles in the condensation, droplet and coarse modes contributed 6-539 7%, 81-86% and 8-12%, respectively, to the estimated b_{sp}. OM and EC were the 540 dominant contributors, accounting for 32-41% and 30-37%, respectively, of the 541 542 estimated b_{sp} in the condensation mode. OM and secondary inorganic aerosols (sum of (NH₄)₂SO₄ and NH₄NO₃) were the dominant contributors, accounting for 27-44% 543 544 and 27-34%, respectively, of the estimated b_{sp} in the droplet mode. Unidentified fraction, crustal element oxides and OM were the dominant contributors, accounting 545 for 26-47%, 16-29% and 19-27%, respectively, of the estimated b_{sp} in the coarse 546 547 mode. The sum of the dominant contributors, including OM, EC, secondary inorganic aerosols and crustal element oxides, accounted for 70-79% of the estimated b_{sp} in the 548 four seasons. In contrast, the sum of the other chemical species (including NaCl, 549 NaNO₃, Na₂SO₄, K₂SO₄, CaSO₄, Ca(NO₃)₂, H₂O) accounted for 5-10% and the 550 unidentified fraction, 12-23% of the estimated b_{sp}. In conclusion, visibility 551 degradation was determined by the dominant chemical species (e.g. OM, EC, 552 secondary inorganic aerosols and crustal element oxides) in the fine mode (both 553 condensation and droplet), which agreed with the results of the original and revised 554 555 IMPORVE formulas (Pitchford et al., 2007).

- 556
- 557

Insert Figure 7

3.3 Key factors for variations of particle and chemical species MSEs

560 **3.3.1 The estimated MSEs of particle and chemical species**

561 To conveniently explore the control factors of particle MSE, the dominant chemical species' MSEs were estimated by their mass concentrations and the estimated 562 b_{sp}, according to the measured chemical species mass concentrations in section 3.1 and 563 the estimated b_{sp} in section 3.2. Here, only the MSEs of (NH₄)₂SO₄, NH₄NO₃, OM, 564 565 EC, crustal element oxides and unidentified fraction in the condensation, droplet, fine (sum of condensation and droplet), and coarse modes were estimated (Table 3), 566 567 considering these chemical species accounted for more than 90% of the estimated b_{sp}. However, particle MSEs in the condensation, droplet, fine and coarse modes were 568 estimated by sum of b_{sp} from individual chemical species divided by sum of particle 569 570 mass concentration according to formula (9). Moreover, an external mixing of 571 individual chemical species was assumed in the estimation. Generally, good correlations ($R^2 > 0.79$) were found between the measured and estimated b_{sp} using the 572 573 average MSEs of chemical species in Table 3 with the slopes being 0.85, 0.84, 0.76 and 0.84 in spring, summer, autumn and winter, respectively (Fig. S8). Thus, the estimated 574 MSEs of chemical species in Table 3 were underestimated. 575

576

577

Insert Table 3

578

579 Undoubtedly, the particle MSE should be also underestimated because the 580 estimated b_{sp} was 11-15% less of the measured b_{sp} in four seasons, as discussed in 581 section 3.2. The measured b_{sp} would be biased low by about 3% due to the evaporation 582 of NH₄NO₃, while the NO₃⁻ mass concentrations based the filter measurements were 583 biased low by 5%, 3%, 9% and 6% in spring, summer, autumn and winter, respectively. Thus, the MSEs of NO_3^- would be underestimated by 9%, 13%, 6% and 5% in the respective season in the real world. In conclusion, the MSEs of particle and chemical species were underestimated by less than 13%.

On annual average, the estimated particle MSEs in the condensation, droplet and 587 coarse modes were 2.1 ± 0.2 m² g⁻¹, 4.3 ± 0.2 m² g⁻¹ and 0.5 ± 0.0 m² g⁻¹, respectively. The 588 estimated particle MSE in the fine (sum of condensation and droplet) mode, similar to 589 PM_{2.5}) was 3.7 ± 0.2 m² g⁻¹, which was slightly higher than the value of 3.5 m² g⁻¹ 590 estimated in 2009-2010 in urban Guangzhou (Tao et al., 2014). Seasonal variations of 591 the estimated MSEs in the fine mode followed the sequence of winter $(3.9\pm0.2 \text{ m}^2 \text{ g}^-)$ 592 ¹) > autumn (3.8±0.2 m² g⁻¹) > summer (3.6±0.2 m² g⁻¹) > spring (3.5±0.1 m² g⁻¹). 593 Evidently, the estimated MSEs in the fine mode were slightly higher in autumn and 594 595 winter than spring and summer, which also agreed with the previous studies in urban 596 Guangzhou (Andreae et al., 2008; Jung et al., 2009a).

On annual average, the estimated MSEs of (NH₄)₂SO₄, NH₄NO₃, OM and crustal 597 598 element oxides (equal to fine soil in the IMPROVE formulas) in the fine mode were 4.4 ± 0.8 , 4.5 ± 1.5 , 4.6 ± 0.3 and 2.6 ± 0.1 m² g⁻¹, respectively, which were higher than those 599 $(3.0, 3.0, 4.0 \text{ and } 1.0 \text{ m}^2 \text{ g}^{-1}$, respectively) from using the original IMPROVE formula 600 (Hand and Malm, 2007; Malm and Hand, 2007; Pitchford et al., 2007). As shown in 601 602 Table 3, the MSEs of (NH₄)₂SO₄, NH₄NO₃, OM and crustal element oxides in the fine 603 mode depended on their mass fractions in the droplet mode with high MSEs. In the original IMPROVE formula, MSEs of these chemical species were estimated using the 604 multiple linear regression model according to the chemical components in PM2.5 and 605 b_{sp} from IMPROVE network, noting that significant mass fractions of particle were in 606 the condensation mode at the regional sites of IMPROVE network and an urban site in 607 U.S.A. (Cabada et al., 2004; Hand et al., 2002; Malm et al., 2003). In contrast, in the 608

present study most mass fractions of the dominant chemical species (e.g. (NH₄)₂SO₄, 609 NH₄NO₃ and OM) in the fine mode were distributed in the droplet rather than 610 condensation mode. These results suggested the higher MSEs of (NH₄)₂SO₄, NH₄NO₃ 611 and OM in the fine mode in this study were likely due to their significant mass fractions 612 in the droplet mode. In fact, the MSE of fine soil in the IMPROVE formulas would 613 represent the MSE of the bulk mode rather than the fine mode (Hand and Malm, 2007). 614 The average MSEs of the bulk mode was 1.0 ± 0.2 m² g⁻¹ in this study, which was similar 615 to that in the IMPROVE formulas. 616

617 On annual average, the estimated MSEs of (NH₄)₂SO₄, NH₄NO₃ and OM were 4.7 ± 0.6 , 4.8 ± 0.9 and 5.3 ± 0.2 m² g⁻¹ in the droplet mode, and were 2.1 ± 0.5 , 2.3 ± 0.8 and 618 $2.7\pm0.1 \text{ m}^2 \text{ g}^{-1}$ in the condensation mode, respectively, which were lower than those in 619 the large mode (similar to droplet mode) and were slightly lower than those in the small 620 621 mode (similar to condensation mode) in the revised IMPROVE formula (Pitchford et al., 2007). Theoretically, the highest MSEs of (NH₄)₂SO₄, NH₄NO₃ and OM would be 622 623 found at about 0.55 µm in geometric mass mean diameters (GMMD) at the wavelength 550 nm according to Mie theory. However, the MMADs of (NH₄)₂SO₄, NH₄NO₃ and 624 OM were 0.76 - 0.80 µm (equal to about 0.60-0.64 µm in GMMD) in the droplet mode 625 and were 0.21 µm (equal to about 0.16-0.18 µm in GMMD) in the condensation mode 626 in this study, which were larger than 0.50 µm in GMMD in the large mode and were 627 628 lower than 0.20 µm in GMMD in the small mode in the revised IMPROVE formula. Thus, the higher GMMDs in the droplet mode and the lower GMMDs of (NH₄)₂SO₄, 629 NH4NO3 and OM in the condensation mode in this study likely resulted in their lower 630 631 MSEs compared with those in the revised IMPROVE formula. In addition, the underestimated b_{sp} would also result in underestimating their MSEs in the condensation 632 and droplet modes in this study. 633

Although the contribution of EC to b_{sp} was not considered in the IMPROVE 634 formulas, its mass extinction efficiency (10 m² g⁻¹) considered both scattering and 635 absorption abilities (Hand and Malm, 2007). In fact, the theoretical average mass 636 absorption efficiency (MAE) of EC in fine particle was 7.5 m² g⁻¹ at the wavelength 637 550 nm (Wu et al., 2016). Thus, mass extinction efficiency of EC was also about 10 m^2 638 g-1 in this study, suggesting the estimated EC MSEs were comparable with the 639 IMPROVE formulas. The estimated MSEs of coarse particle was 0.5±0.0 m² g⁻¹, which 640 was also comparable with the value of $0.6 \text{ m}^2 \text{ g}^{-1}$ in the IMPROVE formulas. Noticeably, 641 642 sea salt was mainly distributed in the coarse mode rather than droplet mode in this study. In addition, the unidentified fraction with large mass fraction and the high MSE in the 643 fine mode was not considered in the IMPROVE formulas, although it accounted for a 644 significant contribution of the estimated b_{sp} in this study (Fig. 7). In conclusion, EC 645 and unidentified fraction rather than sea salt should be considered in estimating b_{sp} , 646 especially when EC and unidentified fraction accounted for significant mass fractions 647 of fine particles. 648

649 3.3.2 Impact of size distribution on particle and chemical species MSE

650 As discussed in section 3.3.1, seasonal average MSEs in the coarse mode fluctuated in a small range of 0.4-0.5 m² g⁻¹, while those in the fine mode in a slightly 651 larger range of 3.5-3.9 m² g⁻¹, but the percentage changes are in similar magnitudes (10-652 20%). Only variations of fine particle MSE were discussed below as an example. It is 653 worth to mention that fine particle MSE increased with its mass concentrations in 654 IMPROVE network (Lowenthal and Kumar, 2004), but such a phenomenon was not 655 founded in the present study. As shown in Fig. 8, the seasonal variations of fine particle 656 MSE were mainly caused by particle fractions in the size range of 0.4-0.9 µm, which 657

658	belong to the droplet mode. In this mode, the MSEs of $(NH_4)_2SO_4$ and NH_4NO_3 and
659	OM were higher while those of the other chemical species were lower than the overall
660	particle MSE. Note that the overall particle MSE depends on the mass concentrations
661	and MSEs of individual chemical components. Thus, the seasonal average MSEs of
662	fine particle were dominated by the seasonal average mass fractions and associated
663	MSEs of (NH ₄) ₂ SO ₄ and NH ₄ NO ₃ and OM in the droplet mode.
664	
665	Insert Figure 8
666	

The sum of the products of seasonal average mass concentration and MSEs of the above three chemical species in the droplet mode was 1.8, 2.1, 2.3 and 2.5 m² g⁻¹ in spring, summer, autumn and winter, respectively. As expected, the seasonal variations of fine particle MSE followed the sequences of winter $(3.9\pm0.2 \text{ m}^2 \text{ g}^{-1}) >$ autumn $(3.8\pm0.2 \text{ m}^2 \text{ g}^{-1}) >$ summer $(3.6\pm0.2 \text{ m}^2 \text{ g}^{-1}) >$ spring $(3.5\pm0.1 \text{ m}^2 \text{ g}^{-1})$. Noticeably, fine particle MSE was determined by the average MSEs of the dominant chemical species, rather than their mass fractions which were much smaller than 1.0.

Different from the approach used for fine particle MSE, the MSEs of $(NH_4)_2SO_4$, NH4NO3 and OM in the droplet mode were determined using measurement-based their mass size distributions prescribed as log-normal size distributions. In theory (section 2.4), the log-normal size distribution of chemical species is determined by three parameters include mass concentration (in the range of 0.43 - 2.1 µm), MMAD and standard deviation (σ), which control the area, mode and scale of the log-normal size

680	distribution, respectively. Thus, the MSEs of (NH ₄) ₂ SO ₄ , NH ₄ NO ₃ and OM should
681	depend on their MMADs and σ values. Seasonal average σ values of $(NH_4)_2SO_4,$
682	NH4NO3 and OM were in the range of 0.18-0.21, 0.18-0.21 and 0.22-0.26, respectively,
683	while the corresponding MMADs in the range of 0.72-0.92, 0.75-0.90 and 0.73-0.78
684	$\mu m,$ respectively (Fig. 9). Generally, the seasonal average MSEs of $(NH_4)_2SO_4,$
685	NH_4NO_3 and OM in the droplet mode were higher with the lower σ values (or MMADs)
686	when MMADs (σ values) were close. However, the MSE of OM in summer was 5.2 m^2
687	g ⁻¹ , which was lower than 5.3 m^2 g ⁻¹ in autumn, although σ values and MMADs in
688	summer were lower than those in autumn. This was mainly related with the evident
689	fluctuation the MSE of OM in the range of 0.6-0.7 μ m.
690	
691	Insert Figure 9
692	
693	In conclusion, the fine particle MSE was determined by the sum of the products
694	of average mass fractions and MSEs of $(NH_4)_2SO_4$ and NH_4NO_3 and OM in the droplet
695	mode. The MSEs of the above three chemical species in the droplet mode depended on
695 696	mode. The MSEs of the above three chemical species in the droplet mode depended on both their σ value and MMADs. Generally, fine particle MSE mainly related with OM
695 696 697	mode. The MSEs of the above three chemical species in the droplet mode depended on both their σ value and MMADs. Generally, fine particle MSE mainly related with OM due to its high mass and MSE in the droplet mode in urban Guangzhou.
695 696 697 698	mode. The MSEs of the above three chemical species in the droplet mode depended on both their σ value and MMADs. Generally, fine particle MSE mainly related with OM due to its high mass and MSE in the droplet mode in urban Guangzhou. 4. Summary and implication
695696697698699	 mode. The MSEs of the above three chemical species in the droplet mode depended on both their σ value and MMADs. Generally, fine particle MSE mainly related with OM due to its high mass and MSE in the droplet mode in urban Guangzhou. 4. Summary and implication Size- and chemically-resolved particle number and mass concentration were
 695 696 697 698 699 700 	mode. The MSEs of the above three chemical species in the droplet mode depended on both their σ value and MMADs. Generally, fine particle MSE mainly related with OM due to its high mass and MSE in the droplet mode in urban Guangzhou. 4. Summary and implication Size- and chemically-resolved particle number and mass concentration were measured in urban Guangzhou in different seasons during 2015-2016 and the data were

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EC in both condensation and droplet modes, and particle mass, NO3⁻, OC, Na⁺, Ca²⁺ 702 and Cl⁻ in both droplet and coarse modes. The estimated b_{sp} can represent 85-89% of 703 704 the measured b_{sp} based on the size-segregated chemical compositions according to ISORROPIA II thermodynamic equilibrium model and Mie theory model. The largest 705 706 contributors to b_{sp} were the chemical species in the droplet mode with the highest MSEs. 707 MSEs of the dominant chemical species were noticeably different in this study than those in the original and revised IMPROVE formulas. The MSEs of (NH₄)₂SO₄, 708 NH₄NO₃ and OM in the fine mode were higher than those in the original IMPROVE 709 710 formula, and in the droplet mode were lower than those in the revised IMPROVE 711 formula. In any case, b_{sp} would be underestimated in urban Guangzhou using the 712 original or revised IMPROVE formulas because the unidentified chemical species (and 713 associated mass fractions) in the droplet mode accounted for a large fraction of b_{sp} and this portion was not included in these formulas. Moreover, MSEs of chemical species 714 715 would be overestimated in the original and revised IMPROVE formulas using multiple 716 linear regression model when the unidentified species was ignored. In addition, sea salt 717 was found in the coarse mode in this study, differing from the set up in the IMPROVE formulas which is in the droplet mode. It can be concluded that the estimated b_{sp} in 718 Guangzhou based on the revised IMPROVE formula would have large biases, even 719 though good correlations between estimated and measured b_{sp} was found. 720

MSEs of fine particles are controlled by the relative mass fractions of the dominant chemical components (e.g., $(NH_4)_2SO_4$, NH_4NO_3 and OM) and associated size distributions (e.g. σ and MMAD). Localized b_{sp} formulas are thus needed for better

31

- restimating particle MSE because particle size distributions of individual chemical
- species vary significantly in space and time.
- 726 Data availability. Data used in this study are available from Jun Tao (taojun@scies.org).
- 727 Competing interests. The authors declare that they have no conflict of interest.
- 728

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- 985 2018.

Season Date		Date Sample type		Sample duration	Sample number
Summer	15 July- 6 August in 2015			24h	23 sets
Autumn	15 October- 5 November in 2015			24h	22 sets
Winter	4-20 January - 19-22 February in 2016	Size-segregated samples	Anderson 8-stage air samplers	24h	21 sets
Spring	8-20 April and 4-14 May in 2016			48h	10 sets
Summer	15 July- 6 August in 2015				23 sets
Autumn	15 October- 5 November in 2015	DM. and DM. appendix	CSADM	24 h	22 sets
Winter	4-20 January - 19-22 February in 2016	PW12.5 and PW10 samples	USAPM	24 n	21 sets
Spring	8-20 April and 4-14 May in 2016				20 sets
Summer	15 July- 6 August in 2015				
Autumn	15 October- 5 November in 2015	Particle number concentration		5 min	
Winter	4-20 January - 19-22 February in 2016	in the range of 14 nm - 615	SMPS, ISI Model 3936		
Spring	8-20 April and 4-14 May in 2016	1111			
Summer	15 July- 6 August in 2015				
Autumn15 October- 5 November in 2015Winter4-20 January - 19-22 February in 2016		Particle number concentration		<u>ب</u>	
		in the range of 542 nm - 10	APS, 1SI Model 3321	5 min	
Spring	8-20 April and 4-14 May in 2016	μπ			
Summer	15 July- 6 August in 2015				
Autumn	15 October- 5 November in 2015		Nephelometer, Ecotech, Model	<i>-</i> .	
Winter	4-20 January - 19-22 February in 2016	Dry b _{sp}	Aurora1000G	5 min	
Spring	8-20 April and 4-14 May in 2016				
Summer	15 July- 6 August in 2015	NO_3 in PM_{10}			
Autumn	15 October- 5 November in 2015	NO ₃ ⁻ in PM _{2.5}		11	
Winter	4-20 January in 2016	NO ₃ ⁻ in PM _{2.5}	IGAC, Model S-611	l h	
Spring	4-14 May in 2016	NO ₃ ⁻ in PM _{2.5}			

Table 1. Summary of the sampling information

Chamiaal		Annual		Spring		Summer		Autumn		Winter	
composition	Size mode	MMAD ^(b) (µm)	Mass (µg m ⁻³)	MMAD (µm)	Mass (µg m ⁻³)						
PM ^(a)	Condensation(<0.43µm)	_	5.7±2.3 (10±2%)	_	6.6±3.0 (10±3%)	—	4.0±1.3 (8±1%)	—	7.0±1.9 (10±2%)	0.21±0.00	5.7±2.2 (10±2%)
	Droplet(0.43 -2.1µm)	0.78±0.07	29.1±11.8(48±7%)	0.87±0.13	31.9±8.7(50±8%)	0.78±0.05	20.4±8.0(42±8%)	0.74±0.06	35.6±9.7(46±4%)	0.79±0.05	30.6±13.2(52±5%)
	Coarse(2.1 -10µm)	4.57±0.42	25.5±10.1(42±8%)	4.37±0.37	25.3±7.0(40±7%)	4.47±0.35	23.1±4.9(50±7%)	4.90±0.46	30.8±11.8(44±6%)	4.47±0.24	22.5±11.7(38±6%)
	Condensation(<0.43µm)	_	1.0±0.5 (12%)	_	0.9±0.3 (10%)	—	0.9±0.3 (15%)	—	1.4±0.5 (13%)	0.21±0.00	0.6±0.3 (10%)
SO4 ²⁻	Droplet(0.43 -2.1µm)	0.80±0.08	6.5±2.9 (77%)	0.86±0.07	7.3±2.3 (79%)	0.79±0.07	4.9±2.6 (75%)	0.77±0.08	8.5±2.6 (75%)	0.82±0.08	5.8±2.7 (79%)
	Coarse(2.1 -10µm)	4.17±0.44	0.9±0.6 (11%)	4.34±0.59	0.9±0.6 (11%)	4.09±0.16	0.6±0.3 (10%)	4.08±0.22	1.4±0.8 (12%)	4.20±0.59	0.8±0.5 (11%)
	Condensation(<0.43µm)	—	0.4±0.3 (10%)		0.4±0.2 (6%)	—	0.2±0.2 (9%)	—	0.4±0.3 (10%)	0.21±0.00	0.6±0.3 (13%)
NO ₃ -	Droplet(0.43 -2.1µm)	0.85±0.21	2.2±2.2 (46%)	0.87±0.07	3.2±2.1 (51%)	0.94±0.35	0.8±0.5 (35%)	0.80±0.09	2.1±1.7 (39%)	0.80±0.07	3.2±2.9 (63%)
	Coarse(2.1 -10µm)	4.38±0.61	1.8±1.4 (44%)	4.47±0.62	2.4±1.2 (43%)	4.15±0.52	1.3±0.7 (56%)	4.36±0.31	2.4±1.7 (51%)	4.74±0.76	1.3±1.5 (24%)
	Condensation(<0.43µm)	_	0.2±0.2 (6%)	_	0.2±0.1 (6%)	—	0.1±0.1 (5%)	—	0.2±0.2 (7%)	0.21±0.00	0.2±0.2 (6%)
$\mathrm{NH_4^+}$	Droplet(0.43 -2.1µm)	0.76±0.13	2.4±1.5 (89%)	0.86±0.17	2.8±1.1 (89%)	0.70±0.11	1.4±1.1 (91%)	0.73±0.12	3.1±1.4 (90%)	0.82±0.10	2.5±1.7 (86%)
	Coarse(2.1 -10µm)	3.25±0.69	0.1±0.1 (5%)	3.13±1.16	0.2±0.2 (6%)	3.36±0.68	0.0±0.0 (4%)	3.01±0.23	0.1±0.1 (3%)	3.45±0.70	0.2±0.1 (8%)
-	Condensation(<0.43µm)	0.21±0.00	1.2±0.6 (13±4%)	_	1.4±0.4 (19±4%)	—	0.8±0.3 (11±4%)	—	1.6±0.5 (14±2%)	0.21±0.00	1.2±0.6 (13±4%)
OC	Droplet(0.43 -2.1µm)	0.76±0.07	5.5±2.4 (62±9%)	0.73±0.06	3.9±1.6 (51±6%)	0.77±0.07	4.1±1.3 (63±9%)	0.78±0.06	6.9±2.0 (58±5%)	0.75±0.08	6.5±2.6 (69±7%)
	Coarse(2.1 -10µm)	3.73±0.58	2.2±1.1 (25±8%)	3.99±0.25	2.2±0.7 (30±3%)	3.50±0.73	1.7±0.9 (26±9%)	4.14±0.24	3.3±1.0 (28±4%)	3.44±0.39	1.7±0.9 (18±8%)
-	Condensation(<0.43µm)	_	1.1±0.4 (31±7%)	_	1.1±0.1 (36±9%)	0.21±0.00	0.8±0.2 (32±5%)	—	1.0±0.4 (24±3%)	0.21±0.00	1.4±0.6 (35±6%)
EC	Droplet(0.43 -2.1µm)	0.66±0.08	2.0±1.0 (55±7%)	0.65±0.08	1.8±0.8 (54±9%)	0.61±0.08	1.3±0.5 (50±5%)	0.71±0.04	2.7±0.9 (62±6%)	0.67±0.07	2.1±0.9 (54±5%)
	Coarse(2.1 -10µm)	3.69±0.65	0.5±0.3 (14±7%)	3.54±0.61	0.3±0.2 (10±6%)	3.48±0.52	0.5±0.3 (18±6%)	4.17±0.24	0.6±0.2 (14±5%)	3.50±0.75	0.4±0.3 (11±8%)
	Condensation(<0.43µm)	—	0.1±0.1 (11%)	_	0.1±0.0 (9%)	—	0.0±0.0 (5%)	—	0.1±0.1 (16%)	0.21±0.00	0.1±0.0 (11%)
Na^+	Droplet(0.43 -2.1µm)	0.86±0.12	0.4±0.2 (48%)	0.84±0.10	0.3±0.0 (48%)	0.96±0.11	0.4±0.1 (45%)	0.81±0.09	0.4±0.3 (52%)	0.80±0.11	0.3±0.2 (48%)
	Coarse(2.1 -10µm)	3.75±0.38	0.4±0.3 (41%)	3.90±0.63	0.3±0.2 (43%)	3.60±0.19	0.6±0.4 (50%)	3.64±0.27	0.3±0.3 (32%)	3.94±0.38	0.3±0.2 (41%)
	Condensation(<0.43µm)	_	0.1±0.0 (13%)	_	0.0±0.0 (10%)	—	0.1±0.0 (16%)	—	0.1±0.0 (12%)	0.21±0.00	0.1±0.0 (12%)
\mathbf{K}^+	Droplet(0.43 -2.1µm)	0.69±0.08	0.3±0.2 (78%)	0.76±0.07	0.3±0.1 (76%)	0.64±0.08	0.3±0.1 (72%)	0.67±0.07	0.4±0.2 (87%)	0.73±0.06	0.4±0.2 (77%)
	Coarse(2.1 -10µm)	3.74±0.51	0.0±0.0 (9%)	3.94±0.40	0.1±0.0 (14%)	3.74±0.64	0.0±0.0 (12%)	3.30±0.38	0.0±0.0 (1%)	3.78±0.35	0.0±0.0 (11%)
	Condensation(<0.43µm)	—	0.0±0.0 (4%)	_	0.1±0.0 (7%)	—	0.0±0.0 (4%)	—	0.0±0.0 (3%)	0.21±0.00	0.0±0.0 (5%)
Ca ²⁺	Droplet(0.43 -2.1µm)	0.91±0.12	0.2±0.1 (24%)	0.88±0.13	0.3±0.1 (36%)	1.00±0.11	0.3±0.1 (30%)	0.81±0.10	0.2±0.1 (16%)	0.92±0.09	0.2±0.1 (21%)
	Coarse(2.1 -10µm)	4.57±0.54	0.8±0.4 (72%)	5.02±0.58	0.6±0.2 (57%)	4.10±0.42	0.7±0.3 (66%)	4.72±0.47	1.1±0.5 (81%)	4.73±0.38	0.7±0.3 (74%)
	Condensation(<0.43µm)	_	0.0±0.0 (5%)	_	0.1±0.0 (5%)	—	0.0±0.0 (2%)	—	0.0±0.0 (5%)	0.21±0.00	0.0±0.0 (10%)
Cl-	Droplet(0.43 -2.1µm)	0.89±0.13	0.2±0.3 (24%)	0.89±0.10	0.7±0.7 (37%)	0.92±0.20	0.0±0.0 (9%)	0.89±0.05	0.0±0.0 (17%)	0.85±0.08	0.2±0.2 (42%)
	Coarse(2.1 -10µm)	3.77±0.35	0.4±0.4 (71%)	3.97±0.12	0.8±0.4 (58%)	3.70±0.23	0.4±0.3 (89%)	3.72±0.21	0.3±0.2 (78%)	3.80±0.50	0.4±0.6 (48%)

 Table 2. Summary of concentrations of chemical compositions in the different size modes

^(a)PM: Particulate matter; ^(b) MMAD is mass mean aerodynamic diameter.

	Size mode	Annual		Spring		Summer		Autumn		Winter	
Chemical species		MMAD ^(c) (µm)	MSE ^(d) (m ² g ⁻¹)	MMAD (µm)	MSE (m ² g ⁻¹)						
	Condensation(<0.43µm)	—	2.1±0.2	_	1.9±0.2	_	2.0±0.1	_	2.1±0.1	0.21±0.00	2.2±0.2
	Droplet(0.43 -2.1µm)	0.78±0.07	4.3±0.2	0.87±0.13	4.0±0.1	0.78±0.05	4.2±0.1	0.74±0.06	4.3±0.2	0.79±0.05	4.4±0.2
PM ^(a)	Coarse(2.1 -10µm)	4.57±0.42	0.5±0.0	4.37±0.37	0.6±0.1	4.47±0.35	0.5±0.0	4.90±0.46	0.5±0.0	4.47±0.24	0.5±0.0
	Fine mode(<2.1µm) ^(b)		3.7±0.2		3.5±0.1	1	3.6±0.2		3.8±0.2		3.9±0.2
	Condensation(<0.43µm)	—	2.1±0.5	_	1.9±0.6	-	2.6±0.2	_	2.0±0.5	0.21±0.00	1.9±0.5
$(NH_4)_2SO_4$	Droplet(0.43 -2.1µm)	0.79±0.17	4.7±0.6	0.92±0.13	4.3±0.3	0.74±0.20	4.8±0.6	0.72±0.16	4.9±0.7	0.84±0.13	4.6±0.7
	Fine mode(<2.1µm)		4.4±0.8		4.1±0.4	1	4.5±0.6		4.6±0.8		4.3±0.9
	Condensation(<0.43µm)	0.21±0.00	2.3±0.8	_	2.0±0.8	_	2.9±0.3	_	2.6±1.0	0.21±0.00	2.3±0.7
NH_4NO_3	Droplet(0.43 -2.1µm)	0.80±0.16	4.8±0.9	0.90±0.18	4.5±0.8	0.77±0.17	4.9±0.8	0.75±0.13	5.1±1.0	0.82±0.14	4.7±0.8
	Fine mode(<2.1µm)		4.5±1.5		4.2±1.2	†	4.7±0.9		4.9±2.0	1	4.4±1.3
	Condensation(<0.43µm)	—	2.7±0.1	_	2.5±0.1	_	2.8±0.2	_	2.6±0.1	0.21±0.00	2.8±0.1
OM	Droplet(0.43 -2.1µm)	0.76±0.07	5.3±0.2	0.73±0.06	5.4±0.1	0.77±0.07	5.2±0.2	0.78±0.06	5.3±0.2	0.75±0.08	5.5±0.2
OW	Coarse(2.1 -10µm)	3.73±0.58	0.8±0.1	3.99±0.25	0.8±0.0	3.50±0.73	0.8±0.1	4.14±0.24	0.7±0.0	3.44±0.39	0.8±0.1
	Fine mode(<2.1µm)		4.6±0.3		4.4±0.2	1	4.6±0.2		4.5±0.1		4.9±0.3
	Condensation(<0.43µm)	—	2.9±0.1	_	2.9±0.1	_	2.9±0.1	_	3.0±0.1	0.21±0.00	2.9±0.1
FC	Droplet(0.43 -2.1µm)	0.66±0.08	2.3±0.2	0.65±0.08	2.3±0.2	0.61±0.08	2.3±0.2	0.71±0.04	2.2±0.1	0.67±0.07	2.3±0.2
EC	Coarse(2.1 -10µm)	3.69±0.65	0.4±0.0	3.54±0.61	0.4±0.0	3.48±0.52	0.4±0.0	4.17±0.24	0.4±0.0	3.50±0.75	0.5±0.0
	Fine mode(<2.1µm)		2.6±0.1		2.6±0.1	1	2.6±0.2		2.5±0.1	1	2.6±0.1
	Condensation(<0.43µm)	_	0.7±0.0	_	0.7±0.0	-	0.7±0.1	_	0.7±0.0	0.21±0.00	0.7±0.0
Crustal element	Droplet(0.43 -2.1µm)	0.91±0.12	2.9±0.2	0.88±0.13	3.0±0.2	1.00±0.11	2.9±0.2	0.81±0.10	2.8±0.2	0.92±0.09	2.8±0.2
oxides	Coarse(2.1 -10µm)	4.57±0.54	0.4±0.0	5.02±0.58	0.4±0.0	4.10±0.42	0.5±0.0	4.72±0.47	0.4±0.0	4.73±0.38	0.4±0.0
	Fine mode(<2.1µm)		2.4±0.2	t	2.4±0.1	1	2.5±0.2	t	2.4±0.2	1	2.3±0.2
	Condensation(<0.43µm)		1.3±0.2	_	1.2±0.4	<u> </u>	1.2±0.2	_	1.4±0.1	0.21±0.00	1.3±0.2
Unidentified	Droplet(0.43 -2.1µm)	0.85±0.26	3.8±0.6	1.00±0.20	3.5±0.8	0.74±0.44	3.9±0.9	0.84±0.10	3.9±0.2	0.90±0.20	3.7±0.4
Unidentified	Coarse(2.1 -10µm)	5.74±1.52	0.4±0.1	4.55±0.71	0.5±0.1	6.46±1.14	0.4±0.1	6.33±1.62	0.4±0.1	4.91±0.90	0.5±0.1
	Fine mode(<2.1µm)		3.1±0.8		2.9±0.9		2.6±1.0		3.3±0.3		3.1±0.5
NaCl	Coarse(2.1 -10µm)	4.88 ± 0.41	0.5±0.1	5.14±0.70	0.5±0.1	4.49±0.38	0.6 ± 0.0	5.38±0.43	0.5±0.0	4.66±0.65	0.5±0.0

Table 3. Summary of the estimated MSEs of particle and the dominant chemical composition at the wavelength of 550nm under dry condition (relative humidity =40%)

^(a)PM: Particulate matter; ^(b)Fine mode = sum of condensation and droplet modes; ^(c)MMAD is mass mean aerodynamic diameter; ^(d)MSE is mass scattering efficiency.

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Fig. 1. The sampling location in urban Guangzhou in the Pearl River Delta (PRD) region of China.



Fig. 2. Continuous log-normal size distributions of chemical species mass concentrations in four seasons ($dlogD_a=0.01\mu m$).



Fig. 3. Continuous log-normal size distributions of the estimated chemical species number concentrations in four seasons ($dlogD_a=0.01\mu m$).



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Fig. 9. Continuous log-normal size distributions of $(NH_4)_2SO_4$ (a), NH_4NO_3 (b) and OM (c) mass scattering efficiencies (MSEs), mass concentrations, their σ values and MMADs in the droplet mode at wavelength of 550 nm under dry condition (relative humidity =40%).