

## Responses to Referee#2

We greatly appreciate all of the comments that help us improve the paper. Our point-by-point responses are detailed below.

(1) Methods: MSP high flow impactor was used to collect aerosol samples in this study. This sampler usually performs well. However, the filter samples are NOT suitable for analysis of OC/EC using thermo-optical instrument. The analysis method used in this work (NIOSH 5040) requires highly uniform distribution of aerosol particles on the filters, whereas the samples from MSP impactor, particularly the first 3 stages, cannot meet the requirement. Thus the measurements of OC and EC in this work could be associated with high uncertainties.

Response: This study focuses on the development of an alternative method for estimating  $f_{sp}(RH)$ . Hence, the calculation method was provided in detail, while the chemical analysis procedures were only described briefly. In the revised paper, we have clarified ambiguous points and provided more descriptions on the experimental section, especially on the OC/EC measurements.

Two stages were performed in the experiments to determine carbonaceous aerosols. The first stage of carbon analysis was in an inert helium atmosphere and consisted of four temperature steps: 250 °C (60 s), 500 °C (60 s), 650 °C (60 s), and 850 °C (120 s). The second stage was conducted under an environment of 2% O<sub>2</sub>/98% He, and the temperature was set as 550 °C (45 s), 625 °C (45 s), 700 °C (45 s), 775 °C (45 s), 850 °C (45 s), and 870 °C (120 s). Due to the non-uniform particle deposition on the filters collected by the cascade impactor, laser correction did not work properly to separate OC and EC based on this protocol. Hence, we defined OC as the fraction of carbon that evolved at or below 850 °C in a helium atmosphere (in the first stage), and EC as the fraction of carbon that evolved after oxygen was introduced to the carrier gas (in the second stage). A similar approach was applied in a previous study (Huang and Yu, 2008).

In fact, the MSP high flow impactor, with an inlet and regular stages with cut-point diameters of 18, 10, 2.5, 1.4, 1.0, 0.44 and 0.25 µm, was employed in this work to collect size-segregated aerosols. The carbonaceous aerosols in the first 2 stages (>18µm and 10-18µm) were not determined in this study because particles in these size ranges widely deposited on the filter that cannot be covered by the punch area (1.5cm<sup>2</sup>) required by the analyzer.

On the other hand, PM<sub>2.5</sub> and PM<sub>10</sub> samples were also collected by two aerosol samplers (BGI Incorporated, Waltham, MA, U.S.A., Model PQ200) at the same monitoring site on November 12, 14, 16 and 18, 2010. Both samplers were operated at the flow rate of 16.7 L min<sup>-1</sup>. One sampler was equipped with a PM<sub>2.5</sub> cut cyclone (Model VSCC), while the other was equipped with a PM<sub>10</sub> cut cyclone. The quartz filter was analyzed for the OC/EC fractions following the IMPROVE thermal/optical reflectance (TOR) protocol on a DRI model 2001 carbon analyzer (Atmoslytic, Inc., Calabasas, CA, USA) (Chow et. al., 2007). This analysis acquired 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 attains its original intensity after oxygen [O<sub>2</sub>] was added to the analysis atmosphere), and three EC fractions (EC1, EC2, and EC3 at 580 °C, 740 °C and 840 °C, respectively, in a 2% O<sub>2</sub>/98% He atmosphere). IMPROVE\_TOR OC is operationally defined as OC1 + OC2 + OC3 + OC4 + OP and EC is defined as EC1 + EC2 + EC3 – OP (Chow et. al., 2007).

The comparison of the carbon fraction measurement results of the high flow impactor with those of BGI aerosol samplers is presented in Figure 1. Although only four data points were available for comparison, an excellent agreement was found in total carbon (TC) between the two different measurement methods. However, the bias of OC between the analysis method employed in this study and IMPROVE TOR is estimated to be about +10%, while the bias of EC is about -30%. The bias may be aroused from the different thermal gradient program and the laser correction. A sensitivity test was thus conducted to quantify the impact of the uncertainties in OC/EC separation on the  $b_{sp}$  results. It was found that a 10% variation in OC only resulted in a 3% variation in  $b_{sp}$ , while a 30% variation in EC only resulted in a 1% variation in  $b_{sp}$ . Uncertainties in  $b_{sp}$  will cause uncertainties in the calculated  $f_{sp}(RH)$ . As shown in Figure 2, the impact of the uncertainties from the measured mass size distributions of OC and EC should only cause no more than 3% uncertainties in the calculated  $f_{sp}(RH)$  in this study.

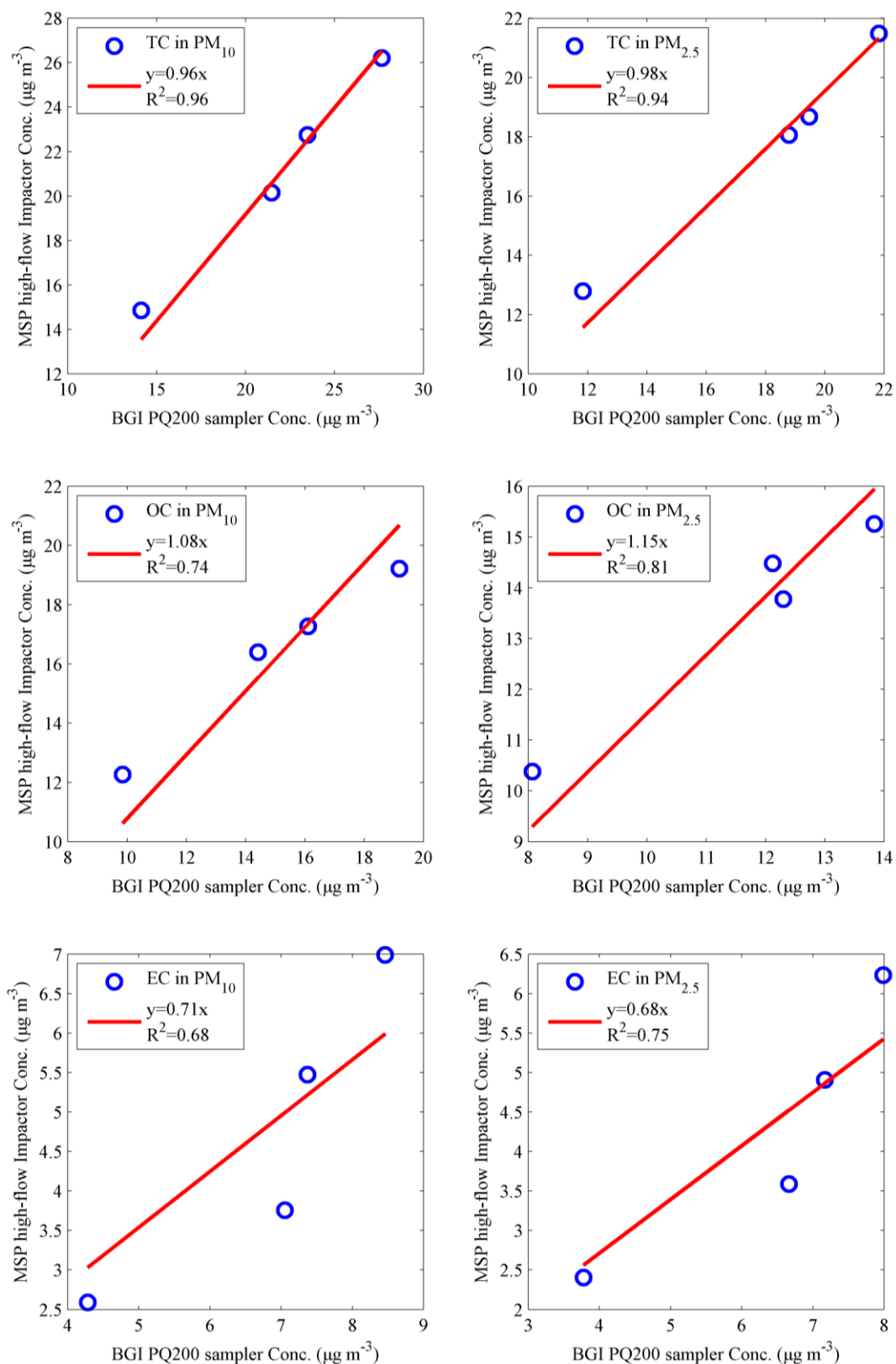


Figure 1. Comparison between the measurement results of MSP high-flow Impactor and BGI PQ200 sampler.

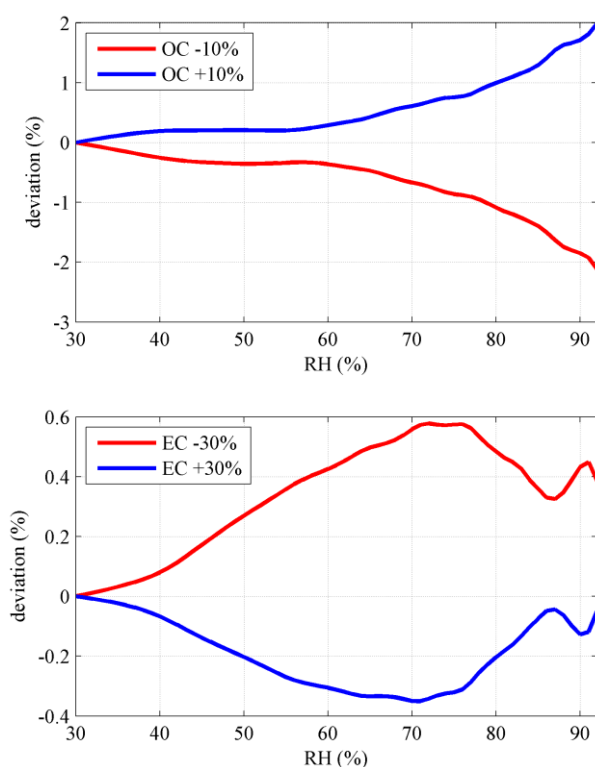


Figure 2. Deviation of  $f_{sp}(RH)$  due to the mass variations of OC and EC

(2) Methods: Mie calculation is very sensitive to the size distribution of aerosol species. However, the size distribution data from a high-flow impactor are usually suffering from particle bounce. This is particularly concerned in case where filters, instead of metal foils with grease coating, are used as the substrate. Thus I suggest make an uncertainty evaluation upon the size distribution measurement in this work.

Response: Although bounce can be avoided by coating substrate with oil or grease, it will definitely affect the result of the chemical species measurement. Furthermore, the metal foils substrate cannot meet the requirement for carbon analysis. As a result, we used the quartz fiber membrane filters to collect particles in this study, where the particles can be inset into the membrane structure. An earlier study (Chang et. al., 1999) also suggested that better collection efficiencies for particles can be obtained by using glass fiber filter instead of aluminum as impaction substrate. The performance for collection efficiency by using glass fiber filter sometime can be as good as that of using oil-coated substrate. Considering the similar membrane structure and silicon-based material between quartz fiber filter and glass fiber filter, the particle bounce effect caused by cascade impactor can be reduced to some extent.

As noted above, TC in  $PM_{2.5}$  and  $PM_{10}$  samples shows excellent agreement between MSP high flow impactor and BGI aerosol samplers (see Figure 1 and related responses above). Therefore, the bounce of particles was insignificant in this study.

(3) Results 3.1: The analysis of charge balance in aerosols (Figure 2a) is wrong. The calculation should be based on “charge equivalence”, not on “molar concentration”.

Response: The figure in ACPD version of the manuscript did consider the balance of charge equivalence between the input cations and anions, but this was not reflected in

the axis titles. The revised figure (Figure 3) will be used in the revised manuscript.

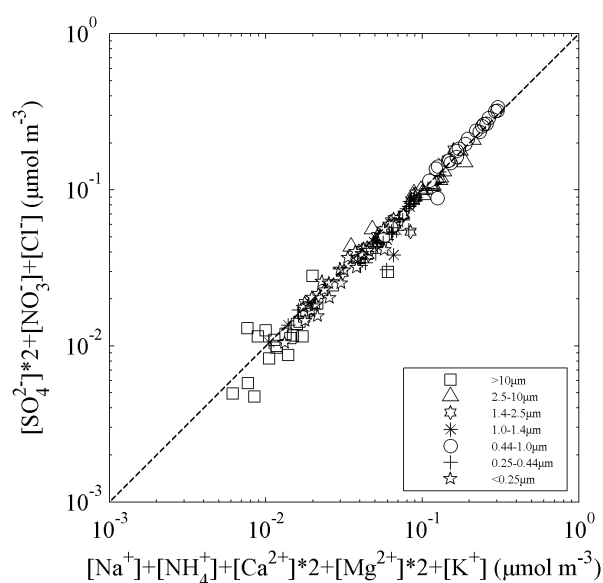


Figure 3. The balance of charge equivalence between the cations and anions

(4) Results 3.1: The relationship between OC and EC is in an unusual pattern. This could be a result of the mismatch between sampling and analysis methods.

Response: Thanks for the careful review. We apologize for using the wrong dataset in this plot. Specifically, we compared this plot (Figure 2b in ACPD version of the manuscript) with another figure (Figure 4 in ACPD version of the manuscript) and then found out this mistake. The corrected plot (in Figure 4 below) has been used in the revised manuscript.

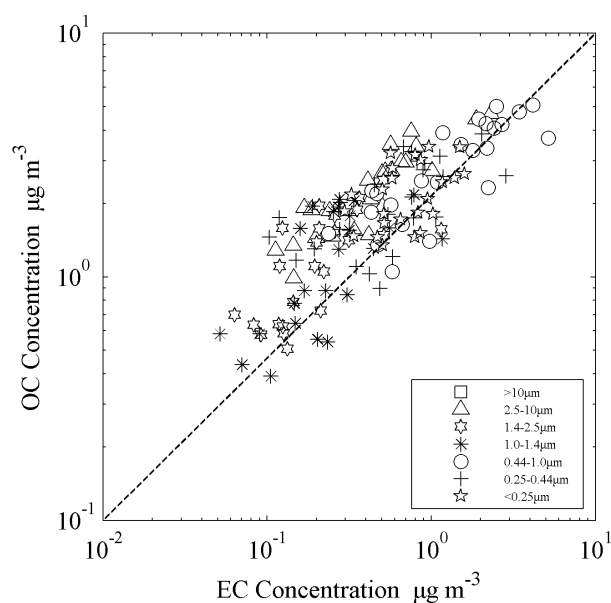


Figure 4. Comparison between the mass of OC and EC

(5) Results:  $\text{Na}_2\text{SO}_4$  showed peak in submicron size range (Figures 3-4). As particulate sodium comes mostly from sea sprays, it is unusual to have the species existing mostly in submicron range. I strongly suspect the occurrence of particle bounce in the impactor.

Response: It is true that particulate sodium is mostly observed in coarse particles, and sodium is usually regarded as an indicator of sea salt aerosols. However, substantial sodium content has also been detected in anthropogenic plumes associated with coal combustion (Takuwa et. al., 2006). Our previous study (Tao et. al., 2012) also reported a considerable amount of sodium in  $\text{PM}_{10}$  at the same site of Guangzhou where is not near the ocean.

As mentioned in the response to question 2 above, the bounce of particles is insignificant in this study. Size-segregated aerosol samples were also collected using the same model cascade impactor at a coastal site (Zhuhai) of the Pearl River Delta region during the same period as of this study. As shown in Figure 5, the size distribution of sodium at this site was characterized by a unimodal pattern peaking at coarse mode during the wet season when air masses were mostly originated from the ocean. It is clearly shown in Figure 5c that no substantial sodium was found in the fine mode at the Zhuhai site even at sodium-rich atmosphere. However, a substantial amount of sodium occurred in the fine mode during dry season when air masses coming from mainland China.

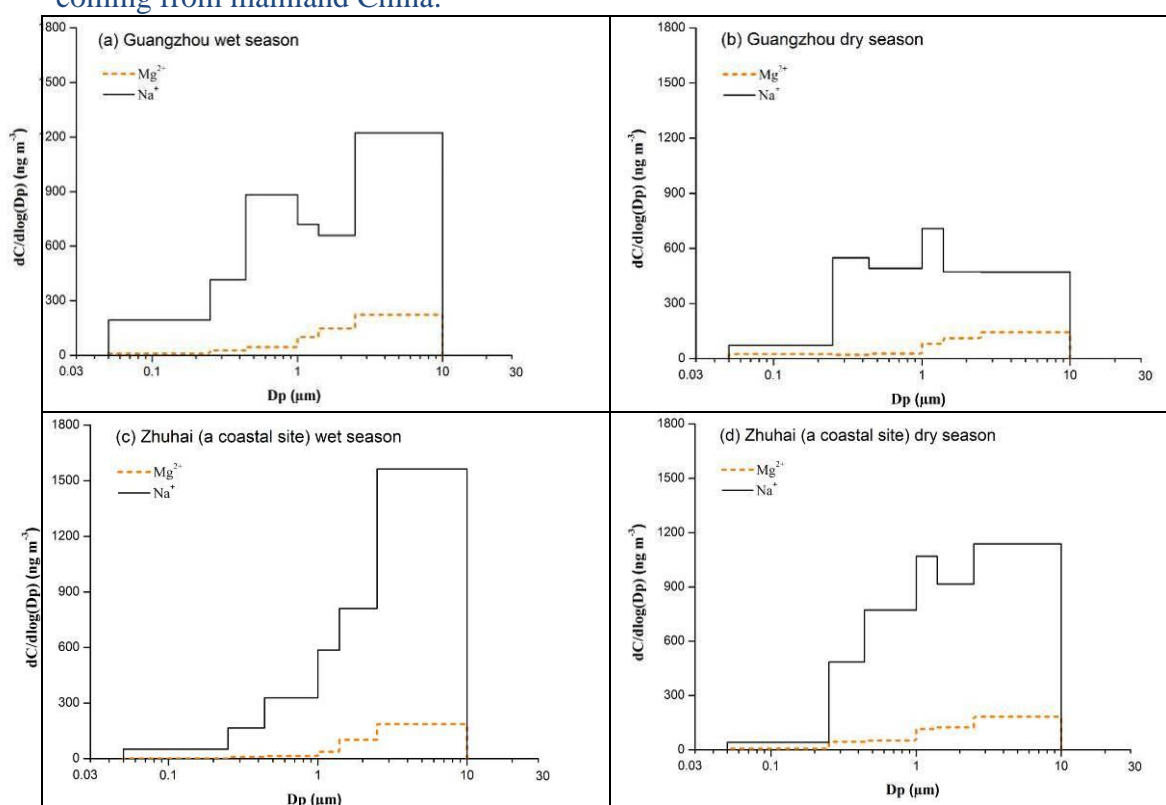


Figure 5. The size distributions of  $\text{Na}^+$  and  $\text{Mg}^{2+}$  at Guangzhou during (a) wet season and (b) dry season in this study, as well as that at a coastal site (Zhuhai) at PRD region during (c) wet season and (d) dry season

Moreover,  $\text{Na}^+$  and  $\text{Cl}^-$  mass concentrations in  $\text{PM}_{2.5}$  in Zhuhai, Shenzhen, Dongguan, Guangzhou, Conghua (a rural site near Guangzhou) and Foshan in summer time in 2010 were also collected (Figures 6 and 7 – data yet to be published in a separate

study). The  $\text{PM}_{2.5}$  samples were collected using low-flow air samplers (MiniVol TAC, AirMetrics Corp., Eugene, OR, USA). Evidently,  $\text{Na}^+$  concentrations in coastal sites (Zhuhai, Shenzhen) were lower than those in inland urban or rural sites (Guangzhou, Foshan, Conghu). This suggests that higher  $\text{Na}^+$  concentrations in  $\text{PM}_{2.5}$  in Guangzhou likely caused by coal combustion or other anthropogenic sources. Thus, we believe the sodium measured in the submicron size range was not from particle bounces in the collection process.

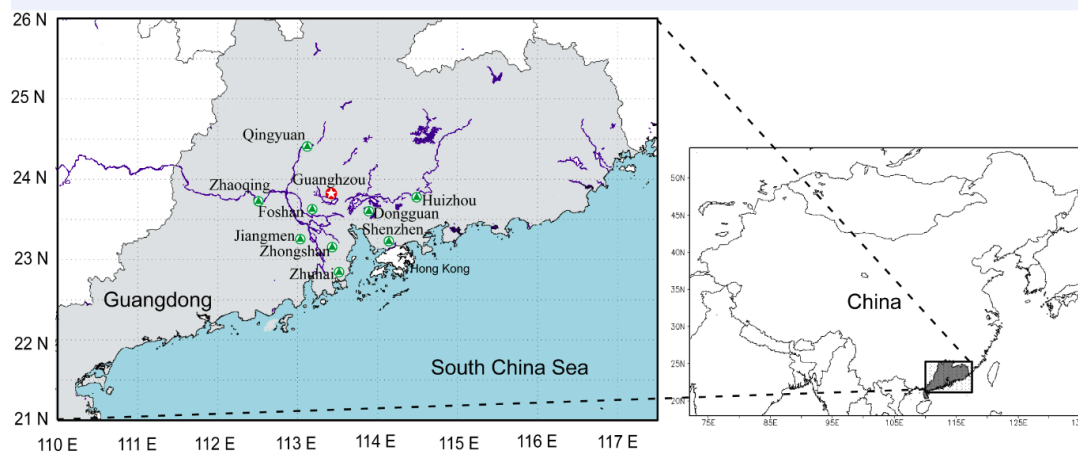


Figure 6. The map showing the locations of the 6 sites where also collected  $\text{PM}_{2.5}$ .

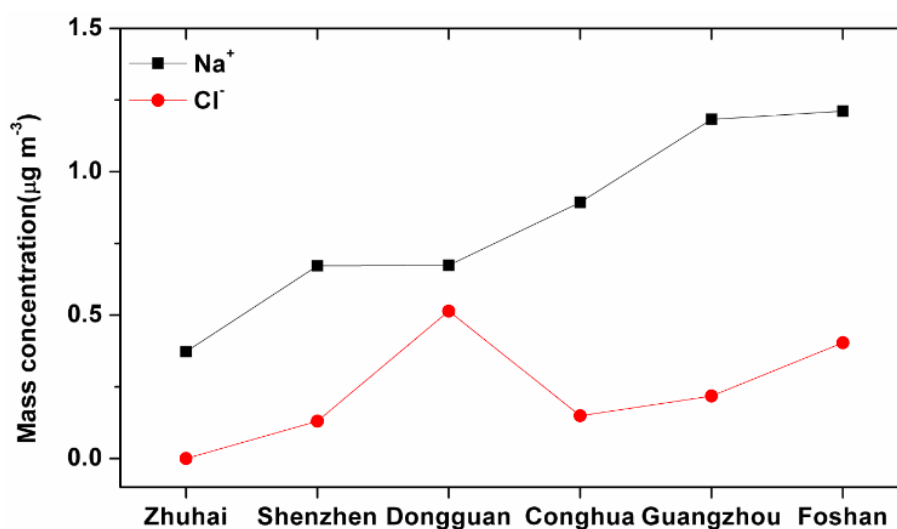


Figure 7. The mass concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  in  $\text{PM}_{2.5}$  samples collected in the 6 sites.

(6) Results 3.3: The parameterization of growth factor,  $f(\text{RH})$ , is the core of this work. I suggest make a detailed evaluation upon the improvement of your method with the previous ones. Showing the sample table of statistics is not enough to convince a scientist. As shown in Figure 6, it's hard to make judgment upon the differences between the results of this work and the others. Moreover, as shown in your previous relevant paper published in 2013, the old method has been good enough to give a prediction of  $f(\text{RH})$  within the uncertainties of measurement. Thus I'm not convinced that the improvement proposed here is significant.

Response: We agree that the method proposed in the present study and the one in our previous study can both give reasonable results on predicting  $f(\text{RH})$  within the uncertainties of measurement. However, the new method here has significant improvements in several aspects as detailed below.

The previous study only considered particles in the size range of 0.5-2.5  $\mu\text{m}$  due to the limitations in measurement technique. The present study made use of size-segregated chemical composition to derive particle number concentration in seven different size ranges (<0.25  $\mu\text{m}$ , 0.25-0.44  $\mu\text{m}$ , 0.44-1  $\mu\text{m}$ , 1-1.4  $\mu\text{m}$ , 1.4-2.5  $\mu\text{m}$ , 2.5-10  $\mu\text{m}$ , >10  $\mu\text{m}$ ). This approach enables us to investigate the properties of particles smaller than 0.5 $\mu\text{m}$  which have significant contributions to  $b_{\text{sp}}$ . Regarding the current study, particles smaller than 0.44  $\mu\text{m}$  accounted for 10-24% of contribution to the calculated  $b_{\text{sp}}$ . Thus, the new method is more accurate when calculating  $b_{\text{sp}}$  using Mie Model.

The previous study calculated the optical refractive index of  $\text{PM}_{0.5-2.5}$  based on the chemical composition of  $\text{PM}_{2.5}$  (also due to the limitations in measurement technique), which uniformized the size distribution of optical refractive index and underestimated the mass fraction of water-soluble species in particles of certain size range (especially in coarse particles). The present study took advantage of the measured size distribution of chemical composition to better describe the size distribution of optical refractive index. Therefore, the new method has higher accuracy in Mie Model calculation.

The new method in the current study also has significant scientific implications since various aerosol mixing states (“Internal” “External” and “Core-Shell”) were simulated thanks to the better size distribution of aerosol chemical composition obtained in this work. This type of study may become more important for studying  $b_{\text{ap}}$  in the near future with the increase of size- and chemically-resolved aerosol data. Moreover, the contributions of each chemical component to  $b_{\text{sp}}$  and  $b_{\text{ap}}$  can be separately quantified when assuming the particles are externally mixed.

We have also compared the  $f_{\text{sp}}(\text{RH})$ -curve (without parameterization) from this work with that in our previous study (Figure 8). We found that the curve in the previous paper overestimated the hygroscopic growth rate at RH of 30%-76% and underestimated the growth rate at higher RH. The fact that our previous work underestimated the mass fraction of water-soluble species in particles of certain size range is probably responsible, at least to some extent, for this phenomenon.

The comparison between the curves from this study and other literatures (Cheng et. al., 2008; Liu et. al., 2008; Malm et. al., 2003) further convinced us that the result from this paper is more reasonable than that from our previous paper. We have added some discussions on this point in the revised manuscript.



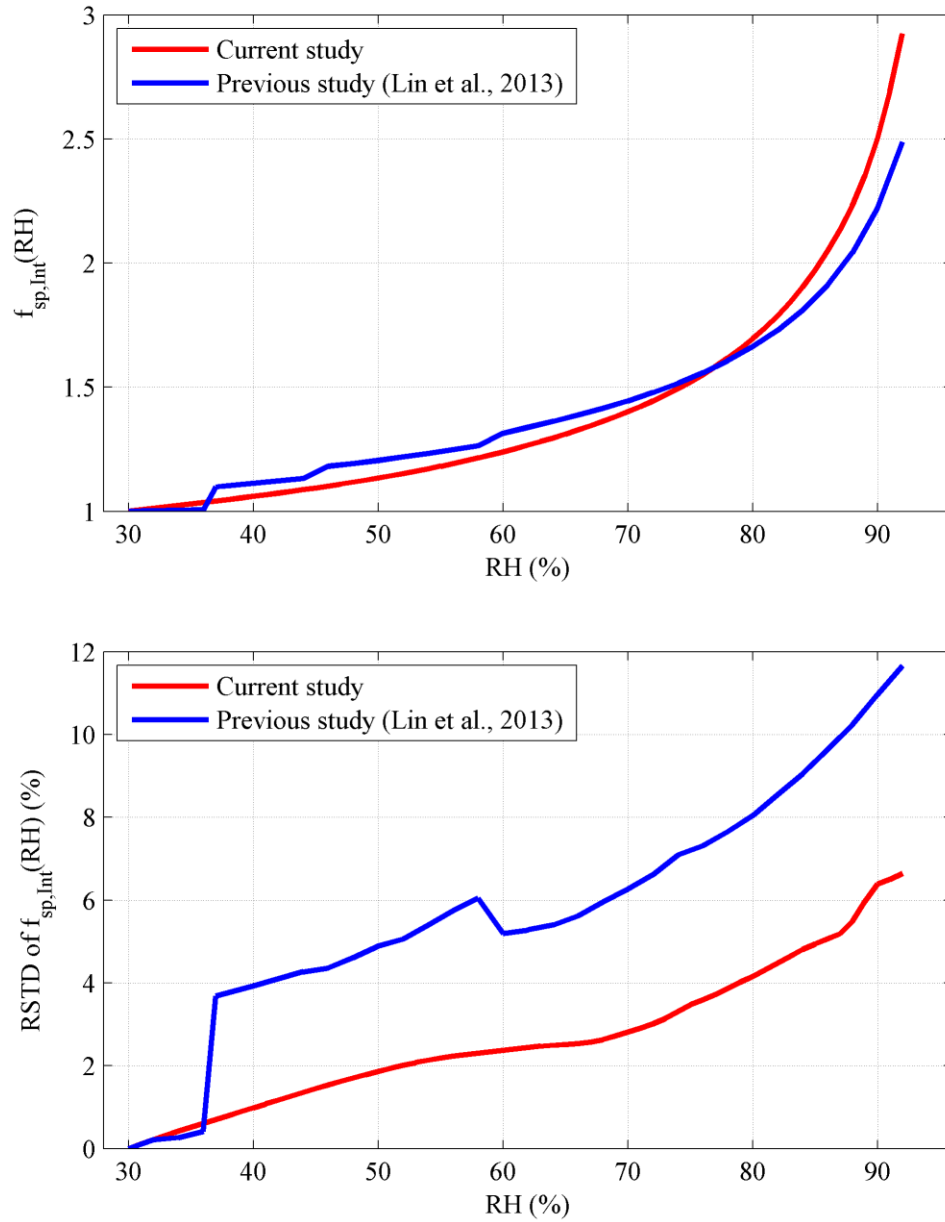


Figure 8. Comparison between the estimated  $f_{sp}(RH)$  based on the method proposed in the current study and the one in a previous study.

## References

- Chang, M., Kim, S. and Sioutas, C.: Experimental studies on particle impaction and bounce: effects of substrate design and material, *Atmospheric Environment*, 33, 2313 - 2322, 10.1016/S1352-2310(99)00082-5, 1999.
- Cheng, Y. F., Wiedensohler, A., Eichler, H., Heintzenberg, J., Tesche, M., Ansmann, A., Wendisch, M., Su, H., Althausen, D., Herrmann, H., Gnauk, T., Brüggemann, E., Hu, M. and Zhang, Y. H.: Relative humidity dependence of aerosol optical properties and direct radiative forcing in the surface boundary layer at Xinken in Pearl River Delta of China: An observation based numerical study, *Atmospheric Environment*, 42, 6373-6397, 2008.
- Chow, J. C., Watson, J. G., Chen, L. W. A., Chang, M. C. O., Robinson, N. F., Trimble, D. and Kohl, S.: The IMPROVE\_A Temperature Protocol for Thermal/Optical Carbon Analysis: Maintaining Consistency with a Long-Term Database, *Journal of the Air & Waste Management Association*, 57, 1014-1023, 10.3155/1047-3289.57.9.1014, 2007.
- Huang, X. F. and Yu, J. Z.: Size distributions of elemental carbon in the atmosphere of a coastal urban area in South China: characteristics, evolution processes, and implications for the mixing state, *Atmospheric Chemistry and Physics*, 8, 5843--5853, 10.5194/acp-8-5843-2008, 2008.
- Liu, X. G., Cheng, Y. F., Zhang, Y. H., Jung, J. S., Sugimoto, N., Chang, S., Kim, Y. J., Fan, S. J. and Zeng, L. M.: Influences of relative humidity and particle chemical composition on aerosol scattering properties during the 2006 PRD campaign, *Atmospheric Environment*, 42, 1525-1536, 2008.
- Malm, W. C., Day, D. E., Kreidenweis, S. M., Collett, J. L. and Lee, T.: Humidity-dependent optical properties of fine particles during the Big Bend Regional Aerosol and Visibility Observational Study, *Journal of Geophysical Research: Atmospheres*, 108, 4279, 10.1029/2002JD002998, 2003.
- Takuwa, T., Mkilaha, I. S. N. and Naruse, I.: Mechanisms of fine particulates formation with alkali metal compounds during coal combustion, *Fuel*, 85, 671-678, 10.1016/j.fuel.2005.08.043, 2006.
- Tao, J., Shen, Z. X., Zhu, C. S., Yue, J. H., Cao, J. J., Liu, S. X., Zhu, L. H. and Zhang, R. J.: Seasonal variations and chemical characteristics of sub-micrometer particles (PM<sub>1</sub>) in Guangzhou, China, *Atmospheric Research*, 118, 222 - 231, 10.1016/j.atmosres.2012.06.025, 2012.