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

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Abstract. To grasp the key factors affecting particle mass scattering efficiency (MSE), particle mass and number size distribution, bulk PM$_{2.5}$ and PM$_{10}$ and their major chemical compositions, and particle scattering coefficient ($b_{sp}$) under dry condition were measured at an urban site in Guangzhou, south China during 2015-2016. On annual average, 10±2%, 48±7% and 42±8% of PM$_{10}$ mass were in the condensation, droplet and coarse modes, with mass median aerodynamic diameters (MMADs) of 0.21±0.00, 0.78±0.07 and 4.57±0.42 μm, respectively. The identified chemical species mass concentrations can explain 79±3%, 82±6% and 57±6% of the total particle mass in the condensation, droplet and coarse mode, respectively. Organic matter (OM) and elemental carbon (EC) in the condensation mode, OM, (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$ and crustal element oxides in the droplet mode, and crustal element oxides, OM and CaSO$_4$ in the coarse mode were the dominant chemical species in their respective modes. The measured $b_{sp}$ can be reconstructed to the level of 91±10% using Mie theory with input of the estimated chemically-resolved number concentrations of NaCl, NaNO$_3$, Na$_2$SO$_4$, NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, K$_2$SO$_4$, CaSO$_4$, Ca(NO$_3$)$_2$, OM, EC, crustal element oxides and unidentified fraction. MSEs of bulk particle and individual chemical species were underestimated by less than 13% in any season based on the estimated $b_{sp}$ and chemical species mass concentrations. Seasonal average MSEs varied in a small range of 3.5±0.1 to 3.9±0.2 m$^2$ g$^{-1}$ for fine particles, which was mainly caused by seasonal variations of the mass fractions and MSEs of OM in the droplet mode.

Keywords: particle size distribution, particle chemical composition, particle mass scattering efficiency
1. Introduction

Light extinct coefficient ($b_{\text{ext}}$) of atmospheric particles, which is the sum of their scattering ($b_{\text{sp}}$) and absorption ($b_{\text{ap}}$) coefficients, is a key index of haze weather (Hand and Malm, 2007). In most cases, $b_{\text{ap}}$ accounted for more than 90% of $b_{\text{ext}}$ (Takemura et al., 2002; Tao et al., 2017a). Numerous studies have demonstrated that haze is mainly caused by high concentrations of fine particles (PM$_{2.5}$, with aerodynamic diameter smaller than 2.5 μm) (Hand and Malm, 2007; Huang et al., 2012; Malm et al., 1994; Malm et al., 2000; Malm et al., 2003; Malm and Hand, 2007; Sisler and Latimer, 1993; Sisler et al., 1996; Sisler and Malm, 2000; Wang et al., 2014b; Zhao et al., 2013). Knowledge of the dominant chemical species in PM$_{2.5}$ (e.g. (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$ and OM) and their contributions to $b_{\text{ap}}$ is crucial in making feasible policies for alleviating haze (Watson, 2002).

Generally, $b_{\text{ap}}$ can be estimated in reasonable accuracy using Mie theory when size distributions of dominant chemical species are known (Cheng et al., 2008; Cheng et al., 2009; Gao et al., 2015; Malm et al., 2003; Watson et al., 2008). However, routinely monitoring of the size distributions of all the dominant chemical components is impractical. To evaluate haze in the national parks in U.S.A. under the Regional Haze Rule, the original and revised IMPROVE formulas were developed for reconstructing $b_{\text{ap}}$ based on the chemical species in PM$_{2.5}$ and coarse particle mass concentrations monitored in the IMPROVE network (Pitchford et al., 2007; Watson, 2002). The MSEs of chemical species are the important parameters of the IMPROVE formulas for building the relationships between chemical species and $b_{\text{ap}}$ (Hand and
The recommended MSEs of $(NH_4)_2SO_4$, NH$_4$NO$_3$, OM and fine soil (estimated from crustal elements) in PM$_{2.5}$ were 3.0, 3.0, 4.0 and 1.0 $m^2$ g$^{-1}$, respectively, in the original IMPROVE formula. However, MSEs of any particle species vary with its mass concentrations and size distributions (Lowenthal and Kumar, 2004; Malm et al., 2003; Malm and Hand, 2007; Malm and Pitchford, 1997). Subsequently, the MSEs and mass concentrations of $(NH_4)_2SO_4$, NH$_4$NO$_3$ and OM in the PM$_{2.5}$ were separated into small and large modes in the revised IMPROVE formula (Hand and Malm, 2007).

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

According to Mie theory, variations in size distributions (e.g. MMADs and mass fractions) of chemical components are the most important factors for hindering the applications of the IMPROVE formulas and multiple linear regression models. Although many studies have conducted on understanding size distributions and chemical compositions of fine particles in China, few studies have explored the relationship between the size distribution of major chemical species and their MSEs (Cheng et al., 2008; Cheng et al., 2009; Gao et al., 2015). To fill this knowledge gap, size-segregated particle mass, PM\(_{10}\), PM\(_{2.5}\) and their major chemical components, and online data including size distribution of particle number, \( b_{np} \) under dry conditions and water-soluble inorganic ions were synchronously measured at an urban site in Guangzhou covering four seasons in 2015-2016. Size distributions of dominant chemical components were first characterized in section 3.1, followed by discussions on the closures of particle mass and number concentration and \( b_{sp} \) in 3.2. Key factors controlling the variations of chemical species and their MSEs were then discussed in section 3.3. Knowledge gained from the present study will improve the assessments of air-quality and climate impact caused by atmospheric particles.

2. Methodology

2.1 Site description

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

2.2 Field sampling

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

Bulk PM₁₀ and PM₁₀ samples were collected using two Gravisol Sequential Ambient Particulate Monitor (GSAPM) samplers (APM Inc., Korea) at a flow rate of 16.7 L min⁻¹. Samples were collected on 47 mm quartz fiber filter (Whatman QM-A). Sampling durations were the same as those for collecting size-segregated samples in every season. The sampling information is summarized in Table 1. Moreover, 8 sets of
blank samples were also collected for each of the size-segregated particle, PM$_{2.5}$ and PM$_{10}$ samples during the whole sampling period. The aerosol-loaded filter samples were stored in a freezer at -18 °C before analysis to prevent volatilization of particles.

*Insert Table 1*

The background water-soluble inorganic ions (WSII) (e.g. Na$^+$, Ca$^{2+}$) of quartz fiber filter were slightly high in general. Thus, 47mm and 81mm quartz fiber filters were first baked at 500 °C for 3 h to remove adsorbed organic vapors; they were then soaked in distilled-deionized water for 3 h for several times to remove WSII until the background values were less than 0.01 mg L$^{-1}$. Finally, the quartz fiber filters were dried through baking at 200 °C. All blank quartz fiber filters were stored in desiccators.

Particle number concentration for particles in the range of 14 nm - 615 nm in mobility diameter (default as geometric diameter (D$_g$)) was measured using a scanning mobility particle sizer (SMPS; TSI Model 3936, TSI, Inc., St. Paul, MN) combined with a long differential mobility analyzer (DMA; TSI Model 3080) and a condensation particle counter (CPC; TSI Model 3010), and for particles in the range of 542 nm - 10 µm aerodynamic diameter (D$_a$) using an Aerodynamics Particle Sizer (APS; TSI Model 3321), both at 5 min resolution. Dry $b_{dp}$ was measured using a single wavelength integrating nephelometer (Ecotech Pty Ltd, Australia, Model Aurora1000G) at the wavelength of 520 nm. Ambient air passed through three total suspended particulate (TSP) cyclones, then stainless steel tubes and the Nafion driers prior to sampling by the SMPS, APS and nephelometer. RH of aerosol samples was controlled to be lower than 30% by sweeping dry air from a compressed air pump.
Water-soluble inorganic ion (NO$_3^-$) was measured using an In-situ instrument of Gas and Aerosol Composition (IGAC, Model S-611, Machine Shop, Fortelice International Co., Ltd., Taiwan, China) at a resolution of 1-h (Tao et al., 2018).

### 2.3 Lab chemical analysis and data quality assurance and control

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

Three pieces of 0.526 cm$^2$ punches from each 47 mm quartz filter samples and one-fourth of each 81 mm quartz filter samples were used to determine water-soluble inorganic ions. The extraction of water-soluble species from each filter was put into a separate 4 mL bottle, followed by 4 mL distilled-deionized water (with a resistivity of $>18$ MΩ), and then subjected to ultrasonic agitation for 1 h for complete extraction of the ionic compounds. The extract solutions were filtered (0.25 μm, PTFE, Whatman, USA) and stored at 4 °C in pre-cleaned tubes until analysis. Cation (Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$) concentrations were determined by ion chromatography (Dionex ICS-1600) using a CS12A column with 20 mM Methanesulfonic Acid eluent. Anions (SO$_4^{2-}$, NO$_3^-$, Cl$^-$, and F$^-$) were separated on an AS19 column in ion chromatography (Dionex ICS-2100), using 20 mM KOH as the eluent. A calibration was performed for each analytical sequence. Procedural blank values were subtracted.
from sample concentrations. Method detection limits (MDL) of ions were within the range of 0.001 to 0.002 mg L\(^{-1}\).

OC and EC were analyzed using a DRI model 2001 carbon analyzer (Atmoslytic, Inc., Calabasas, CA, USA). An area of 0.526 cm\(^2\) punched from each 47mm quartz filter and 1-4 dots punched from each 81mm quartz filter were analyzed for four OC fractions (OC1, OC2, OC3, and OC4 at 140 °C, 280 °C, 480 °C, and 580 °C, respectively, in a helium [He] atmosphere); OP (a pyrolyzed carbon fraction determined when transmitted laser light attained its original intensity after oxygen [O\(_2\)] was added to the analyzed atmosphere); and three EC fractions (EC1, EC2, and EC3 at 580 °C, 740 °C, and 840 °C, respectively, in a 2% O\(_2\)/98% He atmosphere). Here, OC is operationally defined as OC1 + OC2 + OC3 + OC4 + OP and EC is defined as EC1 + EC2 + EC3 – OP for 47mm samples. However, OC is operationally defined as OC1 + OC2 + OC3 + OC4 and EC is defined as EC1 + EC2 + EC3 for 81mm samples due to extremely low OP level. Average field blanks were subtracted from each sample filter. MDLs of OC and EC were 0.41±0.2 μgC cm\(^{-2}\) and 0.03±0.2 μgC cm\(^{-2}\), respectively.

To obtain high quality data of the size distributions of major chemical components, bulk PM\(_{2.5}\) and PM\(_{10}\) samples were synchronously collected and the same chemical components were analyzed. Generally, good correlations (\(R^2>0.90\)) were found in the mass concentrations of the total particle and major chemical components (including total carbon (TC), NO\(_3^-\) and SO\(_4^{2-}\)) between the size-segregated samples (PM\(_{10}\) and PM\(_{2.5}\)) and the GSAPM samplers (PM\(_{10}\) and PM\(_{2.5}\)). The regression slopes were in the range of 0.91-1.05, suggesting good and
acceptable data quality of the size distributions of the major chemical components (Fig. S1).

2.4 Data analysis methods

In this work, the cut-off point 2.1 \( \mu \text{m} \) was chosen to separate the fine and coarse mode particles for investigating the impact of aerosol size distribution on their respective MSEs. Moreover, the cut sizes of <0.43 \( \mu \text{m} \) and 0.43 - 2.1 \( \mu \text{m} \) were used to separate the condensation mode and droplet mode, respectively. Continuous size-distribution profiles of major chemical components are needed in order to accurately calculate \( b_{sp} \) using Mie theory, and are obtained from the inversion of the measured mass concentration distribution in the size bins of the Anderson 8-stage air samplers using the technique described by Dong et al. (2004). However, this approach is not applicable for the condensation mode because there is only one size bin in this mode. Thus, MMADs of this mode are used for generating the continuous size distributions of all the concerned chemical species. MMADs of this mode are calculated according to:

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D_p = (D_{p1} \times D_{p2})^{0.5}
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(1)

Where \( D_{p1} \) and \( D_{p2} \) represent the lower (0.10 \( \mu \text{m} \), limits of detection of Anderson 8-stage air sampler) and upper (0.43 \( \mu \text{m} \)) boundaries of this size bin, respectively. To improve the resolution of \( b_{sp} \), 401 bins were used for chemical species ranging from 10 nm to 100 \( \mu \text{m} \), with a constant ratio between the adjacent size bins, defined as \( \log(D_{p2}/D_{p1}) = 0.01 \). Further increasing the number of size bins does not have any significant impact on the results, e.g., the changes in \( b_{sp} \) are smaller than 1\% even if the above ratio of 0.01 is replaced with 0.001.

The ISORROPIA II model was run at the reserved mode (Fountoukis and Nenes, 2007) with input data of K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), NH\(_4^+\), Na\(^+\), SO\(_4^{2-}\), NO\(_3^-\), Cl\(^-\), RH (40\%), and

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\text{RH} (40\%)
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temperature (25°C), to estimate the size-resolved mass concentrations of NaCl, 
NaNO₃, Na₂SO₄, NH₄Cl, NH₄NO₃, (NH₄)₂SO₄, KCl, KNO₃, K₂SO₄, MgCl₂, 
Mg(NO₃)₂, MgSO₄, CaCl₂, Ca(NO₃)₂, CaSO₄ and H₂O.

3. Results and Discussion

3.1 Size distributions of total particle mass and major chemical components

3.1.1 Total particle mass

Generally, any particle size distribution can be fitted into a combination of 
condensation, droplet and coarse modes (John et al., 1990). Continuous log-normal 
size distributions of particle mass including the condensation, droplet and coarse 
modes were calculated using the method described in section 2.4 and are summarized 
in Table 2. On annual average, 10±2%, 48±7% and 42±8% of PM₁₀ mass were in the 
condensation, droplet and coarse modes, with the average MMADs of 0.21±0.00, 
0.78±0.07 and 4.57±0.42, respectively. This result was comparable with those 
observed by the Micro-Orifice Uniform Deposit Impactor (MOUDI) in other cities 
(e.g. Shenzhen and Hong Kong) of the PRD region (Bian et al., 2014; Lan et al., 2011; 
Yu et al., 2010).

The estimated annual PM₂.₅ concentration based on the continuous log-normal 
size distribution was 36.4±13.2 μg m⁻³, which was close to the synchronously 
measured PM₂.₅ (36.8±15.3 μg m⁻³), although slightly higher than the sum of the mass 
concentrations (34.9±13.8 μg m⁻³) in the condensation and droplet modes. Thus, the 
fine (sum of condensation and droplet) mode particles can reasonably represent PM₂.₅.

Seasonal average particle mass concentrations were evidently lower in summer than 
in the other seasons for all the three modes, were close during the other seasons for 
the condensation and droplet modes, and were slightly higher in autumn and spring 
than winter for the coarse mode. These results agree with the seasonal variations of
PM$_{2.5}$ observed at the same site in 2009-2010 (Tao et al., 2014b).

Insert Table 2

3.1.2 Water-soluble inorganic ions

Generally, SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ are the dominant WSII s, especially in the condensation and droplet modes. They are mainly formed through aqueous-phase reactions in moisture conditions in the PRD region (Lan et al., 2011; Yu et al., 2010).

As expected, 77±6% SO$_4^{2-}$, 46±16% NO$_3^-$ and 89±7% NH$_4^+$ mass concentrations were in the droplet mode on annual average (Table 2). Much lower fractions for NO$_3^-$ than SO$_4^{2-}$ and NH$_4^+$ in the droplet mode were mostly due to the high volatility of NH$_3$NO$_3$ (Zhang et al., 2008). The MMADs of the three ions in the droplet mode were in the range of 0.70-0.94 µm, comparable with MOUDI measurements (0.78-1.03 µm) conducted in the PRD region (Bian et al., 2014; Lan et al., 2011; Yu et al., 2010).

Small fractions of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ masses were distributed in the condensation mode, e.g., 12±4%, 10±4% and 6±5%, respectively, on annual average. The mass fractions of SO$_4^{2-}$ in the condensation mode shown above were much lower than those (24-29%) observed in urban Guangzhou in 2006-2007 (Yu et al., 2010), suggesting gas-phase chemical reactions of SO$_2$ has become less important in the formation of SO$_4^{2-}$, likely due to the dramatic reduction of SO$_2$ emissions in urban or suburban Guangzhou in the recent decade (Zheng et al., 2009; Zheng et al., 2018).

Note that the MMAD in the condensation mode was 0.21 µm in Yu et al. (2010), a value that is comparable with those (0.23-0.42 µm) measured using MOUDI at urban sites in the PRD region (Bian et al., 2014; Lan et al., 2011; Yu et al., 2010).

11±5% SO$_4^{2-}$, 44±18% NO$_3^-$ and 5±4% NH$_4^+$ mass concentrations were
distributed in the coarse mode. In general, NO$_3^-$ mainly exists in the form of NH$_4$NO$_3$
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in the condensation and droplet modes and associates with base cations in the coarse
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mode (e.g., Ca(NO$_3$)$_2$ and NaNO$_3$) (Zhang et al., 2015a). More than 50% NO$_3^-$ mass
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concentrations were distributed in the coarse mode in summer and autumn when
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ambient temperatures were high. The MMADs of NO$_3^-$ in the coarse mode were
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4.15±0.52 and 4.36±0.31 µm in summer and autumn, respectively, slightly lower than
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those of Ca$^{2+}$ (4.10±0.42 and 4.72±0.47 µm in the same seasons), but evidently higher
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than those of Na$^+$ (3.60±0.19 and 3.64±0.27 µm) (Table 2). This suggests that
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NH$_4$NO$_3$ was prone to dissociate to HNO$_3$(g) in summer and autumn due to the high
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ambient temperatures with released HNO$_3$(g) further reacting with mineral dust and to
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a less extent with sea salt particles. In comparison, the MMADs of SO$_4^{2-}$ in the coarse
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mode were in between of those of Ca$^{2+}$ and Na$^+$, likely due to uptake of H$_2$SO$_4$(g) by
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both mineral dust and sea salt particles (Zhang et al., 2015a). In contrast, the MMAD
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of NH$_4^+$ in the coarse mode was 3.25±0.69 µm, much smaller than those of SO$_4^{2-}$ and
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NO$_3^-$, suggesting that NH$_4^+$ in the coarse mode was likely from hygroscopic growth of
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NH$_4^+$ in the droplet mode (Tian et al., 2014a).

It is also worth mentioning that most of Cl$^-$ was distributed in the coarse mode
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and its MMAD (3.77±0.35 µm) was very close to that of Na$^+$ (3.75±0.38 µm),
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especially in summer when air masses were originated from the China South Sea (Tao
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et al., 2017b; Xia et al., 2017). The mole ratios of Cl$^-$/Na$^+$ were less than 1.0 in all the
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seasons but spring due to the reactions between sea salt and acid gasses (HNO$_3$(g) and
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H$_2$SO$_4$(g)) (Zhuang et al., 1999a). The excess Cl$^-$ in the coarse mode in spring was
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likely due to the aged biomass burning particles from the southeast Asian. In fact, the
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concentration of the typical biomass burning tracer K$^+$ in the coarse mode was higher
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in spring than in the other seasons (Zhang et al., 2015c). In any case, sea salt was
mainly distributed in the coarse mode rather than the droplet mode in urban Guangzhou.

### 3.1.3 OC and EC

OC and EC in fine particles can be produced from both primary emissions of vehicle exhaust, coal combustion, biomass burning and secondary formation (Chow et al., 2011; Gentner et al., 2012; Gentner et al., 2017; Hallquist et al., 2009; Zheng et al., 2006). In general, fresh OC and EC particles emitted from vehicle exhaust, coal combustion and biomass burning should be distributed in the condensation mode (Schwarz et al., 2008; Zhang et al., 2012b). Only 13±4% of OC and 31±7% of EC mass concentrations were distributed in the condensation mode in the present study (Table 2). OC/EC ratios were in the range of 0.9-1.6 in the condensation mode, suggesting that vehicle exhaust was the dominant source of OC and EC in this particle size range (Huang et al., 2006a; Schwarz et al., 2008; Shiraiwa et al., 2007; Watson et al., 2001; Wu et al., 2017). 62±9% of OC and 55±7% of EC mass concentrations were distributed in the droplet mode (Table 2), similar to that of $\text{SO}_4^{2-}$. These numbers were similar to those observed in the other cities of the PRD region, and was previously identified to be mainly caused by in-cloud aerosol processing (Huang et al., 2006b). Cloud processing indeed plays important roles in forming droplet mode aerosols in urban Guangzhou (Tao et al., 2018). OC/EC ratios were in the range of 2.2-3.2 in the droplet mode, much higher than those in the condensation mode, suggesting that OC in the droplet mode was mainly aged or secondary particles (Day et al., 2015; Huang et al., 2006a; Wu and Yu, 2016).

Although only one size bin was available in the condensation mode in this study, the estimated MMADs of OC and EC in this mode were comparable with those (0.25-0.34 µm) measured using MOUDI with 3 bins in this size range at suburban...
sites (e.g. Hong Kong and Shenzhen) (Lan et al., 2011; Yu et al., 2010). The MMADs of OC and EC in the droplet mode were 0.76±0.07 µm and 0.66±0.08 µm, respectively, which were slightly lower than those (0.7-1.0 µm for OC and 0.8-1.0 µm for EC) found in earlier studies in the PRD region (e.g. Guangzhou, Hong Kong and Shenzhen) (Lan et al., 2011; Yu et al., 2010). Noticeably, the MMADs of OC and EC in the droplet mode were very close to those (0.73 µm for OC and 0.77 µm for EC) measured in summer at a suburban site of Hong Kong, where the loadings of the dominant chemical components (e.g. OC, EC and SO$_4^{2-}$) were low (Yu et al., 2010).

Road dust and biogenic aerosols were generally considered as the major sources of OC and EC in the coarse mode (Ho et al., 2003; Zhang et al., 2015b). Significant fractions of OC (25±8%) and EC (14±7%) mass concentrations were distributed in the coarse mode. These numbers were comparable with those (13-38% for OC and 4-16% for EC) measured at suburban sites of Guangzhou, Shenzhen and Hong Kong (Lan et al., 2011; Yu et al., 2010), but were lower than those (51-57% for OC and 17-21% for EC) measured in urban Guangzhou in 2006-2007. The MMADs of OC (3.73±0.58 µm) and EC (3.69±0.65 µm) in the coarse mode were close to those (3.8-4.3 µm for OC and 3.7-4.1 µm for EC) measured in suburban of Hong Kong, although smaller than those (4.8-5.2 µm for OC and 5.0-5.2 µm for EC) measured in suburban of Shenzhen and urban of Guangzhou (Lan et al., 2011; Yu et al., 2010). These results suggested that the MMADs of OC and EC might decrease with their decreasing coarse mode mass fractions. Annual PM$_{10}$ concentrations in 2015-2016 in this study were 40% lower than those in 2006-2007 in the PRD region, which further supported the above hypothesis (Yu et al., 2010).
3.2 Closures of particle mass and number concentrations and $b_{sp}$

3.2.1 Closure of particle mass concentration

To investigate the impact of chemical species in different size modes on $b_{sp}$, particle mass concentrations in the different modes were first reconstructed based on mass concentrations of individual known chemical components. The dominant water-soluble inorganic species including NaCl, NaNO$_3$, Na$_2$SO$_4$, NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, K$_2$SO$_4$, CaSO$_4$ and Ca(NO$_3$)$_2$ were determined using the ISORROPIA II thermodynamic equilibrium model as mentioned in section 2.4. A ratio of OM to OC of 1.4, 1.6 and 1.6 would be appropriate for the condensation, droplet and coarse mode, respectively, which was based on the findings of a previous study that suggested an average OM/OC ratio of 1.57 and a range of 1.4-1.8 in an urban environment of the PRD region (He et al., 2011). In our previous study (Tao et al., 2017b), mass concentration of crustal element oxides in PM$_{2.5}$ was estimated from the measurements of five crustal elements (Al, Si, Ca, Fe and Ti) in urban Guangzhou. This approach cannot be used in the present study due to the lack of crustal elements measurements. Alternatively, crustal element oxides mass concentration was estimated from Ca$^{2+}$ mass concentration because of their good correlations as was found in our previous study (Fig. S2) (Tao et al., 2017b). Moreover, source profiles of soil dust (representing crustal element oxides) in cities of southern China also suggested that Ca$^{2+}$ accounted for 5% of total soil dust in PM$_{2.5}$ (Sun et al., 2019). On annual average, the estimated crustal element oxides accounted for 8±2%, 10±4% and 29±5% of the total particle mass concentrations in the condensation, droplet and coarse mode, respectively. The reconstructed mass concentrations accounted for 79±3%, 82±6% and 57±6% of the total in the condensation, droplet and coarse mode, respectively.
As shown in Fig. 2, OM, EC, (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$ and crustal element oxides dominated in different modes in four seasons. For example, OM and EC accounted for 31-39% and 14-19%, respectively, of particle mass in the condensation mode, OM, (NH$_4$)$_2$SO$_4$, crustal element oxides and NH$_4$NO$_3$ accounted for 19-34%, 18-22%, 6-15% and 4-11%, respectively, in the droplet mode, and crustal element oxides, OM and CaSO$_4$ accounted for 22-34%, 12-17% and 4-5%, respectively, in the coarse mode. In addition, the total of the other identified chemical species only accounted for less than 10% of the total particle mass in every mode. For example, Na$_2$SO$_4$ and K$_2$SO$_4$ mainly distributed in the droplet mode and together they accounted for only 2-5% of the particle mass in this mode. NaCl, NaNO$_3$ and Ca(NO$_3$)$_2$ mainly distributed in the coarse mode and each of these species accounted for less than 2% of the total particle mass in this mode.

Insert Figure 2

3.2.2 Closure of particle number concentration

To estimate the contribution of individual chemical species on $b_{wp}$ using Mie theory, number size distributions of the dominant chemical species were needed and were calculated according to the method described in Lin et al. (2014). As shown in Fig. 3, most chemical species (except (NH$_4$)$_2$SO$_4$ in summer) had much higher number concentrations in the condensation than droplet or coarse mode. Although the estimated number median aerodynamic diameters (NMADs) of the number concentrations of individual chemical species mainly distributed in the range of 100-120 nm, the estimated NMADs of particle number concentrations were always close to about 100 nm in four seasons. This was because the estimated MMADs of
particle mass concentrations were a constant value (0.21 µm) based on only one bin in
the condensation mode. Moreover, average densities of particle in the condensation
mode only changed a little in four seasons because OM and EC were always the
dominant chemical species in this mode.

In contrast, the NMADs of particle number concentrations simultaneously
measured by the SMPS and APS distributed in the range of 40-80 nm (Fig. 4), which
shifted to smaller sizes than those estimated from the size-segregated chemical
species mass concentrations. This was because SMPS and APS collected dried
particles while the size-segregated sampler collected ambient particles. Dₚ of particles
measured by SMPS can be converted to Dₚ using the average particle density
calculated from the synchronously measured size-segregated individual chemical
species mass concentrations and densities. In any case, the NMADs of particle
number concentrations were less than 100 nm regardless of using SMPS and APS
measurements or the estimated size-segregated chemical species mass concentrations.

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

NMADs estimated from the size-segregated chemical species mass
concentrations were close to those measured by the SMPS and APS in spring and
autumn, resulting in the close estimation of particle number concentrations to the
measured ones. In contrast, the estimated particle number concentrations from the the
size-segregated chemical species mass concentrations were evidently lower than those measured by the SMPS and APS in summer and winter, due to the much higher NMADs (100 nm) estimated from the size-segregated chemical species mass concentrations than those (about 30 or 40 nm) measured by the SMPS and APS. Fortunately, the single particle scattering efficiencies of chemical species in the condensation mode at the wavelength 520 nm were much lower than those in the droplet mode and the coarse mode (Fig S3).

To exclude the large uncertainties in the estimated particle number concentration caused by condensation mode particles (which were due to the design flaws of size-segregated sampler), particles smaller than 430 nm were not included in the calculation below. The estimated particle number concentrations in the range of 430 nm-10 μm based on the size-segregated chemical species mass concentrations were only slightly higher than those measured by the SMPS and APS. This was likely because particles in the droplet mode may shift to the smaller sizes (<430 nm) during the dry process by Nafion tube. Moreover, most of EC particles in the droplet mode were internally mixed with OM or inorganic salts in the real world, which also may result in overestimating the particle number concentrations by the size-segregated chemical species mass concentrations (Wu et al., 2016; Yu et al., 2010). Correlation coefficients between the estimated and measured particle number concentrations in the range of 430 nm-10 μm were significantly improved when the intercepts in the linear regression equations were retained. To some extent, the intercepts represented the measurement or estimation errors of SMPS and APS and models. In any case, good correlations ($R^2>0.81$) between the estimated daily particle number concentrations and the measured ones were found and the slopes ranged from 0.79 to 1.03 in the four seasons (Fig. 5). These results suggested that the estimated particle
number concentrations were acceptable in the range of 430 nm-10 µm, noting that particles in this size range dominate particle scattering efficiency.

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

Although the number concentrations in the condensation mode were underestimated, good correlations ($R^2 > 0.92$) were found between the measured and estimated $b_{sp}$ with the slopes being 0.87, 0.87, 0.85 and 0.89 in spring, summer, autumn and winter, respectively (Fig 6). On annual arithmetic average, the estimated $b_{sp}$ can explain $91\pm10\%$ of the measured $b_{sp}$. The residual fractions were likely related to the chosen convert factor between OM and OC, measurements and sampling errors of chemical species (especially NO$_3^-$), errors from the models (ISORROPIA II model, Mie model, and especially the inversion technique method), and measurement errors caused by the size-segregated sampler (Vaughan, 1989). Magnitudes of the uncertainties caused by these sources are discussed below.

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

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

Different from the other chemical species, NH$_4$NO$_3$ can dissociate into HNO$_3$(g) and NH$_3$(g) during the filter gravimetric weighing process under dry condition. To evaluate the evaporative loss of NH$_4$NO$_3$, synchronous online data of NO$_3^-$ were also measured by an In-situ Gas and Aerosol Composition monitoring system at hourly temporal resolution (Fig. S4). Seasonal average NO$_3^-$ concentrations were 42% (PM$_{2.5}$), 39% (PM$_{10}$), 42% (PM$_{2.5}$) and 19% (PM$_{2.5}$) less from filter measurements than online measurements in spring, summer, autumn and winter, respectively. Adjusting the filter NO$_3^-$ data using the above ratios can increase the estimated b$_{sp}$ by 7%, 2%, 4% and 2% in the respective season.

Meanwhile, the measured b$_{sp}$ could also be underestimated due to the dissociation of NH$_4$NO$_3$ during the dry processes of ambient particles through the Nafion dryer. A previous study indicated the measured b$_{sp}$ being decreased by less than 10% due to the dissociation of NH$_4$NO$_3$ in a heated nephelometer (Bergin et al., 1997). In the present study, the chamber temperatures of nephelometer were less than 300 K and the particle residence time in both the Nafion dryer and the nephelometer chamber was about 7 seconds. Thus, the bias in the measured b$_{sp}$ should be less than 2% in any season according to the relationship among the loss of b$_{sp}$, residence time and the temperature in chamber in a previous study (Bergin et al., 1997). Combining all of the above-mentioned factors, the adjusted estimated b$_{sp}$ would increase to the level of 92%, 87%, 87% and 89% of the measured b$_{sp}$ in
spring, summer, autumn and winter, respectively. This means the above methods for estimating \( b_{sp} \) were reasonable with the adjusted estimated values explaining 87-92\% of the measured values after the filter-based NO\(_3^−\) concentrations were adjusted based on the online data. Thus, the errors from the models and size-segregated samplers may account for remaining 8-13\% of the measured \( b_{sp} \).

Generally, the estimated seasonal average \( b_{sp} \) were 146±40 Mm\(^{-1}\), 99±33 Mm\(^{-1}\), 169±54 Mm\(^{-1}\) and 151±71 Mm\(^{-1}\) in spring, summer, autumn and winter, respectively (Fig. 7). The particles in the condensation, droplet and coarse modes contributed 6-7\%, 81-86\% and 8-12\%, respectively, to the estimated \( b_{sp} \). OM and EC were the dominant contributors, accounting for 32-41\% and 30-37\%, respectively, of the estimated \( b_{sp} \) in the condensation mode. OM and secondary inorganic aerosols (sum of (NH\(_4\))\(_2\)SO\(_4\) and NH\(_4\)NO\(_3\)) were the dominant contributors, accounting for 27-44\% and 27-34\%, respectively, of the estimated \( b_{sp} \) in the droplet mode. Unidentified fraction, crustal element oxides and OM were the dominant contributors, accounting for 26-47\%, 16-29\% and 19-27\%, respectively, of the estimated \( b_{sp} \) in the coarse mode. The sum of the dominant contributors, including OM, EC, secondary inorganic aerosols and crustal element oxides, accounted for 70-79\% of the estimated \( b_{sp} \) in the four seasons. In contrast, the sum of the other chemical species (including NaCl, NaNO\(_3\), Na\(_2\)SO\(_4\), K\(_2\)SO\(_4\), CaSO\(_4\), Ca(NO\(_3\))\(_2\), H\(_2\)O) accounted for 5-10\% and the unidentified fraction, 12-23\% of the estimated \( b_{sp} \). In conclusion, visibility degradation was determined by the dominant chemical species (e.g. OM, EC, secondary inorganic aerosols and crustal element oxides) in the fine mode (both condensation and droplet), which agreed with the results of the original and revised IMPORVE formulas (Pitchford et al., 2007).
3.3 Key factors for variations of particle and chemical species MSEs

3.3.1 The estimated MSEs of particle and chemical species

To conveniently explore the control factors of particle MSE, the dominant chemical species’ MSEs were estimated by their mass concentrations and the estimated $b_{sp}$, according to the measured chemical species mass concentrations in section 3.1 and the estimated $b_{sp}$ in section 3.2. Here, only the MSEs of particle, ($\text{NH}_4)_2\text{SO}_4$, $\text{NH}_4\text{NO}_3$, OM, EC, crustal element oxides and unidentified fraction in the condensation, droplet, coarse, and fine modes (sum of condensation and droplet modes) were estimated (Table 3), considering these chemical species accounted for more than 90% of the estimated $b_{sp}$. Moreover, an external mixing of individual chemical species was assumed in the estimation.

Undoubtedly, the particle MSE should be underestimated because the estimated $b_{sp}$ was 11-15% less of the measured $b_{sp}$ in four seasons, as discussed in section 3.2.

The measured $b_{sp}$ would be biased low by about 3% due to the evaporation of $\text{NH}_4\text{NO}_3$, while the $\text{NO}_3^-$ mass concentrations based the filter measurements were biased low by 5%, 3%, 9% and 6% in spring, summer, autumn and winter, respectively. Thus, the MSEs of $\text{NO}_3^-$ would be underestimated by 9%, 13%, 6% and 5% in the respective season in the real world. In conclusion, the MSEs of particle and chemical species were underestimated by less than 13%.

On annual average, the estimated particle MSEs in the condensation, droplet and
coarse modes were 2.1±0.2 m² g⁻¹, 4.3±0.2 m² g⁻¹ and 0.5±0.0 m² g⁻¹, respectively. The estimated particle MSE in the fine mode (sum of condensation and droplet modes, similar to PM₂.₅) was 3.7±0.2 m² g⁻¹, which was slightly higher than the value of 3.5 m² g⁻¹ estimated in 2009-2010 in urban Guangzhou (Tao et al., 2014b). Seasonal variations of the estimated MSEs in the fine mode followed the sequence of winter (3.9±0.2 m² g⁻¹) > autumn (3.8±0.2 m² g⁻¹) > summer (3.6±0.2 m² g⁻¹) > spring (3.5±0.1 m² g⁻¹). Evidently, the estimated MSEs in the fine mode were slightly higher in autumn and winter than spring and summer, which also agreed with the previous studies in urban Guangzhou (Andreae et al., 2008; Jung et al., 2009a).

On annual average, the estimated MSEs of (NH₄)₂SO₄, NH₄NO₃, OM and crustal element oxides (equal to fine soil in the IMPROVE formulas) in the fine mode were 4.4±0.8, 4.5±1.5, 4.6±0.3 and 2.6±0.1 m² g⁻¹, respectively, which were higher than those (3.0, 3.0, 4.0 and 1.0 m² g⁻¹, respectively) from using the original IMPROVE formula (Hand and Malm, 2007; Malm and Hand, 2007; Pitchford et al., 2007). As shown in Table 3, the MSEs of (NH₄)₂SO₄, NH₄NO₃, OM and crustal element oxides in the fine mode depended on their mass fractions in the droplet mode with high MSEs. In the original IMPROVE formula, MSEs of these chemical species were estimated using the multiple linear regression model according to the chemical components in PM₂.₅ and b_sp from IMPROVE network, noting that significant mass fractions of particle were in the condensation mode at the regional sites of IMPROVE network and an urban site in U.S.A. (Cabada et al., 2004; Hand et al., 2002; Malm et al., 2003). In contrast, in the present study most mass fractions of the dominant chemical species (e.g. (NH₄)₂SO₄, NH₄NO₃ and OM) in the fine mode were distributed in the droplet rather than condensation mode. These results suggested the higher MSEs of (NH₄)₂SO₄, NH₄NO₃ and OM in the fine mode in this study were
likely due to their significant mass fractions in the droplet mode. In fact, the MSE of fine soil in the IMPROVE formulas would represent the MSE of the bulk mode rather than the fine mode (Hand and Malm, 2007). The average MSEs of the bulk mode was 1.0±0.2 m² g⁻¹ in this study, which was similar to that in the IMPROVE formulas.

On annual average, the estimated MSEs of (NH₄)₂SO₄, NH₄NO₃ and OM were 4.7±0.6, 4.8±0.9 and 5.3±0.2 m² g⁻¹ in the droplet mode, and were 2.1±0.5, 2.3±0.8 and 2.7±0.1 m² g⁻¹ in the condensation mode, respectively, which were lower than those in the large mode (similar to droplet mode) and were slightly lower than those in the small mode (similar to condensation mode) in the revised IMPROVE formula (Pitchford et al., 2007). Theoretically, the highest MSEs of (NH₄)₂SO₄, NH₄NO₃ and OM would be found in about 0.55 µm in mass median geometric diameters (MMGD) at the wavelength 550 nm according to Mie theory. However, the MMADs of (NH₄)₂SO₄, NH₄NO₃ and OM were 0.76 - 0.80 µm (equal to about 0.60-0.64 µm in MMGD) in the droplet mode and were 0.21 µm (equal to about 0.16-0.18 µm in MMGD) in the condensation mode in this study, which were larger than 0.50 µm in MMGD in the large mode and were lower than 0.20 µm in MMGD in the small mode in the revised IMPROVE formula. Thus, the higher MMGDs in the droplet mode and the lower MMGDs of (NH₄)₂SO₄, NH₄NO₃ and OM in the condensation mode in this study maybe result in their lower MSEs compared with those in the revised IMPROVE formula. In addition, the underestimated b_sp would also result in underestimating their MSEs in the condensation and droplet modes in this study.

Although the contribution of EC to b_sp was not considered in the IMPROVE formulas, its mass extinction efficiency (10 m² g⁻¹) considered both scattering and absorption abilities (Hand and Malm, 2007). In fact, the theoretical average mass absorption efficiency (MAE) of EC in fine particle was 7.5 m² g⁻¹ at the wavelength 25
550 nm (Wu et al., 2016). Thus, mass extinction efficiency of EC was also about 10 m$^2$ g$^{-1}$ in this study, suggesting the estimated EC MSEs were comparable with the IMPROVE formulas. The estimated MSEs of coarse particle was 0.5±0.0 m$^2$ g$^{-1}$, which was also comparable with the value of 0.6 m$^2$ g$^{-1}$ in the IMPROVE formulas. Noticeably, sea salt was mainly distributed in the coarse mode rather than droplet mode in this study. In addition, the unidentified fraction with large mass fraction and the high MSE in the fine mode was not considered in the IMPROVE formulas, although it accounted for a significant contribution of the estimated $b_{sp}$ in this study (Fig. 7). In conclusion, EC and unidentified fraction rather than sea salt should be considered in estimating $b_{sp}$, especially when EC and unidentified fraction accounted for significant mass fractions of fine particles.

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

As discussed in section 3.3.1, seasonal average MSEs in the coarse mode fluctuated in a small range of 0.4-0.5 m$^2$ g$^{-1}$, while those in the fine mode in a slightly larger range of 3.5-3.9 m$^2$ g$^{-1}$, but the percentage changes are in similar magnitudes (10-20%). Only variations of fine particle MSE were discussed below as an example. It is worth to mention that fine particle MSE increased with its mass concentrations in IMPROVE network (Lowenthal and Kumar, 2004), but such a phenomenon was not founded in the present study. As shown in Fig. 8, the seasonal variations of fine particle MSE were mainly caused by particle fractions in the size range of 0.4-0.9 µm, which belong to the droplet mode. In this mode, the MSEs of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ and OM were higher while those of the other chemical species were lower than the overall particle MSE. Note that the overall particle MSE depends on the mass concentrations and MSEs of individual chemical components. Thus, the seasonal
average MSEs of fine particle were dominated by the seasonal average mass fractions and associated MSEs of \((\text{NH}_4)_2\text{SO}_4\) and \(\text{NH}_4\text{NO}_3\) and OM in the droplet mode.

\[ \text{Insert Figure 8} \]

The sum of the products of seasonal average mass concentration and MSEs of the above three chemical species in the droplet mode was 1.8, 2.1, 2.3 and 2.5 m\(^2\) g\(^{-1}\) in spring, summer, autumn and winter, respectively. As expected, the seasonal variations of fine particle MSE followed the sequences of winter \((3.9\pm0.2 \text{ m}^2 \text{ g}^{-1}) > \) autumn \((3.8\pm0.2 \text{ m}^2 \text{ g}^{-1}) > \) summer \((3.6\pm0.2 \text{ m}^2 \text{ g}^{-1}) > \) spring \((3.5\pm0.1 \text{ m}^2 \text{ g}^{-1})\).

Noticeably, fine particle MSE was determined by the average MSEs of the dominant chemical species, rather than their mass fractions which were much smaller than 1.0.

Different from the approach used for fine particle MSE, the MSEs of \((\text{NH}_4)_2\text{SO}_4\), \(\text{NH}_4\text{NO}_3\) and OM in the droplet mode were determined using measurement-based their mass size distributions prescribed as log-normal size distributions. The three parameters describing the log-normal size distributions include mass concentration (in the range of 0.43 - 2.1 \(\mu\)m), MMAD and standard deviation (\(\sigma\)). Thus, the MSEs of \((\text{NH}_4)_2\text{SO}_4\), \(\text{NH}_4\text{NO}_3\) and OM should depend on their MMADs and \(\sigma\) values. Seasonal average \(\sigma\) values of \((\text{NH}_4)_2\text{SO}_4\), \(\text{NH}_4\text{NO}_3\) and OM were in the range of 0.18-0.21, 0.18-0.21 and 0.22-0.26, respectively, while the corresponding MMADs in the range of 0.72-0.92, 0.75-0.90 and 0.73-0.78 \(\mu\)m, respectively (Fig. 9). Generally, the seasonal average MSEs of \((\text{NH}_4)_2\text{SO}_4\), \(\text{NH}_4\text{NO}_3\) and OM in the droplet mode were
higher with the lower σ values (or MMADs) when MMADs (σ values) were close. However, the MSE of OM in summer was 5.2 m$^2$ g$^{-1}$, which was lower than 5.3 m$^2$ g$^{-1}$ in autumn, although σ values and MMADs in summer were lower than those in autumn. This was mainly related with the evident fluctuation the MSE of OM in the range of 0.6-0.7 μm.

Insert Figure 9

In conclusion, the fine particle MSE was determined by the sum of the products of average mass fractions and MSEs of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ and OM in the droplet mode. The MSEs of the above three chemical species in the droplet mode depended on both their σ value and MMADs. Generally, fine particle MSE mainly related with OM due to its high mass and MSE in the droplet mode in urban Guangzhou.

4. Summary and implication

Size- and chemically-resolved particle number and mass concentration were measured in urban Guangzhou in different seasons during 2015-2016 and the data were used to estimate particle MSE. SO$_4^{2-}$ and NH$_4^+$ mainly distributed in the droplet mode, EC in both condensation and droplet modes, and bulk particle, NO$_3^-$, OC, Na$^+$, Ca$^{2+}$ and Cl$^-$ in both droplet and coarse modes. The estimated $b_{sp}$ can represent 85-89% of the measured $b_{sp}$ based on the size-segregated chemical compositions according to ISORROPIA II thermodynamic equilibrium model and Mie theory model. The largest
contributors to $b_{sp}$ were the chemical species in the droplet mode with the highest MSEs.

MSEs of the dominant chemical species were noticeably different in this study than those in the original and revised IMPROVE formulas. The MSEs of (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$ and OM in the fine mode were higher than those in the original IMPROVE formula, and in the droplet mode were lower than those in the revised IMPROVE formula. In any case, $b_{sp}$ would be underestimated in urban Guangzhou using the original or revised IMPROVE formulas because the unidentified chemical species (and associated mass fractions) in the droplet mode accounted for a large fraction of $b_{sp}$ and this portion was not included in these formulas. Moreover, MSEs of chemical species would be overestimated in the original and revised IMPROVE formulas using multiple linear regression model when the unidentified species was ignored. In addition, sea salt was found in the coarse mode in this study, differing from the set up in the IMPROVE formulas which is in the droplet mode. It can be concluded that the estimated $b_{sp}$ in Guangzhou based on the revised IMPROVE formula would have large biases, even though good correlations between estimated and measured $b_{sp}$ was found.

MSEs of fine particles are controlled by the relative mass fractions of the dominant chemical components (e.g., (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$ and OM) and associated size distributions (e.g. $\sigma$ and MMAD). Localized $b_{sp}$ formulas are thus needed for better estimating particle MSE because particle size distributions of individual chemical species vary significantly in space and time.
Data availability. Data used in this study are available from Jun Tao (taojun@scies.org).

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

Acknowledgments

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<th>Season</th>
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<th>Sampler</th>
<th>Sample duration</th>
<th>Sample number</th>
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**Table 1** Summary of sampling information in urban Guangzhou

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Table 2: Summary of chemical compositions concentrations in the different modes in urban Guangzhou

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<th>Cockroach</th>
<th>Ethanol</th>
<th>Food</th>
<th>Smoke</th>
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<tbody>
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<td>0.1±0.1</td>
<td>0.1±0.1</td>
<td>0.1±0.1</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.1±0.1</td>
<td>1.2</td>
<td>0.1±0.1</td>
<td>0.1±0.1</td>
<td>0.1±0.1</td>
<td>0.1±0.1</td>
<td>0.1±0.1</td>
<td>0.1±0.1</td>
<td>0.1±0.1</td>
<td>0.1±0.1</td>
</tr>
</tbody>
</table>

Note: Concentrations are given in micrograms per cubic meter (µg/m³) ± standard deviation.
Table 3 Summary of the estimated MSEs of particle and the dominant chemical species in urban Guangzhou

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
<th>MMAD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coarse mode</strong></td>
<td>4.88±0.74</td>
<td>5.38±0.65</td>
<td>2.14±0.26</td>
<td>2.55±0.43</td>
<td>0.5±0.0</td>
</tr>
<tr>
<td><strong>Fine mode</strong></td>
<td>5.74±0.57</td>
<td>6.57±0.82</td>
<td>2.58±0.65</td>
<td>3.48±0.82</td>
<td>0.5±0.0</td>
</tr>
</tbody>
</table>

*PM: Particulate matter; **Fine mode = sum of condensation and droplet modes.*
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