

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

Jun Tao^{1,*}, Zhisheng Zhang¹, Yunfei Wu², Leiming Zhang^{3,*}, Zhijun Wu⁴, Peng Cheng⁵, Mei Li⁵, Laiguo Chen¹, Renjian Zhang², Junji Cao⁶

¹South China Institute of Environmental Sciences, Ministry of Environmental Protection, Guangzhou, China

²RCE-TEA, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China

³Air Quality Research Division, Science and Technology Branch, Environment and Climate Change Canada, Toronto, Canada

⁴State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China

⁵Institute of Mass Spectrometer and Atmospheric Environment, Jinan University, Guangzhou, China

⁶Key Laboratory of Aerosol Chemistry and Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China

*Correspondence to: (Leiming Zhang) leiming.zhang@canada.ca or (Jun Tao) taojun@scies.org

1 **Abstract.** To grasp the key factors affecting particle mass scattering efficiency (MSE),
2 particle mass and number size distribution, PM_{2.5} and PM₁₀ and their major chemical
3 compositions, and particle scattering coefficient (b_{sp}) under dry condition were
4 measured at an urban site in Guangzhou, south China during 2015-2016. On annual
5 average, 10±2%, 48±7% and 42±8% of PM₁₀ mass were in the condensation, droplet

6 and coarse modes, respectively, with mass mean aerodynamic diameters (MMADs) of
7 0.78 ± 0.07 in the droplet mode and 4.57 ± 0.42 μm in the coarse mode. The identified
8 chemical species mass concentrations can explain $79\pm 3\%$, $82\pm 6\%$ and $57\pm 6\%$ of the
9 total particle mass in the condensation, droplet and coarse mode, respectively. Organic
10 matter (OM) and elemental carbon (EC) in the condensation mode, OM, $(\text{NH}_4)_2\text{SO}_4$,
11 NH_4NO_3 and crustal element oxides in the droplet mode, and crustal element oxides,
12 OM and CaSO_4 in the coarse mode were the dominant chemical species in their
13 respective modes. The measured b_{sp} can be reconstructed to the level of $91\pm 10\%$ using
14 Mie theory with input of the estimated chemically-resolved number concentrations of
15 NaCl , NaNO_3 , Na_2SO_4 , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, K_2SO_4 , CaSO_4 , $\text{Ca}(\text{NO}_3)_2$, OM, EC,
16 crustal element oxides and unidentified fraction. MSEs of particle and individual
17 chemical species were underestimated by less than 13 % in any season based on the
18 estimated b_{sp} and chemical species mass concentrations. Seasonal average MSEs varied
19 in the range of 3.5 ± 0.1 to 3.9 ± 0.2 $\text{m}^2 \text{g}^{-1}$ for fine particles (aerodynamic diameter
20 smaller than 2.1 μm), which was mainly caused by seasonal variations of the mass
21 fractions and MSEs of the dominant chemical species (OM, NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$) in
22 the droplet mode. MSEs of the dominant chemical species were determined by their
23 log-normal size distribution parameters including MMADs and standard deviation (σ)
24 in the droplet mode.

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

27 **1. Introduction**

28 Light extinct coefficient (b_{ext}) of atmospheric particles, which is the sum of their
29 scattering (b_{sp}) and absorption (b_{ap}) coefficients, is a key index of haze weather (Hand
30 and Malm, 2007). In most cases, b_{sp} accounted for more than 90% of b_{ext} (Takemura et
31 al., 2002; Tao et al., 2017a). Numerous studies have demonstrated that haze is mainly

32 caused by high concentrations of fine particles ($PM_{2.5}$, with aerodynamic diameter
33 smaller than $2.5 \mu m$) (Hand and Malm, 2007; Huang et al., 2012; Malm et al., 1994;
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).
36 Knowledge of the dominant chemical species in $PM_{2.5}$ (e.g. $(NH_4)_2SO_4$, NH_4NO_3 and
37 OM) and their contributions to b_{sp} is crucial in making feasible policies for alleviating
38 haze (Watson, 2002).

39 Generally, b_{sp} can be estimated in reasonable accuracy using Mie theory when size
40 distributions of the dominant chemical species are known (Cheng et al., 2008; Cheng
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
44 Rule, the original and revised empirical formulas from the Interagency Monitoring of
45 Protected Visual Environments (IMPROVE) network were developed for
46 reconstructing b_{sp} based on the chemical species in $PM_{2.5}$ and coarse particle mass
47 concentrations monitored in the IMPROVE network (Pitchford et al., 2007; Watson,
48 2002). MSEs of the chemical species are important parameters not only for building the
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 $(NH_4)_2SO_4$, NH_4NO_3 , OM and fine soil (estimated from crustal
52 elements) in $PM_{2.5}$ were 3.0, 3.0, 4.0 and $1.0 m^2 g^{-1}$, 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 $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and OM in $\text{PM}_{2.5}$
57 were separated into small and large modes in the revised IMPROVE formula (Hand
58 and Malm, 2007).

59 China has been suffering from severe $\text{PM}_{2.5}$ pollution and haze weather (Li et al., 2016;
60 Ming et al., 2017; Wang et al., 2017; Zhang et al., 2013). To investigate the formation
61 of haze, the original and revised IMPROVE formulas have been directly applied in
62 many cities in China (Hua et al., 2015; Shen et al., 2014; Tao et al., 2009; Zhang et al.,
63 2012a; Zou et al., 2018). The IMPROVE formulas have been proved to over- or
64 underestimate b_{sp} in urban cities in China (Cao et al., 2012; Cheng et al., 2015; Han et
65 al., 2014; Jung et al., 2009a; Jung et al., 2009b; Tao et al., 2012; Tao et al., 2014), which
66 were likely due to the significantly different size distributions of the major chemical
67 components and related mass fractions in $\text{PM}_{2.5}$ between different countries or even
68 cities (Bian et al., 2014; Cabada et al., 2004; Chen et al., 2017; Guo et al., 2009; Lan et
69 al., 2011; Tian et al., 2014; Yao et al., 2003; Yu et al., 2010; Zhang et al., 2008; Zhuang
70 et al., 1999b). To reduce the uncertainties in the estimated b_{sp} using the original and
71 revised IMPROVE formulas, the average MSEs of the dominant chemical species were
72 typically estimated by the multiple linear regression method (Hand and Malm, 2007).

73 Although the estimated b_{sp} by the multiple linear regression model may be close to the
74 measured b_{sp} , the rationality of the estimated MSEs of chemical species were unknown.
75 Variations in size distributions of the chemical components (e.g., MMADs and mass

76 fractions) are important factors for hindering the application of the IMPROVE formulas
77 and multiple linear regression models. Although many studies have focused on size
78 distributions and chemical compositions of fine particles in China, few studies have
79 explored the relationship between the size distribution of major chemical species and
80 their MSEs (Cheng et al., 2008; Cheng et al., 2009; Gao et al., 2015). To fill this
81 knowledge gap, size-segregated particle mass, PM₁₀, PM_{2.5} and their major chemical
82 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 urban site in Guangzhou covering four seasons in 2015-2016. Size distributions of
85 dominant chemical components were first characterized in section 3.1, followed by
86 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 especially in urban areas.

91 **2. Methodology**

92 **2.1 Site description**

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

99

100

Insert Figure 1

101

102 **2.2 Field sampling**

103 Size-segregated particle samples were collected using Anderson 8-stage air samplers
104 with the cut-off points of 0.43, 0.65, 1.1, 2.1, 3.3, 4.7, 5.8 and 9.0 μm (Thermo-
105 electronic Company, USA). Two sets of samplers were used alternatively due to the
106 need of daily clearance of the instruments. The samplers were operated at an airflow
107 rate of 28.3 L min^{-1} . The sampling flow rate was controlled by a flow meter (Aalborg
108 Inc., USA). Samples were collected on 81 mm quartz fiber filter (Whatman QM-A).
109 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 $\text{PM}_{2.5}$ and PM_{10} samples were collected using two Gravisol Sequential Ambient
115 Particulate Monitor (GSAPM) samplers (APM Inc., Korea) at a flow rate of 16.7 L min^{-1} .
116 Samples were collected on 47 mm quartz fiber filter (Whatman QM-A). Sampling
117 durations were the same as those for collecting size-segregated samples in every season.
118 The sampling information is summarized in Table 1. Moreover, 8 sets of blank samples
119 were also collected for each of the size-segregated particle, $\text{PM}_{2.5}$ and PM_{10} samples
120 during the whole sampling period. Two sets of blank filters in each category were put
121 in the samplers without flow for 24 h when seasonal field campaigns finished. The
122 aerosol-loaded filter samples were stored in a freezer at $-18\text{ }^{\circ}\text{C}$ before analysis to
123 prevent volatilization of particles.

124

125

Insert Table 1

126

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

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

144 To exclude the impact of particle hygroscopic growth on the measured size distribution
145 and b_{sp}, ambient air is forced to pass through three total suspended particulate (TSP)
146 cyclones, then stainless steel tubes and the Nafion driers prior to be sampled by the
147 SMPS, APS and nephelometer. According to the method described in Kulkarni et al.
148 (2011), particle losses in different sizes from the tube are plotted in Fig. S1. Generally,

149 particle losses in the condensation (0.1-0.4 μm), droplet (0.4-2.1 μm) and coarse modes
150 (2.1-10 μm) were less than 1.3%, 0.3% and 0.1%, respectively, suggesting that the
151 particle losses from the tube were minimal. Ambient RH and temperature were
152 measured by an automatic meteorological station (Vaisala Company, Helsinki, Finland,
153 model MAWS201) at the SCIES site, and the seasonal average of these two
154 meteorological parameters were 53-75 % and 15-29 $^{\circ}\text{C}$, respectively. RH of aerosol
155 samples was controlled to be lower than 30% by sweeping dry air from a compressed
156 air pump. NO_3^- was measured using an In-situ instrument of Gas and Aerosol
157 Composition (IGAC, Model S-611, Machine Shop, Fortelice International Co., Ltd.,
158 Taiwan, China) at a resolution of 1-h (Tao et al., 2018).

159 **2.3 Lab chemical analysis and data quality assurance and control**

160 47 mm and 81 mm quartz fiber filters were measured gravimetrically for particle mass
161 concentration using a Sartorius ME 5-F electronic microbalance with a sensitivity of
162 $\pm 1 \mu\text{g}$ (Sartorius, Göttingen, Germany) after 24 h equilibration at temperature of
163 $23 \pm 1 \text{ }^{\circ}\text{C}$ and RH of $40 \pm 5\%$. Microbalance was calibrated by 5 mg, 200 mg and 5000
164 mg weights before weighting. Each filter was weighed at least three times before and
165 after sampling. Differences among replicate weights were mostly less than 20 μg for
166 each sample. Net mass was obtained by subtracting pre-weight from post-weight.

167 Three pieces of 0.526 cm^2 punches from each 47 mm quartz filter samples and one-
168 fourth of each 81 mm quartz filter samples were used to determine water-soluble
169 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 of $>18 \text{ M}\Omega$), and then subjected to ultrasonic agitation for 1 h for complete extraction
172 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^+ , NH_4^+ , K^+ ,
174 Mg^{2+} and Ca^{2+}) concentrations were determined by ion chromatography (Dionex ICS-
175 1600) using a CS12A column with 20 mM Methanesulfonic Acid eluent. Anions (SO_4^{2-} ,
176 NO_3^- , 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 mg L^{-1} .

181 OC and EC were analyzed using a DRI model 2001 carbon analyzer (Atmoslytic, Inc.,
182 Calabasas, CA, USA). An area of 0.526 cm^2 punched from each 47mm quartz filter and
183 1-4 dots punched from each 81mm quartz filter were analyzed for four OC fractions
184 (OC1, OC2, OC3, and OC4 at 140 °C, 280 °C, 480 °C, and 580 °C, respectively, in a
185 helium [He] atmosphere); OP (a pyrolyzed carbon fraction determined when
186 transmitted laser light attained its original intensity after oxygen [O_2] was added to the
187 analyzed atmosphere); and three EC fractions (EC1, EC2, and EC3 at 580 °C, 740 °C,
188 and 840 °C, respectively, in a 2% O_2 /98% He atmosphere). Here, OC is operationally
189 defined as $\text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{OP}$ and EC is defined as $\text{EC1} + \text{EC2} + \text{EC3} -$
190 OP for 47mm samples. However, OC is operationally defined as $\text{OC1} + \text{OC2} + \text{OC3} +$
191 OC4 and EC is defined as $\text{EC1} + \text{EC2} + \text{EC3}$ for 81mm samples due to extremely low
192 OP level. Average field blanks were subtracted from each sample filter. MDLs of OC
193 and EC were $0.41 \pm 0.2 \mu\text{gC cm}^{-2}$ and $0.03 \pm 0.2 \mu\text{gC cm}^{-2}$, respectively.
194 To obtain high quality data of the size distributions of major chemical components, bulk
195 $\text{PM}_{2.5}$ and PM_{10} samples were synchronously collected and the same chemical

196 components were analyzed. Generally, good correlations ($R^2 > 0.90$) were found in the
 197 mass concentrations of the total particle and major chemical components (including
 198 total carbon (TC), NO_3^- and SO_4^{2-}) between the size-segregated samples (PM_{10} and
 199 $\text{PM}_{2.1}$) and the GSAPM samplers (PM_{10} and $\text{PM}_{2.5}$). 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 **2.4 Data analysis methods**

203 The ISORROPIA II model was run at the reserved mode (Fountoukis and Nenes, 2007)
 204 with input data of K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , Na^+ , SO_4^{2-} , NO_3^- , Cl^- , RH (40%), and
 205 temperature (25°C), to estimate the size-resolved mass concentrations of NaCl, NaNO_3 ,
 206 Na_2SO_4 , NaHSO_4 , NH_4Cl , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , K_2SO_4 , KHSO_4 , KNO_3 ,
 207 KCl , MgSO_4 , $\text{Mg}(\text{NO}_3)_2$, MgCl_2 , CaSO_4 , $\text{Ca}(\text{NO}_3)_2$, CaCl_2 and H_2O . 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, NaNO_3 , Na_2SO_4 , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$,
 210 K_2SO_4 , $\text{Ca}(\text{NO}_3)_2$, CaSO_4 and H_2O were used to estimate b_{sp} in this study.

211 In this work, the cut-off point of 2.1 μm was chosen to separate the fine and coarse
 212 mode particles for investigating the impact of aerosol size distribution on their
 213 respective MSEs. Moreover, the cut-off sizes of $<0.43 \mu\text{m}$ and $0.43 - 2.1 \mu\text{m}$ were used
 214 to separate the condensation mode and droplet mode, respectively. Particle MSE was
 215 estimated by the sum of b_{sp} from individual chemical species divided by sum of particle
 216 mass concentration according to:

$$217 \quad \text{MSE} = \frac{\int_0^{D_{i,j}^{\text{max}}} b_{\text{sp}} dD_{i,j}}{\int_0^{D_{i,j}^{\text{max}}} c dD_{i,j}} \quad (1)$$

218 Where i is chemical species, j is chemical species size, $D_{i,j}$ is the chemical species
 219 diameter, and C is chemical species mass concentration.

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

$$221 \quad b_{sp} = \int_0^{D_{i,j}^{max}} \frac{\pi}{4} D_{i,j}^2 Q_{sp}(m_{i,j}, D_{i,j}, \lambda) N_{i,j} dD_{i,j} \quad (2)$$

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

$$225 \quad N = \frac{6C}{\pi\rho D^3} \quad (3)$$

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

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

$$231 \quad D_a = D_g / (\rho)^{0.5} \quad (4)$$

$$232 \quad \rho = \frac{\sum_{chemical\ species} m_i}{\sum_{chemical\ species} \frac{m_i}{\rho_i}} \quad (5)$$

233 Where ρ represents the daily average density of particle, i is chemical species, m_i is
234 chemical species mass concentration in a bin, and ρ_i is chemical species density. The
235 seasonal average densities of particle are shown in Fig. S4.

236 Continuous size-distribution profiles of major chemical species are needed in order to
237 accurately calculate b_{sp} using Mie theory. To improve the resolution of b_{sp} , 401 bins
238 were used for chemical species ranging from 10 nm to 100 μ m, with a constant ratio
239 between the adjacent size bins, defined as $\log_{10}(D_{a2}/D_{a1})=0.01$. Further increasing the
240 number of size bins does not have any significant impact on the results, e.g., the changes
241 in b_{sp} are smaller than 1% even if the above ratio of 0.01 is replaced with 0.001.
242 Continuous size-distribution profiles of major chemical species are obtained from the
243 inversion of the measured mass concentration distribution in the size bins of the

244 Anderson 8-stage air samplers, using the technique described in Dong et al. (2004). The
 245 key formulas to calculate the normal distribution of density function ($f(D, \mu, \sigma)$) were
 246 summarized as follows:

$$247 \quad f(D, \mu, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\left(\frac{(D-\mu)^2}{2\sigma^2}\right)} \quad (6)$$

$$248 \quad \mu = \bar{y} - \mu\bar{x} \quad (7)$$

$$249 \quad \sigma = \frac{n\sum xy - \sum x \times \sum y}{n\sum x^2 - (\sum x)^2} \quad (8)$$

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

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

$$259 \quad \text{MMADs} = (D_{a1} \times D_{a2})^{0.5} \quad (9)$$

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

262 **3. Results and Discussion**

263 **3.1 Size distributions of total particle mass and major chemical components**

264 **3.1.1 Total particle mass**

265 Generally, any particle size distribution can be fitted into a combination of condensation,
 266 droplet and coarse modes (John et al., 1990). Continuous log-normal size distributions
 267 of particle mass including the condensation, droplet and coarse modes were calculated
 268 using the method described in section 2.4 and are summarized in Table 2. On annual

269 average, $10\pm 2\%$, $48\pm 7\%$ and $42\pm 8\%$ of total mass in the size-segregated samples were
270 in the condensation, droplet and coarse modes, respectively, with the average MMADs
271 being $0.78\pm 0.07\ \mu\text{m}$ in the droplet mode and $4.57\pm 0.42\ \mu\text{m}$ in the coarse mode. These
272 values were comparable to those observed by the Micro-Orifice Uniform Deposit
273 Impactor (MOUDI) in the other cities (e.g. Shenzhen and Hong Kong) of the Pearl
274 River Delta (PRD) region (Bian et al., 2014; Lan et al., 2011; Yu et al., 2010).
275 The estimated annual $\text{PM}_{2.5}$ concentration based on the continuous log-normal size
276 distribution was $36.4\pm 13.2\ \mu\text{g m}^{-3}$, which was close to the synchronously measured
277 $\text{PM}_{2.5}$ ($36.8\pm 15.3\ \mu\text{g m}^{-3}$), although slightly higher than the sum of the mass
278 concentrations ($34.9\pm 13.8\ \mu\text{g m}^{-3}$) in the condensation and droplet modes. Thus, the
279 fine (sum of condensation and droplet) mode particles can reasonably represent $\text{PM}_{2.5}$.
280 Seasonal average particle mass concentrations were evidently lower in summer than in
281 the other seasons for the condensation and droplet modes, and were similar during
282 spring, autumn and winter for all the three modes. These results agree with the seasonal
283 variations of $\text{PM}_{2.5}$ observed at the same site in 2009-2010 (Tao et al., 2014).

284

285 *Insert Table 2*

286

287 **3.1.2 Water-soluble inorganic ions**

288 Generally, SO_4^{2-} , NO_3^- and NH_4^+ are the dominant WSIs, especially in the
289 condensation and droplet modes. They are mainly formed through aqueous-phase
290 reactions in moisture conditions in the PRD region (Lan et al., 2011; Yu et al., 2010).
291 As expected, $77\pm 6\%$ SO_4^{2-} , $46\pm 16\%$ NO_3^- and $89\pm 7\%$ of NH_4^+ mass concentrations
292 were in the droplet mode on annual average due to their aqueous-phase formations
293 (Table 2). Much lower fractions for NO_3^- than SO_4^{2-} and NH_4^+ in the droplet mode were

294 mostly due to the high volatility of NH_4NO_3 (Zhang et al., 2008). The MMADs of the
295 three ions in the droplet mode were in the range of 0.70-0.94 μm , comparable with
296 MOUDI measurements (0.78-1.03 μm) conducted in the PRD region (Bian et al., 2014;
297 Lan et al., 2011; Yu et al., 2010).

298 Small fractions of SO_4^{2-} , NO_3^- and NH_4^+ masses were distributed in the condensation
299 mode, e.g., $12\pm 4\%$, $10\pm 4\%$ and $6\pm 5\%$, respectively, on annual average. The mass
300 fractions of SO_4^{2-} in the condensation mode shown above were much lower than those
301 ($24\text{-}29\%$) observed in urban Guangzhou in 2006-2007 (Yu et al., 2010), suggesting gas-
302 phase chemical reactions of SO_2 has become less important in the formation of SO_4^{2-} ,
303 likely due to the dramatic reduction of SO_2 emissions in urban or suburban Guangzhou
304 in the recent decade (Zheng et al., 2009; Zheng et al., 2018).

305 $11\pm 5\%$ SO_4^{2-} , $44\pm 18\%$ NO_3^- and $5\pm 4\%$ of NH_4^+ mass concentrations were distributed
306 in the coarse mode. In general, NO_3^- mainly exists in the form of NH_4NO_3 in the
307 condensation and droplet modes and associates with base cations in the coarse mode
308 (e.g., $\text{Ca}(\text{NO}_3)_2$ and NaNO_3) (Zhang et al., 2015a). More than 50% NO_3^- mass
309 concentrations were distributed in the coarse mode in summer and autumn when
310 ambient temperatures were high. The MMADs of NO_3^- in the coarse mode were
311 4.15 ± 0.52 and 4.36 ± 0.31 μm in summer and autumn, respectively, slightly lower than
312 those of Ca^{2+} (4.10 ± 0.42 and 4.72 ± 0.47 μm in the same seasons), but evidently higher
313 than those of Na^+ (3.60 ± 0.19 and 3.64 ± 0.27 μm) (Table 2). This suggests that NH_4NO_3
314 was prone to dissociate to $\text{HNO}_{3(\text{g})}$ in summer and autumn due to the high ambient
315 temperatures with released $\text{HNO}_{3(\text{g})}$ further reacting with mineral dust and to a less
316 extent with sea salt particles. In comparison, the MMADs of SO_4^{2-} in the coarse mode
317 were in between of those of Ca^{2+} and Na^+ , likely due to uptake of $\text{H}_2\text{SO}_{4(\text{g})}$ by both
318 mineral dust and sea salt particles (Zhang et al., 2015a). In contrast, the MMAD of

319 NH_4^+ in the coarse mode was $3.25 \pm 0.69 \mu\text{m}$, much smaller than those of SO_4^{2-} and NO_3^- ,
320 suggesting that NH_4^+ in the coarse mode was likely from hygroscopic growth of NH_4^+
321 in the droplet mode (Tian et al., 2014).

322 It is also worth mentioning that most of Cl^- was distributed in the coarse mode and its
323 MMAD ($3.77 \pm 0.35 \mu\text{m}$) was very close to that of Na^+ ($3.75 \pm 0.38 \mu\text{m}$), especially in
324 summer when air masses were originated from the China South Sea (Tao et al., 2017b;
325 Xia et al., 2017). The mole ratios of Cl^-/Na^+ were less than 1.0 in all the seasons but
326 spring due to the reactions between sea salt and acid gasses ($\text{HNO}_{3(\text{g})}$ and $\text{H}_2\text{SO}_{4(\text{g})}$)
327 (Zhuang et al., 1999a). The excess Cl^- in the coarse mode in spring was likely due to
328 the aged biomass burning particles from the southeast Asian (Zhang et al., 2015c). In
329 fact, the concentration of the typical biomass burning tracer K^+ in the coarse mode was
330 higher in spring than in the other seasons (Fig. S5). In any case, sea salt was mainly
331 distributed in the coarse mode rather than the droplet mode in urban Guangzhou.

332 **3.1.3 OC and EC**

333 OC and EC in fine particles can be produced from both primary emissions of vehicle
334 exhaust, coal combustion, biomass burning and secondary formation (Chow et al., 2011;
335 Gentner et al., 2012; Gentner et al., 2017; Hallquist et al., 2009; Zheng et al., 2006). In
336 general, fresh OC and EC particles emitted from vehicle exhaust, coal combustion and
337 biomass burning should be distributed in the condensation mode (Schwarz et al., 2008;
338 Zhang et al., 2012b). Only $13 \pm 4\%$ of OC and $31 \pm 7\%$ of EC mass concentrations were
339 distributed in the condensation mode in the present study (Table 2). OC/EC ratios were
340 in the range of 0.9-1.6 in the condensation mode, suggesting that vehicle exhaust was
341 the dominant source of OC and EC in this particle size range (Huang et al., 2006a;
342 Schwarz et al., 2008; Shiraiwa et al., 2007; Watson et al., 2001; Wu et al., 2017). $62 \pm 9\%$
343 of OC and $55 \pm 7\%$ of EC mass concentrations were distributed in the droplet mode

344 (Table 2), similar to that of SO_4^{2-} . These numbers were similar to those observed in the
345 other cities of the PRD region, and was previously identified to be mainly caused by
346 in-cloud aerosol processing (Huang et al., 2006b). Cloud processing indeed plays
347 important roles in forming droplet mode aerosols in urban Guangzhou (Tao et al., 2018).
348 OC/EC ratios were in the range of 2.2-3.2 in the droplet mode, much higher than those
349 in the condensation mode, suggesting that OC in the droplet mode was mainly aged or
350 secondary particles (Day et al., 2015; Huang et al., 2006a; Wu and Yu, 2016).
351 The MMADs of OC and EC in the droplet mode were $0.76\pm 0.07 \mu\text{m}$ and $0.66\pm 0.08 \mu\text{m}$,
352 respectively, which were slightly lower than those ($0.7\text{-}1.0 \mu\text{m}$ for OC and $0.8\text{-}1.0 \mu\text{m}$
353 for EC) found in earlier studies in the PRD region (e.g. Guangzhou, Hong Kong and
354 Shenzhen) (Lan et al., 2011; Yu et al., 2010). Noticeably, the MMADs of OC and EC
355 in the droplet mode were very close to those ($0.73 \mu\text{m}$ for OC and $0.77 \mu\text{m}$ for EC)
356 measured in summer at a suburban site of Hong Kong, where the loadings of the
357 dominant chemical components (e.g. OC, EC and SO_4^{2-}) were low (Yu et al., 2010).
358 Road dust and biogenic aerosols were generally considered as the major sources of OC
359 and EC in the coarse mode (Ho et al., 2003; Zhang et al., 2015b). Significant fractions
360 of OC ($25\pm 8\%$) and EC ($14\pm 7\%$) mass concentrations were distributed in the coarse
361 mode. These numbers were comparable with those ($13\text{-}38\%$ for OC and $4\text{-}16\%$ for EC)
362 measured at suburban sites of Guangzhou, Shenzhen and Hong Kong (Lan et al., 2011;
363 Yu et al., 2010), but were lower than those ($51\text{-}57\%$ for OC and $17\text{-}21\%$ for EC)
364 measured in urban Guangzhou in 2006-2007. The MMADs of OC ($3.73\pm 0.58 \mu\text{m}$) and
365 EC ($3.69\pm 0.65 \mu\text{m}$) in the coarse mode were close to those ($3.8\text{-}4.3 \mu\text{m}$ for OC and 3.7-
366 $4.1 \mu\text{m}$ for EC) measured in suburban of Hong Kong, although smaller than those (4.8-
367 $5.2 \mu\text{m}$ for OC and $5.0\text{-}5.2 \mu\text{m}$ for EC) measured in suburban of Shenzhen and urban
368 of Guangzhou (Lan et al., 2011; Yu et al., 2010). These results suggested that the

369 MMADs of OC and EC might decrease with their decreasing coarse mode mass
370 fractions. Annual average PM₁₀ concentrations (46 μg m⁻³) in 2015-2016 in the PRD
371 region were about 40% lower than that (76 μg m⁻³) in 2006-2007, which further
372 supported the above hypothesis.

373 **3.2 Closure of particle mass, number concentration, and b_{sp}**

374 **3.2.1 Closure of particle mass concentration**

375 To investigate the impact of chemical species in different size modes on b_{sp}, particle
376 mass concentrations in the different modes were first reconstructed based on mass
377 concentrations of individual known chemical components. The dominant water-soluble
378 inorganic species including NaCl, NaNO₃, Na₂SO₄, NH₄NO₃, (NH₄)₂SO₄, K₂SO₄,
379 CaSO₄ and Ca(NO₃)₂ were determined using the ISORROPIA II thermodynamic
380 equilibrium model as mentioned in section 2.4. A ratio of OM to OC of 1.4, 1.6 and 1.6
381 would be appropriate for the condensation, droplet and coarse mode, respectively,
382 which was based on the findings of a previous study that suggested an average OM/OC
383 ratio of 1.57 and a range of 1.4-1.8 in an urban environment of the PRD region (He et
384 al., 2011). In our previous study (Tao et al., 2017b), mass concentration of crustal
385 element oxides in PM_{2.5} was estimated from the measurements of five crustal elements
386 (Al, Si, Ca, Fe and Ti) in urban Guangzhou. This approach cannot be used in the present
387 study due to the lack of crustal elements measurements. Alternatively, crustal element
388 oxides mass concentration was estimated from Ca²⁺ mass concentration because of their
389 good correlations (slope=0.053, R²=0.79) as was found in a previous study (Fig. S6)
390 (Tao et al., 2017b). It was suggested that Ca²⁺ accounted for 5.3% of crustal element
391 oxides in PM_{2.5} in urban Guangzhou, a value that is close to the content of Ca²⁺ (5.0%)
392 in soil dust source profiles (representing crustal element oxides) in PM_{2.5} in cities of
393 southern China (Sun et al., 2019). Because CaSO₄ and Ca(NO₃)₂ were mainly from the

394 reactions between calcium oxide and acids (e.g. H_2SO_4 and HNO_3), the estimated mass
395 concentration of crustal element oxides needs to deduct those of CaSO_4 and $\text{Ca}(\text{NO}_3)_2$.
396 On annual average, the estimated crustal element oxides accounted for $8\pm 2\%$, $10\pm 4\%$
397 and $29\pm 5\%$ of the total particle mass concentrations in the condensation, droplet and
398 coarse mode, respectively. The reconstructed mass concentrations accounted for $79\pm 3\%$,
399 $82\pm 6\%$ and $57\pm 6\%$ of the total in the condensation, droplet and coarse mode,
400 respectively.

401 As shown in Fig. 2, OM, EC, $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and crustal element oxides
402 dominated in different modes in four seasons. For example, OM and EC accounted for
403 31-39% and 14-19%, respectively, of particle mass in the condensation mode, OM,
404 $(\text{NH}_4)_2\text{SO}_4$, crustal element oxides and NH_4NO_3 accounted for 19-34%, 18-22%, 6-15%
405 and 4-11%, respectively, in the droplet mode, and crustal element oxides, OM and
406 CaSO_4 accounted for 22-34%, 12-17% and 4-5%, respectively, in the coarse mode. In
407 addition, the total of the other identified chemical species only accounted for less than
408 10% of the total particle mass in every mode. For example, Na_2SO_4 and K_2SO_4 mainly
409 distributed in the droplet mode and together they accounted for only 2-5% of the
410 particle mass in this mode. NaCl , NaNO_3 and $\text{Ca}(\text{NO}_3)_2$ mainly distributed in the coarse
411 mode and each of these species accounted for less than 2% of the total particle mass in
412 this mode.

413

414 *Insert Figure 2*

415

416 **3.2.2 Closure of particle number concentration**

417 To estimate the contribution of individual chemical species on b_{sp} using Mie theory,
418 number size distributions of the dominant chemical species were needed and were

419 calculated according to the method described in section 2.4. As shown in Fig. 3, most
420 chemical species (except $(\text{NH}_4)_2\text{SO}_4$ in summer) had much higher number
421 concentrations in the condensation than droplet or coarse mode. The estimated number
422 mean aerodynamic diameters (NMADs) of the number concentrations of individual
423 chemical species mainly distributed in the range of 100-120 nm. The estimated NMADs
424 of particle number concentrations (sum of individual chemical species number
425 concentrations in the same size bin) were close to about 100 nm in the four seasons,
426 which was larger than the NMADs (30-70 nm) of the simultaneously measured particle
427 number concentrations by the SMPS and APS (Fig. 4). This was because SMPS and
428 APS collected dried particles while the size-segregated sampler collected ambient
429 particles. D_p of particles measured by SMPS can be converted to D_a using the average
430 particle density calculated from the synchronously measured size-segregated individual
431 chemical species mass concentrations and densities according to the method described
432 in section 2.4. In any case, the NMADs of particle number concentrations were less
433 than 100 nm regardless of using SMPS and APS measurements or the estimated size-
434 segregated chemical species mass concentrations.

435 As shown in Fig. 3 and Fig. 4, most of particle numbers were in the range of 10 - 400
436 nm either observed by the SMPS or estimated from the size-segregated chemical
437 species mass concentrations. Total particle number concentration in the range of 10 nm-
438 10 μm measured by the SMPS and APS were $7038 \pm 2250 \text{ cm}^{-3}$, $9774 \pm 1471 \text{ cm}^{-3}$,
439 $5694 \pm 1942 \text{ cm}^{-3}$ and $10801 \pm 2986 \text{ cm}^{-3}$ in spring, summer, autumn and winter,
440 respectively, which were 1.09 ± 0.24 , 2.66 ± 0.48 , 1.05 ± 0.20 and 2.33 ± 0.67 times of those
441 estimated by the size-segregated chemical species mass concentrations.

442 NMADs estimated from the size-segregated chemical species mass concentrations were
443 close to those measured by the SMPS and APS in spring and autumn, resulting in the

444 close estimation of particle number concentrations to the measured ones. In contrast,
445 the estimated particle number concentrations from the the size-segregated chemical
446 species mass concentrations were evidently lower than those measured by the SMPS
447 and APS in summer and winter, due to the much higher NMADs (100 nm) estimated
448 from the size-segregated chemical species mass concentrations than those (about 30 or
449 40 nm) measured by the SMPS and APS.

450 To exclude the large uncertainties in the estimated particle number concentration caused
451 by condensation mode particles (which were due to the design flaws of size-segregated
452 sampler), particles smaller than 430 nm were not included in the calculation below. On
453 annual average, the estimated particle number concentrations in the range of 430 nm-
454 10 μm based on the size-segregated chemical species mass concentrations were $33\pm 42\%$
455 higher than those measured by the SMPS and APS. This was likely because particles in
456 the droplet mode may shift to the smaller sizes (<430 nm) during the dry process by
457 Nafion tube. Correlation coefficients between the estimated and measured particle
458 number concentrations in the range of 430 nm-10 μm were significantly improved when
459 the intercepts in the linear regression equations were retained. To some extent, the
460 intercepts represent the measurement errors of SMPS and APS and estimation errors of
461 the inversion technique and ISORROPIA II models. In any case, good correlations
462 ($R^2 > 0.81$) between the estimated daily particle number concentrations and the measured
463 ones were found and the slopes ranged from 0.79 to 1.03 in the four seasons (Fig. 5).
464 These results suggested that the estimated particle number concentrations were
465 acceptable in the range of 430 nm-10 μm , noting that particles in this size range
466 dominate particle scattering efficiency.

467

468

Insert Figure 3

469

Insert Figure 4

470

Insert Figure 5

471

472

473 **3.2.3 Closure between the measured and estimated b_{sp}**

474 Daily b_{sp} was estimated using Mie model (in section 2.4) with input parameters
475 including refractive indices, densities and number concentrations in 401 bins of
476 chemical species (NaCl, NaNO₃, Na₂SO₄, (NH₄)₂SO₄, NH₄NO₃, K₂SO₄, CaSO₄,
477 Ca(NO₃)₂, H₂O, OM, EC, crustal element oxides and unidentified fraction). The
478 refractive indices and densities of above chemical species are summarized in Table S1.
479 Although the number concentrations in the condensation mode were underestimated,
480 good correlations ($R^2 > 0.92$) were found between the measured and estimated b_{sp} with
481 the slopes being 0.87, 0.87, 0.85 and 0.89 in spring, summer, autumn and winter,
482 respectively (Fig. 6). On annual arithmetic average, the estimated b_{sp} can explain $91 \pm 10\%$
483 of the measured b_{sp} . The residual fractions were likely related to the chosen convert
484 factor between OM and OC, measurements and sampling errors of chemical species
485 (especially NO₃⁻), errors from the models (ISORROPIA II model, Mie model, and the
486 inversion technique method), and measurement errors caused by the size-segregated
487 sampler (Vaughan, 1989). Magnitudes of the uncertainties caused by these sources are
488 discussed below.

489 Although the convert factor of 1.6 between OM and OC was reasonable in urban
490 environment, a value of as high as 1.8 was found in literature (He et al., 2011). In
491 addition, OC mass concentrations were likely underestimated due to the OC/EC
492 protocol for size-segregated samples. Nevertheless, the estimated b_{sp} can only be
493 increased by less than 3% if increasing the convert factor to 1.8 in the droplet mode.

494 Note that a previous study at the Fresno Supersite increased the estimated b_{sp} by about
495 10% when increasing the convert factor from 1.4 to 1.8, likely due to the high mass
496 fraction of OC in fine particle at this site (Watson et al., 2008).

497 Different from the other chemical species, NH_4NO_3 can dissociate into $HNO_{3(g)}$ and
498 $NH_{3(g)}$ during the filter gravimetric weighing process under dry condition. To evaluate
499 the evaporative loss of NH_4NO_3 , synchronous inline data of NO_3^- were also measured
500 by an In-situ Gas and Aerosol Composition monitoring system at hourly temporal
501 resolution (Fig. S7). Seasonal average NO_3^- concentrations were 42% ($PM_{2.5}$), 39%
502 (PM_{10}), 42% ($PM_{2.5}$) and 19% ($PM_{2.5}$) less from filter measurements than inline
503 measurements in spring, summer, autumn and winter, respectively. Adjusting the filter
504 NO_3^- data using the above ratios can increase the estimated b_{sp} by 7%, 2%, 4% and 2%
505 in the respective season.

506

507 *Insert Figure 6*

508

509 Meanwhile, the measured b_{sp} could also be underestimated due to the dissociation of
510 NH_4NO_3 during the dry processes of ambient particles through the Nafion dryer. A
511 previous study indicated the measured b_{sp} being decreased by less than 10% due to the
512 dissociation of NH_4NO_3 in a heated nephelometer (Bergin et al., 1997). In the present
513 study, the chamber temperatures of nephelometer were less than 300 K and the particle
514 residence time in both the Nafion dryer and the nephelometer chamber was about 7
515 seconds. Thus, the bias in the measured b_{sp} should be less than 2% in any season
516 according to the relationship among the loss of b_{sp} , residence time and the temperature
517 in chamber in a previous study (Bergin et al., 1997). Combining all of the above-
518 mentioned factors, the adjusted estimated b_{sp} would increase to the level of 92%, 87%,

519 87% and 89% of the measured b_{sp} in spring, summer, autumn and winter, respectively.
520 This means the above methods for estimating b_{sp} were reasonable with the adjusted
521 estimated values explaining 87-92% of the measured values after the filter-based NO_3^-
522 concentrations were adjusted based on the inline data. Thus, the errors from the models
523 and size-segregated samplers may account for the remaining 8-13% of the measured
524 b_{sp} . Moreover, the size distributions would be different under dry and ambient
525 conditions due to the particle hygroscopic properties. In fact, the NMADs of particle
526 measured by SMPS and APS under dry condition were less than those measured by the
527 size-segregated sampler under ambient condition according to section 3.2.2. Thus, the
528 estimated b_{sp} based on size distributions of chemical species would be systematically
529 higher to some extent than the measured b_{sp} under dry condition.

530 Generally, the estimated seasonal average b_{sp} were $146 \pm 40 \text{ Mm}^{-1}$, $99 \pm 33 \text{ Mm}^{-1}$, 169 ± 54
531 Mm^{-1} and $151 \pm 71 \text{ Mm}^{-1}$ in spring, summer, autumn and winter, respectively (Fig. 7).
532 The particles in the condensation, droplet and coarse modes contributed 6-7%, 81-86%
533 and 8-12%, respectively, to the estimated b_{sp} . OM and EC were the dominant
534 contributors, accounting for 32-41% and 30-37%, respectively, of the estimated b_{sp} in
535 the condensation mode. OM and secondary inorganic aerosols (sum of $(\text{NH}_4)_2\text{SO}_4$ and
536 NH_4NO_3) were the dominant contributors, accounting for 27-44% and 27-34%,
537 respectively, of the estimated b_{sp} in the droplet mode. Unidentified fraction, crustal
538 element oxides and OM were the dominant contributors, accounting for 26-47%, 16-
539 29% and 19-27%, respectively, of the estimated b_{sp} in the coarse mode. The sum of the
540 dominant contributors, including OM, EC, secondary inorganic aerosols and crustal
541 element oxides, accounted for 70-79% of the estimated b_{sp} in the four seasons. In
542 contrast, the sum of the other chemical species (including NaCl, NaNO_3 , Na_2SO_4 ,
543 K_2SO_4 , CaSO_4 , $\text{Ca}(\text{NO}_3)_2$, H_2O) accounted for 5-10% and the unidentified fraction, 12-

544 23% of the estimated b_{sp} . In conclusion, visibility degradation was determined by the
545 dominant chemical species (e.g. OM, EC, secondary inorganic aerosols and crustal
546 element oxides) in the fine mode (both condensation and droplet), which agreed with
547 the results of the original and revised IMPORVE formulas (Pitchford et al., 2007).

548

549

Insert Figure 7

550

551 **3.3 Key factors for variations of particle and chemical species MSEs**

552 **3.3.1 The estimated MSEs of particle and chemical species**

553 To conveniently explore the control factors of particle MSE, the dominant chemical
554 species' MSEs were estimated by their mass concentrations and the estimated b_{sp} ,
555 according to the measured chemical species mass concentrations in section 3.1 and the
556 estimated b_{sp} in section 3.2. Here, only the MSEs of $(NH_4)_2SO_4$, NH_4NO_3 , OM, EC,
557 crustal element oxides and unidentified fraction in the condensation, droplet, fine (sum
558 of condensation and droplet), and coarse modes were estimated (Table 3), considering
559 these chemical species accounted for more than 90% of the estimated b_{sp} . However,
560 particle MSEs in the condensation, droplet, fine and coarse modes were estimated by
561 sum of b_{sp} from individual chemical species divided by sum of particle mass
562 concentration according to formula (9). Moreover, an external mixing of individual
563 chemical species was assumed in the estimation. Generally, good correlations ($R^2 > 0.79$)
564 were found between the measured and estimated b_{sp} using the average MSEs of
565 chemical species in Table 3 with the slopes being 0.85, 0.84, 0.76 and 0.84 in spring,
566 summer, autumn and winter, respectively (Fig. S8). Thus, the estimated MSEs of
567 chemical species in Table 3 were underestimated.

568

Insert Table 3

569

570

571 Undoubtedly, the particle MSE should be also underestimated because the estimated b_{sp}
572 was 11-15% less of the measured b_{sp} in four seasons, as discussed in section 3.2. The
573 measured b_{sp} would be biased low by about 3% due to the evaporation of NH_4NO_3 ,
574 while the NO_3^- mass concentrations based the filter measurements were biased low by
575 5%, 3%, 9% and 6% in spring, summer, autumn and winter, respectively. Thus, the
576 MSEs of NO_3^- would be underestimated by 9%, 13%, 6% and 5% in the respective
577 season in the real world. In conclusion, the MSEs of particle and chemical species were
578 underestimated by less than 13%.

579 On annual average, the estimated particle MSEs in the condensation, droplet and coarse
580 modes were $2.1 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$, $4.3 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$ and $0.5 \pm 0.0 \text{ m}^2 \text{ g}^{-1}$, respectively. The
581 estimated particle MSE in the fine (sum of condensation and droplet) mode, similar to
582 $PM_{2.5}$ was $3.7 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$, which was slightly higher than the value of $3.5 \text{ m}^2 \text{ g}^{-1}$
583 estimated in 2009-2010 in urban Guangzhou (Tao et al., 2014). Seasonal variations of
584 the estimated MSEs in the fine mode followed the sequence of winter ($3.9 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$
585 1) > autumn ($3.8 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$) > summer ($3.6 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$) > spring ($3.5 \pm 0.1 \text{ m}^2 \text{ g}^{-1}$).
586 Evidently, the estimated MSEs in the fine mode were slightly higher in autumn and
587 winter than spring and summer, which also agreed with the previous studies in urban
588 Guangzhou (Andreae et al., 2008; Jung et al., 2009a).

589 On annual average, the estimated MSEs of $(NH_4)_2SO_4$, NH_4NO_3 , OM and crustal
590 element oxides (equal to fine soil in the IMPROVE formulas) in the fine mode were
591 4.4 ± 0.8 , 4.5 ± 1.5 , 4.6 ± 0.3 and $2.6 \pm 0.1 \text{ m}^2 \text{ g}^{-1}$, respectively, which were higher than those
592 (3.0 , 3.0 , 4.0 and $1.0 \text{ m}^2 \text{ g}^{-1}$, respectively) from using the original IMPROVE formula
593 (Hand and Malm, 2007; Malm and Hand, 2007; Pitchford et al., 2007). As shown in

594 Table 3, the MSEs of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , OM and crustal element oxides in the fine
595 mode depended on their mass fractions in the droplet mode with high MSEs. In the
596 original IMPROVE formula, MSEs of these chemical species were estimated using the
597 multiple linear regression model according to the chemical components in $\text{PM}_{2.5}$ and
598 b_{sp} from IMPROVE network, noting that significant mass fractions of particle were in
599 the condensation mode at the regional sites of IMPROVE network and an urban site in
600 U.S.A. (Cabada et al., 2004; Hand et al., 2002; Malm et al., 2003). In contrast, in the
601 present study most mass fractions of the dominant chemical species (e.g. $(\text{NH}_4)_2\text{SO}_4$,
602 NH_4NO_3 and OM) in the fine mode were distributed in the droplet rather than
603 condensation mode. These results suggested the higher MSEs of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3
604 and OM in the fine mode in this study were likely due to their significant mass fractions
605 in the droplet mode. In fact, the MSE of fine soil in the IMPROVE formulas would
606 represent the MSE of the bulk mode rather than the fine mode (Hand and Malm, 2007).
607 The average MSEs of the bulk mode was $1.0 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$ in this study, which was similar
608 to that in the IMPROVE formulas.

609 On annual average, the estimated MSEs of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and OM were 4.7 ± 0.6 ,
610 4.8 ± 0.9 and $5.3 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$ in the droplet mode, and were 2.1 ± 0.5 , 2.3 ± 0.8 and 2.7 ± 0.1
611 $\text{m}^2 \text{ g}^{-1}$ in the condensation mode, respectively, which were lower than those in the large
612 mode (similar to droplet mode) and were slightly lower than those in the small mode
613 (similar to condensation mode) in the revised IMPROVE formula (Pitchford et al.,
614 2007). Theoretically, the highest MSEs of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and OM would be
615 found at about $0.55 \mu\text{m}$ in geometric mass mean diameters (GMMD) at the wavelength
616 550 nm according to Mie theory. However, the MMADs of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and
617 OM were $0.76 - 0.80 \mu\text{m}$ (equal to about $0.60 - 0.64 \mu\text{m}$ in GMMD) in the droplet mode
618 and were $0.21 \mu\text{m}$ (equal to about $0.16 - 0.18 \mu\text{m}$ in GMMD) in the condensation mode

619 in this study, which were larger than 0.50 μm in GMMD in the large mode and were
620 lower than 0.20 μm in GMMD in the small mode in the revised IMPROVE formula.
621 Thus, the higher GMMDs in the droplet mode and the lower GMMDs of $(\text{NH}_4)_2\text{SO}_4$,
622 NH_4NO_3 and OM in the condensation mode in this study likely resulted in their lower
623 MSEs compared with those in the revised IMPROVE formula. In addition, the
624 underestimated b_{sp} would also result in underestimating their MSEs in the condensation
625 and droplet modes in this study.

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

641 **3.3.2 Impact of size distribution on particle and chemical species MSE**

642 As discussed in section 3.3.1, seasonal average MSEs in the coarse mode fluctuated in
643 a small range of 0.4-0.5 $\text{m}^2 \text{ g}^{-1}$, while those in the fine mode in a slightly larger range

644 of 3.5-3.9 m² g⁻¹, but the percentage changes are in similar magnitudes (10-20%). Only
645 variations of fine particle MSE were discussed below as an example. It is worth to
646 mention that fine particle MSE increased with its mass concentrations in IMPROVE
647 network (Lowenthal and Kumar, 2004), but such a phenomenon was not founded in the
648 present study. As shown in Fig. 8, the seasonal variations of fine particle MSE were
649 mainly caused by particle fractions in the size range of 0.4-0.9 μm, which belong to the
650 droplet mode. In this mode, the MSEs of (NH₄)₂SO₄ and NH₄NO₃ and OM were higher
651 while those of the other chemical species were lower than the overall particle MSE.
652 Note that the overall particle MSE depends on the mass concentrations and MSEs of
653 individual chemical components. Thus, the seasonal average MSEs of fine particle were
654 dominated by the seasonal average mass fractions and associated MSEs of (NH₄)₂SO₄
655 and NH₄NO₃ and OM in the droplet mode.

656

657 *Insert Figure 8*

658

659 The sum of the products of seasonal average mass concentration and MSEs of the above
660 three chemical species in the droplet mode was 1.8, 2.1, 2.3 and 2.5 m² g⁻¹ in spring,
661 summer, autumn and winter, respectively. As expected, the seasonal variations of fine
662 particle MSE followed the sequences of winter (3.9±0.2 m² g⁻¹) > autumn (3.8±0.2 m²
663 g⁻¹) > summer (3.6±0.2 m² g⁻¹) > spring (3.5±0.1 m² g⁻¹). Noticeably, fine particle MSE
664 was determined by the average MSEs of the dominant chemical species, rather than
665 their mass fractions which were much smaller than 1.0.

666 Different from the approach used for fine particle MSE, the MSEs of $(\text{NH}_4)_2\text{SO}_4$,
667 NH_4NO_3 and OM in the droplet mode were determined using measurement-based their
668 mass size distributions prescribed as log-normal size distributions. In theory (section
669 2.4), the log-normal size distribution of chemical species is determined by three
670 parameters include mass concentration (in the range of 0.43 - 2.1 μm), MMAD and
671 standard deviation (σ), which control the area, mode and scale of the log-normal size
672 distribution, respectively. Thus, the MSEs of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and OM should
673 depend on their MMADs and σ values. Seasonal average σ values of $(\text{NH}_4)_2\text{SO}_4$,
674 NH_4NO_3 and OM were in the range of 0.18-0.21, 0.18-0.21 and 0.22-0.26, respectively,
675 while the corresponding MMADs in the range of 0.72-0.92, 0.75-0.90 and 0.73-0.78
676 μm , respectively (Fig. 9). Generally, the seasonal average MSEs of $(\text{NH}_4)_2\text{SO}_4$,
677 NH_4NO_3 and OM in the droplet mode were higher with the lower σ values (or MMADs)
678 when MMADs (σ values) were close. However, the MSE of OM in summer was 5.2 m^2
679 g^{-1} , which was lower than 5.3 $\text{m}^2 \text{g}^{-1}$ in autumn, although σ values and MMADs in
680 summer were lower than those in autumn. This was mainly related with the evident
681 fluctuation the MSE of OM in the range of 0.6-0.7 μm .

682

683

Insert Figure 9

684

685 In conclusion, the fine particle MSE was determined by the sum of the products of
686 average mass fractions and MSEs of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 and OM in the droplet
687 mode. The MSEs of the above three chemical species in the droplet mode depended on

688 both their σ value and MMADs. Generally, fine particle MSE mainly related with OM
689 due to its high mass and MSE in the droplet mode in urban Guangzhou.

690 **4. Summary and implication**

691 Size- and chemically-resolved particle number and mass concentration were measured
692 in urban Guangzhou in different seasons during 2015-2016 and the data were used to
693 estimate particle MSE. SO_4^{2-} and NH_4^+ mainly distributed in the droplet mode, EC in
694 both condensation and droplet modes, and particle mass, NO_3^- , OC, Na^+ , Ca^{2+} and Cl^-
695 in both droplet and coarse modes. The estimated b_{sp} can represent 85-89% of the
696 measured b_{sp} based on the size-segregated chemical compositions according to
697 ISORROPIA II thermodynamic equilibrium model and Mie theory model. The largest
698 contributors to b_{sp} were the chemical species in the droplet mode with the highest MSEs.
699 MSEs of the dominant chemical species were noticeably different in this study than
700 those in the original and revised IMPROVE formulas. The MSEs of $(\text{NH}_4)_2\text{SO}_4$,
701 NH_4NO_3 and OM in the fine mode were higher than those in the original IMPROVE
702 formula, and in the droplet mode were lower than those in the revised IMPROVE
703 formula. In any case, b_{sp} would be underestimated in urban Guangzhou using the
704 original or revised IMPROVE formulas because the unidentified chemical species (and
705 associated mass fractions) in the droplet mode accounted for a large fraction of b_{sp} and
706 this portion was not included in these formulas. Moreover, MSEs of chemical species
707 would be overestimated in the original and revised IMPROVE formulas using multiple
708 linear regression model when the unidentified species was ignored. In addition, sea salt
709 was found in the coarse mode in this study, differing from the set up in the IMPROVE

710 formulas which is in the droplet mode. It can be concluded that the estimated b_{sp} in
711 Guangzhou based on the revised IMPROVE formula would have large biases, even
712 though good correlations between estimated and measured b_{sp} was found.

713 MSEs of fine particles are controlled by the relative mass fractions of the dominant
714 chemical components (e.g., $(NH_4)_2SO_4$, NH_4NO_3 and OM) and associated size
715 distributions (e.g. σ and MMAD). Localized b_{sp} formulas are thus needed for better
716 estimating particle MSE because particle size distributions of individual chemical
717 species vary significantly in space and time.

718 *Data availability. Data used in this study are available from Jun Tao (taojun@scies.org).*

719 *Competing interests. The authors declare that they have no conflict of interest.*

720

721 **Acknowledgments**

722 This study was supported by the National Natural Science Foundation of China
723 (No.41475119, No. 41875160 and 41603119). Original data are available from the
724 corresponding authors.

725 **References**

- 726 Andreae, M. O., Schmid, O., Yang, H., Chand, D., Zhen Yu, J., Zeng, L. M., and Zhang, Y. H.: Optical
727 properties and chemical composition of the atmospheric aerosol in urban Guangzhou, China,
728 *Atmospheric Environment*, 42, 6335-6350, 2008.
- 729 Bergin, M. H., Ogren, J. A., Schwartz, S. E., and McInnes, L. M.: Evaporation of Ammonium Nitrate
730 Aerosol in a Heated Nephelometer: Implications for Field Measurements, *Environmental Science &*
731 *Technology*, 31, 2878-2883, 10.1021/es970089h, 1997.
- 732 Bian, Q., Huang, X. H., and Yu, J. Z.: One-year observations of size distribution characteristics of major
733 aerosol constituents at a coastal receptor site in Hong Kong – Part 1: Inorganic ions and oxalate,
734 *Atmospheric Chemistry and Physics*, 14, 9013-9027, 2014.
- 735 Cabada, J. C., Rees, S., Takahama, S., Khlystov, A., Pandis, S. N., Davidson, C. I., and Robinson, A. L.:
736 Mass size distributions and size resolved chemical composition of fine particulate matter at the Pittsburgh
737 supersite, *Atmospheric Environment*, 38, 3127-3141, 2004.

738 Cao, J., Wang, Q., Chow, J. C., Watson, J. G., Tie, X., Shen, Z., Wang, P., and An, Z.: Impacts of aerosol
739 compositions on visibility impairment in Xi'an, China, *Atmospheric Environment*, 59, 559-566, 2012.

740 Chen, P., Wang, T., Lu, X., Yu, Y., Kasoar, M., Xie, M., and Zhuang, B.: Source apportionment of size-
741 fractionated particles during the 2013 Asian Youth Games and the 2014 Youth Olympic Games in
742 Nanjing, China, *Science of The Total Environment*, 579, 860-870, 2017.

743 Cheng, Y., Wiedensohler, A., Eichler, H., Su, H., Gnauk, T., Brüggemann, E., Herrmann, H.,
744 Heintzenberg, J., Slanina, J., and Tuch, T.: Aerosol optical properties and related chemical apportionment
745 at Xinken in Pearl River Delta of China, *Atmospheric Environment*, 42, 6351-6372, 2008.

746 Cheng, Y. F., Berghof, M., Garland, R. M., Wiedensohler, A., Wehner, B., Muller, T. J., Su, H., Zhang,
747 Y. H., Achtert, P., and Nowak, A.: Influence of soot mixing state on aerosol light absorption and single
748 scattering albedo during air mass aging at a polluted regional site in northeastern China, *Journal of*
749 *Geophysical Research*, 114, 2009.

750 Cheng, Z., Jiang, J. S., Chen, C., Gao, J., Wang, S., Watson, J. G., Wang, H., Deng, J., Wang, B., and
751 Zhou, M.: Estimation of aerosol mass scattering efficiencies under high mass loading: case study for the
752 megacity of Shanghai, China, *Environmental Science & Technology*, 49, 831-838, 2015.

753 Chow, J. C., Watson, J. G., Lowenthal, D. H., Chen, L. W. A., and Motallebi, N.: PM_{2.5} source profiles
754 for black and organic carbon emission inventories, *Atmospheric Environment*, 45, 5407-5414, 2011.

755 Day, M. C., Zhang, M., and Pandis, S. N.: Evaluation of the ability of the EC tracer method to estimate
756 secondary organic carbon, *Atmospheric Environment*, 112, 317-325, 2015.

757 Dong, Y., Hays, M. D., Smith, N. D., and Kinsey, J. S.: Inverting cascade impactor data for size-resolved
758 characterization of fine particulate source emissions, *Journal of Aerosol Science*, 35, 1497-1512, 2004.

759 Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium
760 model for $K^+Ca^{2+}Mg^{2+}NH_4^+Na^+SO_4^{2-}NO_3^-Cl^-H_2O$ aerosols, *Atmospheric Chemistry and*
761 *Physics*, 7, 4639-4659, 2007.

762 Gao, Y., Lai, S., Lee, S. C., Yau, P. S., Huang, Y., Cheng, Y., Wang, T., Xu, Z., Yuan, C., and Zhang, Y.:
763 Optical properties of size-resolved particles at a Hong Kong urban site during winter, *Atmospheric*
764 *Research*, 155, 1-12, 2015.

765 Gentner, D. R., Isaacman, G., Worton, D. R., Chan, A. W. H., Dallmann, T. R., Davis, L. E., Liu, S., Day,
766 D. A., Russell, L. M., and Wilson, K. R.: Elucidating secondary organic aerosol from diesel and gasoline
767 vehicles through detailed characterization of organic carbon emissions, *Proceedings of the National*
768 *Academy of Sciences of the United States of America*, 109, 18318-18323, 2012.

769 Gentner, D. R., Jathar, S. H., Gordon, T. D., Bahreini, R., Day, D. A., Haddad, I. E., Hayes, P. L., Pieber,
770 S. M., Platt, S. M., and De Gouw, J. A.: Review of Urban Secondary Organic Aerosol Formation from
771 Gasoline and Diesel Motor Vehicle Emissions, *Environmental Science & Technology*, 51, 1074-1093,
772 2017.

773 Guo, S., Hu, M., Wang, Z., Slanina, J., and Zhao, Y.: Size-resolved aerosol water-soluble ionic
774 compositions in the summer of Beijing: implication of regional secondary formation, *Atmospheric*
775 *Chemistry and Physics*, 10, 947-959, 2009.

776 Hallquist, M., Wenger, J., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue,
777 N., George, C., and Goldstein, A.: The formation, properties and impact of secondary organic aerosol:
778 current and emerging issues, *Atmospheric Chemistry and Physics*, 9, 5155-5236, 2009.

779 Han, T., Liu, X., Zhang, Y., Qu, Y., Gu, J., Ma, Q., Lu, K., Tian, H., Chen, J., and Zeng, L.: Characteristics
780 of aerosol optical properties and their chemical apportionments during CAREBeijing 2006, *Aerosol and*
781 *Air Quality Research*, 14, 1431-1442, 2014.

782 Hand, J., Kreidenweis, S., Sherman, D. E., Collett, J., Hering, S., Day, D., and Malm, W.: Aerosol size
783 distributions and visibility estimates during the Big Bend regional aerosol and visibility observational
784 (BRAVO) study, *Atmospheric Environment*, 36, 5043-5055, 2002.

785 Hand, J. L., and Malm, W. C.: Review of the IMPROVE equation for estimating ambient light extinction
786 coefficients, CIRA, Colorado State University, 2007.

787 He, L.Y., Huang, X.F., Xue, L., Hu, M., Lin, Y., Zheng, J., Zhang, R., and Zhang, Y.H.: Submicron
788 aerosol analysis and organic source apportionment in an urban atmosphere in Pearl River Delta of China
789 using high-resolution aerosol mass spectrometry, *Journal of Geophysical Research: Atmospheres*, 116,
790 10.1029/2010JD014566, 2011.

791 Ho, K., Lee, S., Chow, J. C., and Watson, J. G.: Characterization of PM₁₀ and PM_{2.5} source profiles for
792 fugitive dust in Hong Kong, *Atmospheric Environment*, 37, 1023-1032, 2003.

793 Hua, Y., Cheng, Z., Wang, S., Jiang, J., Chen, D., Cai, S., Fu, X., Fu, Q., Chen, C., Xu, B., and Yu, J.:
794 Characteristics and source apportionment of PM_{2.5} during a fall heavy haze episode in the Yangtze River
795 Delta of China, *Atmospheric Environment*, 123, 380-391,
796 <https://doi.org/10.1016/j.atmosenv.2015.03.046>, 2015.

797 Huang, K., Zhuang, G., Lin, Y., Fu, J., Wang, Q., Liu, T., Zhang, R., Jiang, Y., Deng, C., and Fu, Q.:
798 Typical types and formation mechanisms of haze in an Eastern Asia megacity, Shanghai, *Atmospheric
799 Chemistry and Physics*, 12, 2012.

800 Huang, X., Yu, J. Z., He, L. Y., and Hu, M.: Size Distribution Characteristics of Elemental Carbon
801 Emitted from Chinese Vehicles: Results of a Tunnel Study and Atmospheric Implications, *Environmental
802 Science & Technology*, 40, 5355-5360, 2006a.

803 Huang, X. F., Yu, J. Z., He, L. Y., and Yuan, Z.: Water - soluble organic carbon and oxalate in aerosols
804 at a coastal urban site in China: Size distribution characteristics, sources, and formation mechanisms,
805 *Journal of Geophysical Research: Atmospheres*, 111, 2006b.

806 John, W., Wall, S. M., Ondo, J. L., and Winklmayr, W.: Modes in the size distributions of atmospheric
807 inorganic aerosol, *Atmospheric Environment*, 24, 2349-2359, 1990.

808 Jung, J., Lee, H., Kim, Y. J., Liu, X., Zhang, Y., Gu, J., and Fan, S.: Aerosol chemistry and the effect of
809 aerosol water content on visibility impairment and radiative forcing in Guangzhou during the 2006 Pearl
810 River Delta campaign, *Journal of Environmental Management*, 90, 3231-3244, 2009a.

811 Jung, J., Lee, H., Kim, Y. J., Liu, X., Zhang, Y., Hu, M., and Sugimoto, N.: Optical properties of
812 atmospheric aerosols obtained by in situ and remote measurements during 2006 Campaign of Air Quality
813 Research in Beijing (CAREBeijing - 2006), *Journal of Geophysical Research: Atmospheres* (1984–
814 2012), 114, 2009b.

815 Kulkarni, P., Baron, P. A., and Willeke, K.: Aerosol measurement: principles, techniques, and
816 applications, John Wiley & Sons, 2011.

817 Lan, Z., Chen, D., Li, X., Huang, X., He, L., Deng, Y., Feng, N., and Hu, M.: Modal characteristics of
818 carbonaceous aerosol size distribution in an urban atmosphere of South China, *Atmospheric Research*,
819 100, 51-60, 2011.

820 Li, H., Wang, Q. G., Yang, M., Li, F., Wang, J., Sun, Y., Wang, C., Wu, H., and Qian, X.: Chemical
821 characterization and source apportionment of PM_{2.5} aerosols in a megacity of Southeast China,
822 *Atmospheric Research*, 181, 288-299, <http://doi.org/10.1016/j.atmosres.2016.07.005>, 2016.

823 Lin, C., Li, Y., Yuan, Z., Lau, A. K. H., Li, C., and Fung, J. C. H.: Using satellite remote sensing
824 data to estimate the high-resolution distribution of ground-level PM_{2.5}, *Remote Sensing of*

825 Environment, 156, 117-128, <https://doi.org/10.1016/j.rse.2014.09.015>, 2015.

826 Lowenthal, D. H., and Kumar, N.: Variation of Mass Scattering Efficiencies in IMPROVE, Journal of
827 The Air & Waste Management Association, 54, 926-934, 2004.

828 Malm, W., Sisler, J., Pitchford, M., Scruggs, M., Ames, R., Copeland, S., Gebhart, K., and Day, D.:
829 IMPROVE (interagency monitoring of protected visual environments): spatial and seasonal patterns and
830 temporal variability of haze and its constituents in the United States: Report III, CIRA Report ISSN,
831 0737-5352, 2000.

832 Malm, W. C., Sisler, J. F., Huffman, D., Eldred, R. A., and Cahill, T. A.: Spatial and seasonal trends in
833 particle concentration and optical extinction in the United States, Journal of Geophysical Research, 99,
834 1347-1370, 1994.

835 Malm, W. C., and Pitchford, M.: Comparison of calculated sulfate scattering efficiencies as estimated
836 from size-resolved particle measurements at three national locations, Atmospheric Environment, 31,
837 1315-1325, 1997.

838 Malm, W. C., Day, D. E., Kreidenweis, S. M., Collett, J. L., and Lee, T.: Humidity-dependent optical
839 properties of fine particles during the Big Bend Regional Aerosol and Visibility Observational Study,
840 Journal of Geophysical Research, 108, 4279, 2003.

841 Malm, W. C., and Hand, J. L.: An examination of the physical and optical properties of aerosols collected
842 in the IMPROVE program, Atmospheric Environment, 41, 3407-3427, 2007.

843 Ming, L., Jin, L., Li, J., Fu, P., Yang, W., Liu, D., Zhang, G., Wang, Z., and Li, X.: PM_{2.5} in the Yangtze
844 River Delta, China: Chemical compositions, seasonal variations, and regional pollution events,
845 Environmental Pollution, 223, 200-212, <https://doi.org/10.1016/j.envpol.2017.01.013>, 2017.

846 Pitchford, M., Malm, W., Schichtel, B., Kumar, N., Lowenthal, D., and Hand, J.: Revised algorithm for
847 estimating light extinction from IMPROVE particle speciation data, Journal of the Air & Waste
848 Management Association, 57, 1326-1336, 2007.

849 Schwarz, J., Gao, R., Spackman, J., Watts, L., Thomson, D., Fahey, D., Ryerson, T., Peischl, J., Holloway,
850 J., and Trainer, M.: Measurement of the mixing state, mass, and optical size of individual black carbon
851 particles in urban and biomass burning emissions, Geophysical Research Letters, 35, 2008.

852 Shen, G., Xue, M., Yuan, S., Zhang, J., Zhao, Q., Li, B., Wu, H., and Ding, A.: Chemical compositions
853 and reconstructed light extinction coefficients of particulate matter in a mega-city in the western Yangtze
854 River Delta, China, Atmospheric Environment, 83, 14-20,
855 <http://dx.doi.org/10.1016/j.atmosenv.2013.10.055>, 2014.

856 Shiraiwa, M., Kondo, Y., Moteki, N., Takegawa, N., Miyazaki, Y., and Blake, D. R.: Evolution of mixing
857 state of black carbon in polluted air from Tokyo, Geophysical Research Letters, 34, 2007.

858 Sisler, J. F., and Latimer, D. A.: Spatial and temporal patterns and the chemical composition of the haze
859 in the United States: An analysis of data from the IMPROVE network, 1988-1991, Cooperative Institute
860 for Research in the Atmosphere, Colorado State University, 1993.

861 Sisler, J. F., Malm, W., Gebhart, K., and Pitchford, M. L.: Spatial and Seasonal Patterns and Long Term
862 Variability of the composition of the Haze in the United States, Report ISSN, 0737-5352, 1996.

863 Sisler, J. F., and Malm, W. C.: Interpretation of Trends of PM_{2.5} and Reconstructed Visibility from the
864 IMPROVE Network, Journal of the Air & Waste Management Association, 50, 775-789, 2000.

865 Sun, J., Shen, Z., Zhang, L., Lei, Y., Gong, X., Zhang, Q., Zhang, T., Xu, H., Cui, S., Wang, Q., Cao, J.,
866 Tao, J., Zhang, N., and Zhang, R.: Chemical source profiles of urban fugitive dust PM_{2.5} samples from
867 21 cities across China, Science of The Total Environment, 649, 1045-1053,
868 <https://doi.org/10.1016/j.scitotenv.2018.08.374>, 2019.

869 Takemura, T., Nakajima, T., Dubovik, O., Holben, B. N., and Kinne, S.: Single-Scattering Albedo and
870 Radiative Forcing of Various Aerosol Species with a Global Three-Dimensional Model, *Journal of*
871 *Climate*, 15, 333-352, 2002.

872 Tao, J., Ho, K., Chen, L., Zhu, L., Han, J., and Xu, Z.: Effect of chemical composition of PM_{2.5} on
873 visibility in Guangzhou, China, 2007 spring, *Particuology*, 7, 68-75, 2009.

874 Tao, J., Cao, J.J., Zhang, R.J., Zhu, L., Zhang, T., Shi, S., and Chan, C.Y.: Reconstructed light extinction
875 coefficients using chemical compositions of PM_{2.5} in winter in Urban Guangzhou, China, *Advances in*
876 *Atmospheric Sciences*, 29, 359-368, 2012.

877 Tao, J., Zhang, L., Ho, K., Zhang, R., Lin, Z., Zhang, Z., Lin, M., Cao, J., Liu, S., and Wang, G.: Impact
878 of PM_{2.5} chemical compositions on aerosol light scattering in Guangzhou - the largest megacity in South
879 China, *Atmospheric Research*, 135-136, 48-58, <http://dx.doi.org/10.1016/j.atmosres.2013.08.015>, 2014.

880 Tao, J., Zhang, L., Cao, J., and Zhang, R.: A review of current knowledge concerning PM_{2.5} chemical
881 composition, aerosol optical properties and their relationships across China, *Atmospheric Chemistry and*
882 *Physics*, 17, 9485-9518, [10.5194/acp-17-9485-2017](https://doi.org/10.5194/acp-17-9485-2017), 2017a.

883 Tao, J., Zhang, L., Cao, J., Zhong, L., Chen, D., Yang, Y., Chen, D., Chen, L., Zhang, Z., Wu, Y., Xia, Y.,
884 Ye, S., and Zhang, R.: Source apportionment of PM_{2.5} at urban and suburban areas of the Pearl River
885 Delta region, south China - With emphasis on ship emissions, *Science of The Total Environment*, 574,
886 1559-1570, <http://dx.doi.org/10.1016/j.scitotenv.2016.08.175>, 2017b.

887 Tao, J., Zhang, Z., Tan, H., Zhang, L., Wu, Y., Sun, J., Che, H., Cao, J., Cheng, P., Chen, L., and Zhang,
888 R.: Observational evidence of cloud processes contributing to daytime elevated nitrate in an urban
889 atmosphere, *Atmospheric Environment*, 186, 209-215, <https://doi.org/10.1016/j.atmosenv.2018.05.040>,
890 2018.

891 Tian, S., Pan, Y., Liu, Z., Wen, T., and Wang, Y.: Size-resolved aerosol chemical analysis of extreme haze
892 pollution events during early 2013 in urban Beijing, China, *Journal of hazardous materials*, 279, 452-
893 460, 2014.

894 Titos, G., Foyo-Moreno, I., Lyamani, H., Querol, X., Alastuey, A., and Alados-Arboledas, L.:
895 Optical properties and chemical composition of aerosol particles at an urban location: An estimation
896 of the aerosol mass scattering and absorption efficiencies, *Journal of Geophysical Research:*
897 *Atmospheres*, 117, [10.1029/2011JD016671](https://doi.org/10.1029/2011JD016671), 2012.

898 Vaughan, N. P.: The Andersen impactor: Calibration, wall losses and numerical simulation, *Journal of*
899 *Aerosol Science*, 20, 67-90, 1989.

900 Wang, H., Shi, G., Tian, M., Zhang, L., Chen, Y., Yang, F., and Cao, X.: Aerosol optical properties and
901 chemical composition apportionment in Sichuan Basin, China, *Science of The Total Environment*, 577,
902 245-257, <http://dx.doi.org/10.1016/j.scitotenv.2016.10.173>, 2017.

903 Wang, Y., Yao, L., Wang, L., Liu, Z., Ji, D., Tang, G., Zhang, J., Sun, Y., Hu, B., and Xin, J.: Mechanism
904 for the formation of the January 2013 heavy haze pollution episode over central and eastern China,
905 *Science China Earth Sciences*, 57, 14-25, 2014.

906 Watson, J. G., Chow, J. C., and Houck, J. E.: PM_{2.5} chemical source profiles for vehicle exhaust,
907 vegetative burning, geological material, and coal burning in Northwestern Colorado during 1995,
908 *Chemosphere*, 43, 1141-1151, 2001.

909 Watson, J. G.: Visibility: Science and regulation, *Journal of the Air & Waste Management Association*,
910 52, 628-713, 2002.

911 Watson, J. G., Chow, J. C., Lowenthal, D. H., and Magliano, K. L.: Estimating aerosol light scattering at
912 the Fresno Supersite, *Atmospheric Environment*, 42, 1186-1196, 2008.

913 Wu, C., and Yu, J. Z.: Determination of primary combustion source organic carbon-to-elemental carbon
914 (OC/EC) ratio using ambient OC and EC measurements: Secondary OC-EC correlation minimization
915 method, *Atmospheric Chemistry and Physics*, 16, 5453-5465, 2016.

916 Wu, Y., Zhang, R., Tian, P., Tao, J., Hsu, S.C., Yan, P., Wang, Q., Cao, J., Zhang, X., and Xia, X.: Effect
917 of ambient humidity on the light absorption amplification of black carbon in Beijing during January 2013,
918 *Atmospheric Environment*, 124, 217-223, 2016.

919 Wu, Y., Wang, X., Tao, J., Huang, R., Tian, P., Cao, J., Zhang, L., Ho, K. F., Han, Z., and Zhang, R.: Size
920 distribution and source of black carbon aerosol in urban Beijing during winter haze episodes,
921 *Atmospheric Chemistry and Physics*, 17, 7965-7975, 10.5194/acp-17-7965-2017, 2017.

922 Xia, Y., Tao, J., Zhang, L., Zhang, R., Li, S., Wu, Y., Cao, J., Wang, X., Ma, Q., and Xiong, Z.: Impact
923 of size distributions of major chemical components in fine particles on light extinction in urban
924 Guangzhou, *Science of The Total Environment*, 587-588, 240-247,
925 <https://doi.org/10.1016/j.scitotenv.2017.02.127>, 2017.

926 Yao, X., Lau, A. P. S., Fang, M., Chan, C. K., and Hu, M.: Size distributions and formation of ionic
927 species in atmospheric particulate pollutants in Beijing, China: 1-inorganic ions, *Atmospheric
928 Environment*, 37, 2991-3000, 2003.

929 Yu, H., Wu, C., Wu, D., and Yu, J.: Size distributions of elemental carbon and its contribution to light
930 extinction in urban and rural locations in the pearl river delta region, China, *Atmospheric Chemistry and
931 Physics*, 10, 5107-5119, 2010.

932 Zhang, F., Xu, L., Chen, J., Yu, Y., Niu, Z., and Yin, L.: Chemical compositions and extinction
933 coefficients of PM_{2.5} in peri-urban of Xiamen, China, during June 2009–May 2010, *Atmospheric
934 Research*, 106, 150-158, 2012a.

935 Zhang, H., Wang, S., Hao, J., Wan, L., Jiang, J. S., Zhang, M., Mestl, H. E. S., Alnes, L. W. H., Aunan,
936 K., and Mellouki, A. W.: Chemical and size characterization of particles emitted from the burning of coal
937 and wood in rural households in Guizhou, China, *Atmospheric Environment*, 51, 94-99, 2012b.

938 Zhang, L., Vet, R., Wiebe, A., Mihele, C., Sukloff, B., Chan, E., Moran, M. D., and Iqbal, S.:
939 Characterization of the size-segregated water-soluble inorganic ions at eight Canadian rural sites,
940 *Atmospheric Chemistry and Physics*, 8, 7133-7151, 2008.

941 Zhang, R., Jing, J., Tao, J., Hsu, S. C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., Zhao, Y., and
942 Shen, Z.: Chemical characterization and source apportionment of PM_{2.5} in Beijing: seasonal perspective,
943 *Atmos. Chem. Phys.*, 13, 7053-7074, 10.5194/acp-13-7053-2013, 2013.

944 Zhang, R., Wang, G., Guo, S., Zamora, M. L., Ying, Q., Lin, Y., Wang, W., Hu, M., and Wang, Y.:
945 Formation of urban fine particulate matter, *Chemical reviews*, 115, 3803-3855, 2015a.

946 Zhang, Z., Engling, G., Zhang, L., Kawamura, K., Yang, Y., Tao, J., Zhang, R., Chan, C., and Li, Y.:
947 Significant influence of fungi on coarse carbonaceous and potassium aerosols in a tropical rainforest,
948 *Environmental Research Letters*, 10, 034015, 2015b.

949 Zhang, Z., Gao, J., Engling, G., Tao, J., Chai, F., Zhang, L., Zhang, R., Sang, X., Chan, C.Y., and Lin, Z.:
950 Characteristics and applications of size-segregated biomass burning tracers in China's Pearl River Delta
951 region, *Atmospheric Environment*, 102, 290-301, 2015c.

952 Zhao, X. J., Zhao, P. S., Xu, J., Meng, W., Pu, W., Dong, F., He, D., and Shi, Q. F.: Analysis of a winter
953 regional haze event and its formation mechanism in the North China Plain, *Atmospheric Chemistry and
954 Physics*, 13, 5685-5696, 2013.

955 Zheng, B., Tong, D., Li, M., Liu, F., Hong, C., Geng, G., Li, H., Li, X., Peng, L., Qi, J., Yan, L., Zhang,
956 Y., Zhao, H., Zheng, Y., He, K., and Zhang, Q.: Trends in China's anthropogenic emissions since 2010 as
957 the consequence of clean air actions, *Atmospheric Chemistry and Physics*, 18, 14095-14111,
958 10.5194/acp-18-14095-2018, 2018.

959 Zheng, J., Zhang, L., Che, W., Zheng, Z., and Yin, S.: A highly resolved temporal and spatial air pollutant
960 emission inventory for the Pearl River Delta region, China and its uncertainty assessment, *Atmospheric*
961 *Environment*, 43, 5112-5122, 2009.

962 Zheng, M., Hagler, G. S. W., Ke, L., Bergin, M. H., Wang, F., Louie, P. K. K., Salmon, L. G., Sin, D. W.
963 M., Yu, J. Z., and Schauer, J. J.: Composition and sources of carbonaceous aerosols at three contrasting
964 sites in Hong Kong, *Journal of Geophysical Research*, 111, 2006.

965 Zhuang, H., Chan, C. K., Fang, M., and Wexler, A. S.: Formation of nitrate and non-sea-salt sulfate on
966 coarse particles, *Atmospheric Environment*, 33, 4223-4233, 1999a.

967 Zhuang, H., Chan, C. K., Fang, M., and Wexler, A. S.: Size distributions of particulate sulfate, nitrate,
968 and ammonium at a coastal site in Hong Kong, *Atmospheric Environment*, 33, 843-853, 1999b.

969 Zou, J., Liu, Z., Hu, B., Huang, X., Wen, T., Ji, D., Liu, J., Yang, Y., Yao, Q., and Wang, Y.: Aerosol
970 chemical compositions in the North China Plain and the impact on the visibility in Beijing and Tianjin,
971 *Atmospheric Research*, 201, 235-246, <https://doi.org/10.1016/j.atmosres.2017.09.014>, 2018.

972

Table 1. Summary of the sampling information

Season	Date	Sample type	Instruments	Sample duration	Sample number
Summer	15 July- 6 August in 2015	Size-segregated samples	Anderson 8-stage air samplers	24h	23 sets
Autumn	15 October- 5 November in 2015			24h	22 sets
Winter	4-20 January - 19-22 February in 2016			24h	21 sets
Spring	8-20 April and 4-14 May in 2016			48h	10 sets
Summer	15 July- 6 August in 2015	PM _{2.5} and PM ₁₀ samples	GSAPM	24 h	23 sets
Autumn	15 October- 5 November in 2015				22 sets
Winter	4-20 January - 19-22 February in 2016				21 sets
Spring	8-20 April and 4-14 May in 2016				20 sets
Summer	15 July- 6 August in 2015	Particle number concentration in the range of 14 nm - 615 nm	SMPS, TSI Model 3936	5 min	
Autumn	15 October- 5 November in 2015				
Winter	4-20 January - 19-22 February in 2016				
Spring	8-20 April and 4-14 May in 2016				
Summer	15 July- 6 August in 2015	Particle number concentration in the range of 542 nm - 10 μ m	APS, TSI Model 3321	5 min	
Autumn	15 October- 5 November in 2015				
Winter	4-20 January - 19-22 February in 2016				
Spring	8-20 April and 4-14 May in 2016				
Summer	15 July- 6 August in 2015	Dry b _{sp}	Nephelometer, Ecotech, Model Aurora1000G	5 min	
Autumn	15 October- 5 November in 2015				
Winter	4-20 January - 19-22 February in 2016				
Spring	8-20 April and 4-14 May in 2016				
Summer	15 July- 6 August in 2015	NO ₃ ⁻ in PM ₁₀	IGAC, Model S-611	1 h	
Autumn	15 October- 5 November in 2015	NO ₃ ⁻ in PM _{2.5}			
Winter	4-20 January in 2016	NO ₃ ⁻ in PM _{2.5}			
Spring	4-14 May in 2016	NO ₃ ⁻ in PM _{2.5}			

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

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

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

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%)

Chemical species	Size mode	Annual		Spring		Summer		Autumn		Winter	
		MMAD ^(c) (μm)	MSE ^(d) ($\text{m}^2 \text{g}^{-1}$)	MMAD (μm)	MSE ($\text{m}^2 \text{g}^{-1}$)	MMAD (μm)	MSE ($\text{m}^2 \text{g}^{-1}$)	MMAD (μm)	MSE ($\text{m}^2 \text{g}^{-1}$)	MMAD (μm)	MSE ($\text{m}^2 \text{g}^{-1}$)
PM ^(a)	Condensation(<0.43 μm)	—	2.1 \pm 0.2	—	1.9 \pm 0.2	—	2.0 \pm 0.1	—	2.1 \pm 0.1	0.21 \pm 0.00	2.2 \pm 0.2
	Droplet(0.43 -2.1 μm)	0.78 \pm 0.07	4.3 \pm 0.2	0.87 \pm 0.13	4.0 \pm 0.1	0.78 \pm 0.05	4.2 \pm 0.1	0.74 \pm 0.06	4.3 \pm 0.2	0.79 \pm 0.05	4.4 \pm 0.2
	Coarse(2.1 -10 μm)	4.57 \pm 0.42	0.5 \pm 0.0	4.37 \pm 0.37	0.6 \pm 0.1	4.47 \pm 0.35	0.5 \pm 0.0	4.90 \pm 0.46	0.5 \pm 0.0	4.47 \pm 0.24	0.5 \pm 0.0
	Fine mode(<2.1 μm) ^(b)	—	3.7 \pm 0.2	—	3.5 \pm 0.1	—	3.6 \pm 0.2	—	3.8 \pm 0.2	—	3.9 \pm 0.2
(NH ₄) ₂ SO ₄	Condensation(<0.43 μm)	—	2.1 \pm 0.5	—	1.9 \pm 0.6	—	2.6 \pm 0.2	—	2.0 \pm 0.5	0.21 \pm 0.00	1.9 \pm 0.5
	Droplet(0.43 -2.1 μm)	0.79 \pm 0.17	4.7 \pm 0.6	0.92 \pm 0.13	4.3 \pm 0.3	0.74 \pm 0.20	4.8 \pm 0.6	0.72 \pm 0.16	4.9 \pm 0.7	0.84 \pm 0.13	4.6 \pm 0.7
	Fine mode(<2.1 μm)	—	4.4 \pm 0.8	—	4.1 \pm 0.4	—	4.5 \pm 0.6	—	4.6 \pm 0.8	—	4.3 \pm 0.9
NH ₄ NO ₃	Condensation(<0.43 μm)	0.21 \pm 0.00	2.3 \pm 0.8	—	2.0 \pm 0.8	—	2.9 \pm 0.3	—	2.6 \pm 1.0	0.21 \pm 0.00	2.3 \pm 0.7
	Droplet(0.43 -2.1 μm)	0.80 \pm 0.16	4.8 \pm 0.9	0.90 \pm 0.18	4.5 \pm 0.8	0.77 \pm 0.17	4.9 \pm 0.8	0.75 \pm 0.13	5.1 \pm 1.0	0.82 \pm 0.14	4.7 \pm 0.8
	Fine mode(<2.1 μm)	—	4.5 \pm 1.5	—	4.2 \pm 1.2	—	4.7 \pm 0.9	—	4.9 \pm 2.0	—	4.4 \pm 1.3
OM	Condensation(<0.43 μm)	—	2.7 \pm 0.1	—	2.5 \pm 0.1	—	2.8 \pm 0.2	—	2.6 \pm 0.1	0.21 \pm 0.00	2.8 \pm 0.1
	Droplet(0.43 -2.1 μm)	0.76 \pm 0.07	5.3 \pm 0.2	0.73 \pm 0.06	5.4 \pm 0.1	0.77 \pm 0.07	5.2 \pm 0.2	0.78 \pm 0.06	5.3 \pm 0.2	0.75 \pm 0.08	5.5 \pm 0.2
	Coarse(2.1 -10 μm)	3.73 \pm 0.58	0.8 \pm 0.1	3.99 \pm 0.25	0.8 \pm 0.0	3.50 \pm 0.73	0.8 \pm 0.1	4.14 \pm 0.24	0.7 \pm 0.0	3.44 \pm 0.39	0.8 \pm 0.1
	Fine mode(<2.1 μm)	—	4.6 \pm 0.3	—	4.4 \pm 0.2	—	4.6 \pm 0.2	—	4.5 \pm 0.1	—	4.9 \pm 0.3
EC	Condensation(<0.43 μm)	—	2.9 \pm 0.1	—	2.9 \pm 0.1	—	2.9 \pm 0.1	—	3.0 \pm 0.1	0.21 \pm 0.00	2.9 \pm 0.1
	Droplet(0.43 -2.1 μm)	0.66 \pm 0.08	2.3 \pm 0.2	0.65 \pm 0.08	2.3 \pm 0.2	0.61 \pm 0.08	2.3 \pm 0.2	0.71 \pm 0.04	2.2 \pm 0.1	0.67 \pm 0.07	2.3 \pm 0.2
	Coarse(2.1 -10 μm)	3.69 \pm 0.65	0.4 \pm 0.0	3.54 \pm 0.61	0.4 \pm 0.0	3.48 \pm 0.52	0.4 \pm 0.0	4.17 \pm 0.24	0.4 \pm 0.0	3.50 \pm 0.75	0.5 \pm 0.0
	Fine mode(<2.1 μm)	—	2.6 \pm 0.1	—	2.6 \pm 0.1	—	2.6 \pm 0.2	—	2.5 \pm 0.1	—	2.6 \pm 0.1
Crustal element oxides	Condensation(<0.43 μm)	—	0.7 \pm 0.0	—	0.7 \pm 0.0	—	0.7 \pm 0.1	—	0.7 \pm 0.0	0.21 \pm 0.00	0.7 \pm 0.0
	Droplet(0.43 -2.1 μm)	0.91 \pm 0.12	2.9 \pm 0.2	0.88 \pm 0.13	3.0 \pm 0.2	1.00 \pm 0.11	2.9 \pm 0.2	0.81 \pm 0.10	2.8 \pm 0.2	0.92 \pm 0.09	2.8 \pm 0.2
	Coarse(2.1 -10 μm)	4.57 \pm 0.54	0.4 \pm 0.0	5.02 \pm 0.58	0.4 \pm 0.0	4.10 \pm 0.42	0.5 \pm 0.0	4.72 \pm 0.47	0.4 \pm 0.0	4.73 \pm 0.38	0.4 \pm 0.0
	Fine mode(<2.1 μm)	—	2.4 \pm 0.2	—	2.4 \pm 0.1	—	2.5 \pm 0.2	—	2.4 \pm 0.2	—	2.3 \pm 0.2
Unidentified	Condensation(<0.43 μm)	—	1.3 \pm 0.2	—	1.2 \pm 0.4	—	1.2 \pm 0.2	—	1.4 \pm 0.1	0.21 \pm 0.00	1.3 \pm 0.2
	Droplet(0.43 -2.1 μm)	0.85 \pm 0.26	3.8 \pm 0.6	1.00 \pm 0.20	3.5 \pm 0.8	0.74 \pm 0.44	3.9 \pm 0.9	0.84 \pm 0.10	3.9 \pm 0.2	0.90 \pm 0.20	3.7 \pm 0.4
	Coarse(2.1 -10 μm)	5.74 \pm 1.52	0.4 \pm 0.1	4.55 \pm 0.71	0.5 \pm 0.1	6.46 \pm 1.14	0.4 \pm 0.1	6.33 \pm 1.62	0.4 \pm 0.1	4.91 \pm 0.90	0.5 \pm 0.1
	Fine mode(<2.1 μm)	—	3.1 \pm 0.8	—	2.9 \pm 0.9	—	2.6 \pm 1.0	—	3.3 \pm 0.3	—	3.1 \pm 0.5
NaCl	Coarse(2.1 -10 μm)	4.88 \pm 0.41	0.5 \pm 0.1	5.14 \pm 0.70	0.5 \pm 0.1	4.49 \pm 0.38	0.6 \pm 0.0	5.38 \pm 0.43	0.5 \pm 0.0	4.66 \pm 0.65	0.5 \pm 0.0

^(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.

List of Figures

- 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 ($d\log D_a=0.01\mu\text{m}$).
- Fig. 3. Continuous log-normal size distributions of the estimated chemical species number concentrations in four seasons ($d\log D_a=0.01\mu\text{m}$).
- Fig. 4. Continuous log-normal size distributions of the measured particle number concentrations in four seasons.
- Fig. 5. Correlations between the estimated and SMPS- and APS-measured particle number concentrations (430 nm-10 μm) in four seasons.
- Fig. 6. Correlations between the measured and estimated b_{sp} in four seasons.
- Fig. 7. The contributions of continuous log-normal size distributions of chemical species on the estimated b_{sp} in four seasons ($d\log D_a=0.01\mu\text{m}$).
- Fig. 8. Continuous log-normal size distributions of fine particle (<2.1 μm) MSEs in four seasons and the MSEs of chemical species at wavelength of 520 nm under dry condition (relative humidity =40%) in urban Guangzhou.
- Fig. 9. Continuous log-normal size distributions of $(\text{NH}_4)_2\text{SO}_4$ (a), NH_4NO_3 (b) and OM (c) mass concentrations and their σ values and MMADs in the droplet mode at wavelength of 520 nm under dry condition (relative humidity =40%).

















