Response to Reviewer #2

We greatly appreciate the reviewer for providing the detailed comments, which have helped us improve the paper quality significantly. We have addressed all of the comments carefully as detailed below. The original comments are in black and our replies are in blue.

One thing that I recommend doing is to calculate your MSEs also by using multiple linear regression (MLR). Now you calculated them with a Mie model. That is fine and scientifically justified but it also has its uncertainties, for instance related to refractive indices etc. Your data is good for MLR and that would give another estimate for the MSEs. MLR is quick and easy to do – even with Excel – and that is also actually inversely the way air quality data would be used for estimating visibility from PM2.5 filter data. Doing that you would have an additional uncertainty estimate and a closure of MSEs.

We agree with the reviewer that it is worth and relatively easy to use the multiple linear regression (MLR) model to estimate MSEs, as we have done in several of our previous studies (Tao et al., 2014a, 2014b, 2015, 2016). In fact, we have recently completed another study comparing MSEs calculated from using various methods including the MLR model. We chose not to present the results here from this particularly method because (1) the paper is already very long, (2) the focus of the present study is to investigate the causes of the variations in the estimated MSEs (not the absolute errors in using the Mie model), and (3) a systematic study on model differences in the calculated MSEs will be presented in a separate study.

Having done that I suggest you make an additional scatter plot and linear regressions of scattering coefficient calculated with the Mie-derived MSEs, with the MLR-derived MSEs and with IMPROVE MSEs vs. measured scattering coefficient. Now you have written in the text new MSEs and written how they differ from the IMPROVE MSEs but the full comparison for the Guangzhou air is missing, that would be the linear regressions I suggested. How well do the different MSEs predict the observed scattering?

As explained in the previous comment, we chose not to present the MLR-derived MSEs in this study. Here, we focused on comparing the differences in the estimated b_{sp} using the estimated MSEs of chemical species and the measured b_{sp} in section 3.3.1. We have revised the explanation as follows: “Generally, good correlations ($R^2 > 0.79$) were found between the measured and estimated b_{sp} using the average MSEs of chemical species in Table 3 with the slopes being 0.85, 0.84, 0.76 and 0.84 in spring, summer, autumn and winter, respectively (Fig. S8). Thus, the estimated MSEs of chemical species in Table 3 were underestimated.”

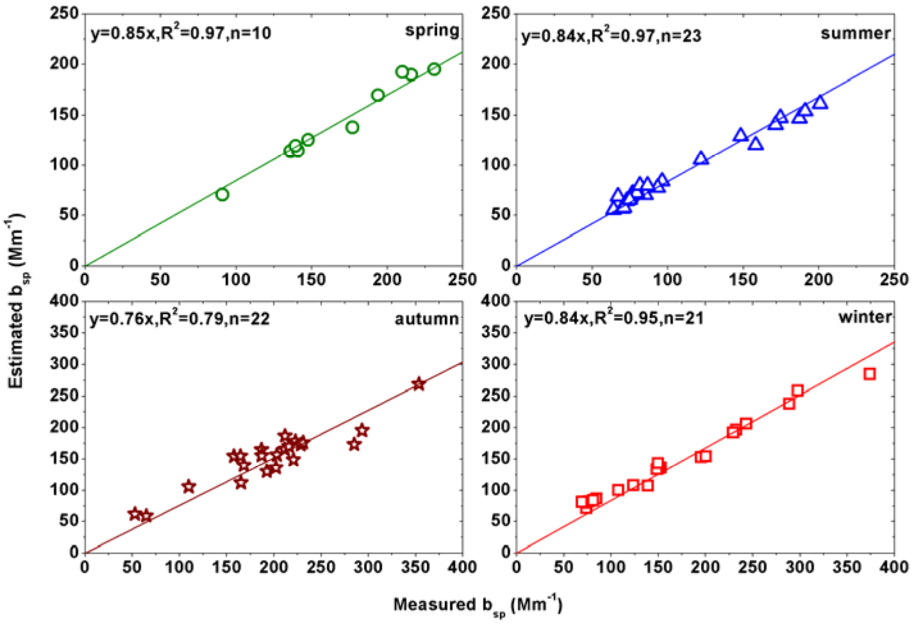

Fig. S8: Correlations between the measured b_{sp} (<100 µm) at wavelength of 520 nm under dry condition (relative humidity <30%) and estimated b_{sp} (<10 µm) using average MSEs of chemical species at wavelength of 550 nm under dry condition (relative humidity =40%) in four seasons.

The estimated b_{sp} depended on both the mass concentrations and MSEs of chemical species. Thus, it is difficult to assess the difference in the estimated b_{sp} only using the MSEs chemical species. In fact, there are large uncertainties from mass concentrations. As mention above, we have recently finished another study to address this issue, which tentatively titled "The differences in the estimated particle scattering coefficient using the different methods in urban Guangzhou of South China".

As Fig 1 and 2 show, on annual average, the estimated mass concentrations of $(NH_4)_2SO_4$ and NH_4NO_3 in $PM_{2.5}$ using the ISORROPIA II model were 42±24% and 33±44%, respectively, lower than those using the original IMPROVE formula. However, the estimated MSEs of the $(NH_4)_2SO_4$, NH_4NO_3 and OM in the fine mode using the multiple models were 47%, 50% and 15%, respectively, higher than those in the original IMPROVE formula. As a result, the differences in annual average contributions of the dominant chemical species were less than 3% between using the multiple models and the original IMPROVE formula. In contrast, the estimated mass concentrations of $(NH_4)_2SO_4$, NH_4NO_3 and organic matter (OM) using the multiple models were 93±16%, 96±9% and 60±32%, respectively, lower in the small mode and 20±50%, 674±569% and 43±68%, respectively, lower in the large mode than those from using the revised IMPROVE formula. The differences in the estimated MSEs of $(NH_4)_2SO_4$, NH_4NO_3 and OM were less than 13% between using the multiple models and the revised IMPROVE formula. Generally, the estimated contributions of the dominant chemical species ($(NH_4)_2SO_4$, NH_4NO_3 and OM) to the measured b_{sp} under dry condition using the original and revised IMPROVE formula were acceptable.

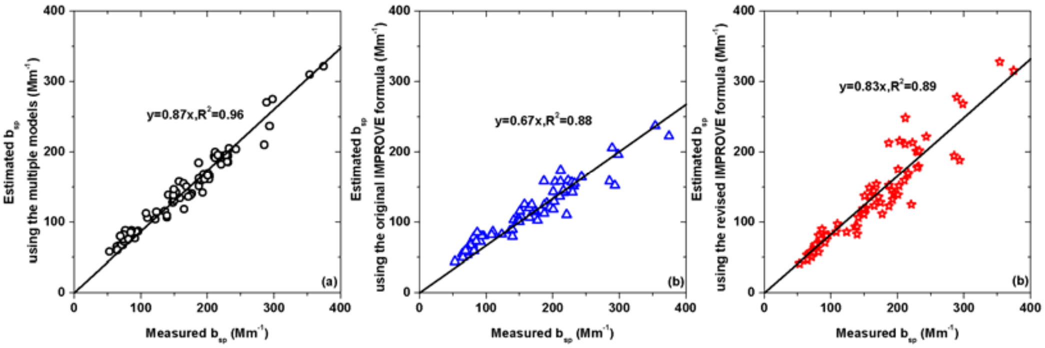

Fig. Suppl.1. Correlations between the measured b_{sp} and the estimated b_{sp} using the multiple models (a), the original IMPROVE formula (b) and the revised IMPROVE formula (c).

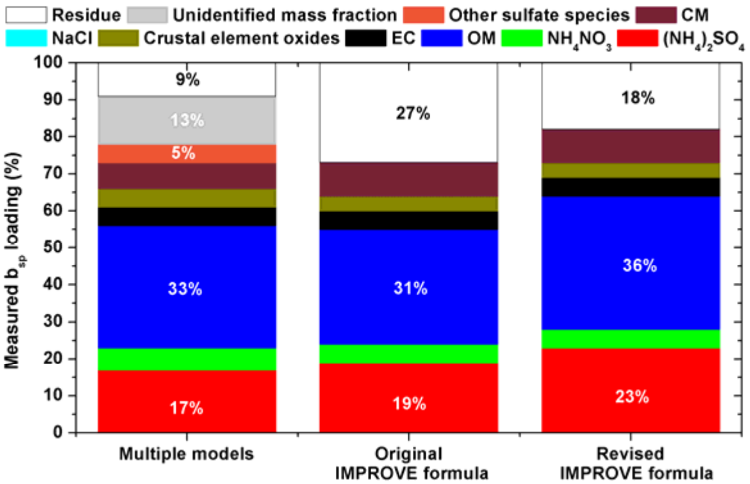

Fig. Suppl.2. Contributions of chemical species to the measured b_{sp} using the multiple models, the original IMPROVE formula and the revised IMPROVE formula.

Another thing I miss is equations. For example equations of how you calculated MSE, the mean diameters you are using and also chemistry: Did you dry the sampling air for the impactor? If not the particles are larger and get collected on the upper stages which affects the inverted size distributions and ultimately the Mie-modeled scattering. At least some discussion of this would be good.

We have added key formulas in section 2.4. We have revised the text as follows: "Particle MSE was estimated by the sum of b_{sp} from individual chemical species divided by sum of particle mass concentration according to:

$$\mathrm{MSE} = \frac{\int_0^{D_{i,j}^{max}} b_{sp}\ dD_{i,j}}{\int_0^{D_{i,j}^{max}} C\ dD_{i,j}} \tag{1}$$

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

Yes, the size segregated samples were collected under the ambient condition rather than the dry condition. We believe the MMADs of chemical species under the ambient would be larger than those under the dry condition due to the particle hygroscopic properties. However, we cannot quantify the difference in the size distribution under the ambient and dry conditions. We highlighted this factor in the analysis of closure between the measured and estimated b_{sp} in section 3.2.3. We have revised the discuss as follows: "Moreover, the size distributions would be different under dry and ambient conditions due to the particle hygroscopic properties. In fact, the NMADs of particle measured by SMPS and APS under dry condition were less than those measured by the size-segregated sampler under ambient condition according to section 3.2.2. Thus, the estimated b_{sp} based on size distributions of chemical species would be systematically higher to some extent than the measured b_{sp} under dry condition."

Detailed comments
L131 " ... geometric diameter (Dg) ..." The widely used meaning of Dg is the geometric mean diameter of a particle number size distribution. So use Dp. for the aerodynamic diameter use Da.

We have revised the descriptions as follows: "Particle number concentration for particles in the range of 14 nm - 615 nm in mobility diameter (D_p) was measured….."

L137-138. Nephelometer: did you calibrate it?

We have added the statement: "Zero calibration was performed every day with zero air, and span check was done every 3 days using HFC-R134a gas."

L197: explain the Mie model in a bit more detail.

We have added the following description in section 2.4:

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

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

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

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

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

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

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

$$\rho=\frac{\sum_{chemical\ species} m_i}{\sum_{chemical\ species}\frac{m_i}{\rho_i}} \tag{5}$$

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

L201, define MMAD and give the formula L206 "limit of detection" is wrong here, that expression is related to concentration measurements

We have given the formula for calculating MMAD in section 2.4. We believe MMAD was related with the mass concentrations in each bin of size-segregated sampler. However, only one bin is designed in the condensation mode, and we thus used formula (9) to estimate MMAD in the condensation mode.

L248 "As expected" – why would you expect this?

It was because SO_4^{2-}, NO_3^- and NH_4^+ are mainly formed through aqueous-phase reactions in moisture conditions in the PRD region. Thus, most of them should be distributed in the droplet mode.

L266 "NO3 mainly exists in the form of ammonium nitrate..." you have data on the inorganic ion concentrations but how did you calculate concentration of ammonium sulfate and ammonium nitrate? Give a couple of formulas.

The chemical species including NH_4NO_3, $(NH_4)_2SO_4$ were estimated by the ISORROPIA II model, which was run at the reserved mode with input data of K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, RH (40%), and temperature (25°C). The ISORROPIA II model has an open source code. The key formulas were described in Fountoukis and Nenes (2007).

L385 "NMAD" – give formula

The NMAD is the number mean aerodynamic diameter, which is calculated the same way as the MMAD (mass mean aerodynamic diameter) except of substituting the mass concentration with number concentration. The actual formula for NMAD calculation can be expressed as:

$$\mathrm{NMAD}=\frac{\int_0^{D_i^{max}}\frac{6C}{\pi\rho {D_i}^2}}{\int_0^{D_i^{max}}\frac{6C}{\pi\rho {D_i}^3}}$$

L574 "mass median geometric diameter (MMGD)" I have never heard of. Define. Consider using some other descriptive diameter that has been presented in literature.

The mass median geometric diameter derived from mass median aerodynamic diameter. The definition of the geometric mass mean (or median) diameters and mass mean (or median) aerodynamic diameters can be found in Hand and Malm (2007). Thus, we revised mass median geometric diameter (MMGD) as geometric mass mean diameters (GMMD).

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

Fig. 4. Are the diameters of the SMPS data and the APS data both aerodynamic or what? The gap is huge, try to explain it.

The diameter of the SMPS data is D_p, while the diameter of the APS data is D_a. the gap of number concentrations between using SMPS and using APS were mainly due to the different dlog(D). The dlog(D_p) and dlog(D_a) were 0.015 and 0.031, which meant the measured number concentration by SMPS would be higher by 2 times (0.031/0.015) than those measured by APS at the same size.

Fig 5. The numbers in the x and y axes cannot be true. In Guangzhou number concentrations are in the range of thousands, now the max concentration is about 400 /cc.

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. As shown in Fig. 4, most of particles distributed in the condensation mode (<430 nm). Here, Fig. 5 shows the correlations between the estimated and SMPS- and APS-measured particle number concentrations (430 nm-10 µm) in four seasons. To avoid misunderstanding, we revised the figure caption as follows: “Fig. 5. Correlations between the estimated and SMPS- and APS-measured particle number concentrations in the size range of 430 nm-10 µm in four seasons.”