

Author's Reply to Anonymous Referees' Comment

First of all, we would thank all anonymous referees for their valuable opinions and suggestions for the manuscript. With a month effort, some modifications and corrections have been made in the revised manuscript. Main features are:

- a. *ISORROPIA II (Fountoukis, C. and Nenes, A., 2007) has been applied to determine the associations among ions and the mass of water uptake at a specific RH. Furthermore, EORI and EGF required by the Mie Model have been re-calculated accordingly.*
- b. *The particles number concentration measured by APS and the light scattering coefficient measured by Nephelometer have been averaged into daily values in order to be compatible with PM_{2.5} sample.*
- c. *The aerosol optical properties have been simulated at the same RH as the one recorded inside Nephelometer. The comparison between modeled result and Nephelometer measurement serves as an indicator of the extent the practical method "captures" the aerosol light scattering coefficient of the real atmosphere.*
- d. *The size distribution and hygroscopicity of modeled optical properties as well as the relevant seasonal variation are discussed. The uncertainties of the measurement and modeling are stated.*

Reply to Anonymous Referee #2

1. SCIES, The acronym of South China Institute of Environmental Sciences, should be defined in the first appearance as it is shown over the whole manuscript. This rule should also apply to other acronyms.

Reply: It has been modified for the revised manuscript

2. In Abstract and line 5 on page 15644, DIR should be corrected to DRI. Same thing to line 7.

Reply: It has been modified for the revised manuscript

3. The data of instruments not used in this manuscript, for examples, MOUDI, TDMPs and HDMPS can be eliminated from "Introduction" section to avoid from distracting the focus of this manuscript.

Reply: We agree with the reviewer's opinion. That has been modified for the revised manuscript

4. The volatilization of aerosol NH_4NO_3 is well acknowledged and this effect on the aerosol chemical properties in this study should be addressed.

Reply: The ISORROPIA II model has been applied in the revised manuscript, which will deal with this problem.

5. It is generally acknowledged that fragile quartz fiber filter is not good for using in mass weighing. Unfortunately, this manuscript used quartz fiber filter for mass weighing, it is suggested to address possible loss of filter debris and thus underestimation of aerosol mass in the weighing process.

Reply: We concur that there are artifacts when using quartz filter for $\text{PM}_{2.5}$ sampling. However, the high loading of $\text{PM}_{2.5}$ in Guangzhou can block the Teflon filter easily, which can affect the flow rate of samplers and increase the sampling errors. Moreover, there are still some previous studies (Shen, et al., 2009; Wang et al., 2011) in China using the quartz filter for the similar reasons. In this study, the field blanks were determined and the average values of 12 blank filters of Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , F , Cl , NO_3^- , and SO_4^{2-} were

0.671±0.091, 0.002±0.002, 0.005±0.006, 0.006±0.007, 0.052±0.064, 0.168±0.036, 0.425±0.094, 0.077±0.096 and 0.362±0.082 mg L⁻¹, respectively. Although the blank value of Na⁺, F, Cl and Ca²⁺ were slightly higher than other species, blank filter was collected every 10 samples and the blank values were quite stable. All results in this study were blank subtracted. Moreover, the values of ambient samples were significantly higher than the blank value, which can reduce the errors.

6. Although the electrical charge neutrality was assumed, a validation of this assumption should be made for the data of this study.

Reply: The ISORROPIA II has been used to determine the associations among ions instead. Moreover, the validation of ISORROPIA II can be referred to in previous literature (Fountoukis, C. and Nenes, A., 2007)

7. POM needs to be defined in line 5 on page 15646.

Reply: It has been modified for the revised manuscript

8. It is hard to assess the adequacy of the factor of 1.8 applied to an urban area like Guangzhou for this study as the cited reference not published in a scientific journal.

Reply: In the last manuscript, the factor of 1.8 is supported by IMPROVE method in the cited reference. On the other hand, in consideration of the local situation, a factor of 1.6 has been adopted for the revised manuscript. This factor is supported by a previous study in China (Cao et al., 2007).

9. On page 15646, the discussion on potential combined forms of inorganic compounds with assumptions of preferential association of NH₄⁺ with SO₄²⁻

or NO_3^- and similar inferences for other ion pairs is speculative. For field with data in this study, preferential reactions are uncertain and assumptions made may not be applicable. For example, Huang et al. (AR 2011, 99:488) observed aerosol data in Guangzhou and found that higher nitrate involving ammonia and nitric acid were observed for $[\text{NH}_4^+]/[\text{SO}_4^{2-}] > 1.5$. Moreover, K^+ only combined with Cl^- at a place very close to biomass burning sites. It is better to apply thermodynamic models such as ISORROPIA II (Fountoukis and Nenes, ACP 2007, 7:4639) and AIM (Ge et al., 2011, Atmos. Environ. 45:561) to this end.

Reply: The ISORROPIA II has been applied to determine those associations among ions in the revised manuscript.

10. Line 2 on page 15647, POM, EC and other unidentified components were assumed not having hygroscopic growth. This might not be true as the salts of minor organic acid such as dicarboxylates are shown to absorb water. An evaluation on the effect of this assumption must be added to the text.

Reply: We agree that this statement had not been properly addressed in the last manuscript. Although we continue to follow the assumption (the hygroscopicity of POM is not considered in the model), we provide supporting reasons for the revised manuscript, which are:

- (1) As a whole, the hygroscopic growth of SOA (Secondary Organic Aerosol) was around 1.2 at 90% RH (Gysel et al., 2007; Stock et al., 2011);*
- (2) The hygroscopicity of some extracts from WSOC was recognized (Gysel et al., 2004). However, there was no WSOC speciation in present study.*
- (3) The water uptake by the aged organic aerosol only accounted for a few percent of total water uptake (Bougiatioti et al., 2009; Engelhart et al., 2011).*
- (4) Not like those inorganic salts, a more accurate RH dependence of POM has not been well established.*

(5) The POM has not been included in the ISORROPIA II model yet.

11.11. The subscript for aerosol component, j , is the same as the j -th size range of aerosol size spectra. Either one of the notations needs to be changed to avoid from confusing. In addition, a (in equations 10, 11, and 12) and a_j (in equation 4) are also confusing.

Reply: It has been corrected for the revised manuscript. The subscript for aerosol component is changed from “ j ” to “ i ” and “ a_j ” to “ a_i ”.

12. The Q values for the calculation of b_{sp} and b_{ap} are suggested listing in a new table in the manuscript.

Reply: They are stated for the revised manuscript.

13. Was the time period for the calculation of $b_{ap, pm2.5}$ the same as the cited study (Wu et al., 2009)? If not, provide a discussion for the effect from this deviation as the relationship should be different.

Reply: This point will not affect the current study as the absorption coefficient of $PM_{2.5}$ is no longer used for the manuscript.

14. Line 15 on page 15651, size should be sizes.

Reply: It has been corrected for the revised manuscript.

15. Was the mass concentration in Figure 3 based on the controlled RH (40%) in the weighing room or the ambient RH or a more complicated way? In calculating “residual” of Figure 3, one needs to know whether the “water” was estimated from ambient RH or the controlled RH in a weighing room.

Reply: The mass concentration in Figure 3 in the last manuscript was based on the ambient RH. Moreover, “Residual” was the difference between mass of $PM_{2.5}$ and estimated water uptake at 40% RH.

16. There are deviations observed from $b_{sp, pm0.5-2.5}$ and $b_{sp, neph}$. Please provide some discussions on the data pair when the deviations are great.

Reply: We agree with the reviewer.

(1) In the revised manuscript, the comparison between modeled result and Nephelometer measurement will serve as an indicator of the extent the practical method presented “captures” the aerosol light scattering coefficient of the real atmosphere.

(2) The more ultra-fine particles in aerosol population, the less sufficiently the APS captures the total particles number concentration of ambient aerosol population. Moreover, a strong linear correlation was found between the particles number concentration and the modeled scattering coefficient. As a result, more ultra-fine particles in October than the other three months may account for the lower correlation coefficient. More detailed discussion on this is presented in the revised manuscript.

17. Please provide more discussions and literature supports on why $PM_{0.5}$ dominated over aerosol mass fractions in Figure 7.

Reply: We concur that the statement in the last manuscript cannot be sufficiently supported by the measurement and modeling result in the current study. Consequently, that statement has been eliminated from the revised manuscript.

18. Fig. 8 (mentioned in line 6 on page 15655) was missing in the manuscript.

Reply: In the last manuscript, the figure was supposed to be Figure 7

References

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