Atmos. Chem. Phys. Discuss., 12, C7556–C7564, 2012
www.atmos-chem-phys-discuss.net/12/C7556/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impact of relative humidity and particles size distribution on aerosol light extinction in urban area of Guangzhou" *by* Z. J. Lin et al.

Z. J. Lin et al.

linzejian@scies.org

Received and published: 28 September 2012

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

PM2.5 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 #3

1. Uncertainty Besides the measurement uncertainties, there are several assumptions made in this study which will impose uncertainties to the simulation of optical properties. These uncertainties should be quantified or at least clearly stated/described in the manuscript. If I understand right, for each PM2.5 sampling period, a constant aerosol chemical composition (derived from the filter analysis) has been assumed for the entire particle size range (0.5-20 micrometer). The refractive index, hygroscopic growth and density etc were all calculated based on this assumption. Uncertainties due to this assumption should be discussed, e.g., in the calculation of the light absorption (as discussed in major comment #2). Besides, to derive bsp,PM0.5 and bap,PM0.5, the author basically used a subtraction method which is subject to uncertainties in Nephelometer measurements, angular correction, Mie simulation of aerosol optical properties in the size range of 0.5 to 2.5 micrometer, as well as in the simple empirical parameterization of light absorption by PM2.5 mass. Given the fact that mass fraction and scattering contribution of PM0.5 are both dominate components in the upper panels of Figure 7, the uncertainties of derived scattering and absorption, as well as the mass of PM0.5 need to be carefully discussed.

Reply: We agree with the reviewer's opinion. (1) The uncertainties of PM2.5 sampling, Ion & OC/EC analysis, Nephelometer, APS, Ambient RH detection are 1.08%, 2.49%, 2.30%, 4.46% and 3.87%, respectively. Accordingly, the modeled aerosol optical property has a total uncertainty of 8.74% (2) As the mass of PM2.5 was found to have a

very strong relationship with the total aerosol light scattering coefficient measured by Nephelometer, the current study tries to work out a practical method to simulate aerosol optical properties on the basis of the chemical composition of PM2.5 and the particles number concentration measured by APS. Furthermore, a highly linear correlation has been found between the modeled light scattering coefficient and the measured particles number concentration in spite of the size-resolved chemical composition and the complicated calculation in the Mie Model. In other words, if the particles number concentration was well measured by APS, the method used in current study is supposed to "capture" the aerosol light scattering coefficient of the real atmosphere efficiently. (3) We concur that using a substraction method to derive bsp,PM0.5 and bap,PM0.5 can't be sufficiently supported by the measurement and modelling in current study. Consequently, the content about the substraction method has been eliminated from the revised manuscript. However, if the SMPS-APS system can be deployed in future study, the optical properties of PM0.5 will probably be quantified.

2. Effect of particle size distribution Beside relative humidity, the manuscript is also titled by the impact of particle size distribution on aerosol light extinction. However, the discussions about the size effects are limited. I would suggest the authors to show at least the monthly averaged particle number size distributions in different seasons to assist the discussion. Or the authors could try higher size-resolution. For example, by using the number size distribution measured by APS, the authors may also calculate and show the size distribution of esp and eap. In addition, Fig. 8 (p15655, l6) is missing, or do the authors mean the lower two panels of Figure 7? As discussed above, for each PM2.5 sampling period, a constant ratio of EC to total particles (+water, according to the chemical composition analysis from the PM2.5 samples) has been assumed for the entire size distribution in this study. This is rarely the case especially for the large particles. I do not think the authors have adequate or enough solid evidence to support the statement that "large particles were more efficient in light absorption" (line 6-7 in page 15655).

Reply: The impact of particles number concentration on optical properties as well as the temporal variation of particles number concentration is illustrated and discussed for the revised manuscript. We agree that there is not enough evidence to support the statement that "large particles were more efficient in light absorption. Consequently, the content of such statement has been eliminated from the revised manuscript.

3. Comparison between Mie simulation and Nephelometer observation The scattering coefficient measured by Nephelometer is the sum of the scattering coefficients of particles in the whole size range. The calculated scattering coefficient (by Mie model) in the range of 0.5 to 2.5 micrometer is a subset of total particle scattering (superset). A comparison between the superset and the subset (as in Fig 5) can NOT serve as a validation of the Mie model simulation. Especially when looking at the upper panels in Figure 7, the extinction of particles smaller than 0.5 (a subtraction between Nephelometer observation and Mie simulation) dominate the total extinction most of the time. And the contribution by particles between 0.5 to 2.5 micrometers is in general small (according to Figure 7), except in April 09. Comparison of the standardized values (in Figure 5) shows if the scattering coefficients of particles from 0.5 to 2.5 micrometer are in the same trend as the total particles scattering. Although good correlation does not mean the Mie calculation is validated, a rather low correlation coefficient as for Oct 09 also does not mean the simulation is poor. Actually, it might be interesting if the author could try to explore why they correlated well to each other sometimes but sometimes not. For example, different trends may due to a change in particle size distribution. The typical number size distribution from 3nm in Oct in Guangzhou may be found in literature. Also, one could also see that there is a significant change (increase) in the mass scattering coefficient (esp, lower panel in Figure7) in the late Oct 09 and early Jan 10 when the correlation is poor. More discussion is needed in this regard.

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.

4. Mixing state of EC The authors discussed about the influence of aged air mass on the mass light absorption coefficient around line 10-20 in page 15655. From my point of view, for a certain size distribution, the light absorption is determined by the refractive index when using Mie model. In the current study, the refractive index is calculated under the assumption of internal mixed aerosol particles. Under such assumption, a lower single scattering albedo either means that the EC mass fraction is high, or the mass fraction of chemical compositions with higher real part of refractive index (e.g., Na2SO4, MgSO4 etc) is relatively low, or the particle number size distribution is different. But it can NOT imply any information about the mixing state of EC, since the basic assumption of the entire calculate (optical, refractive index, density etc) is the aerosol particles are completely internally mixed.

Reply: We agree that discussion about the influence of aged air mass on the mass light absorption coefficient cannot be sufficiently supported by the measurement and modeling result in present study. Consequently, the content of such statement will be eliminated from the revised manuscript.

5. The introduction needs to be re-organized and be more specific and focusing.

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

6. What is the sampling relative humidity of PM2.5? How did you control the sampling and chemical analysis relative humidity at 40% as in Table 1?

Reply: The PM2.5 was sampled by quartz filter at ambient RH, but the PM2.5 quartz fiber filters were weighted at a temperature about 25°C and a relative humidity (RH) about 40%. Each filter was weighed at least three times before and after sampling, and the net mass was obtained by subtracting the average of pre-sampling weights from the average of post-sampling weights.

7. Quartz filter is usually used for thermal EC/OC analyses. To determine the PM2.5mass and aerosol chemical composition, TeïňĆon filter would be much better than Quartz filter. How much uncertainties would be induced by using the Quartz filter to serve this purpose?

Reply: We concur that there are artifacts when using quartz filter for PM2.5 sampling. However, the high loading of PM2.5 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+, NH4+, K+, Mg2+, Ca2+, F-, Cl-, NO3-, and SO42- 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.

8. The relative humidity at ambient, dry or measurement conditions have not been clearly described in this manuscript. For example, what is the sampling relative humidity in Nephelometer (more specific than lower than 70%)? Did the author treat the aerosols inside Nephelometer as dry particles, or also calculated the scattering coefficient according to the instrument-recorded relative humidity inside the Nephelometer when using Eq. 14? Are data in Figure 3 at ambient conditions?

Reply: The relative humidity at ambient, dry and measurement conditions were listed in Table 1 in the last manuscript. More illustrations about RH conditions have been presented for the revised manuscript. The scattering coefficient simulated by the Mie Model is on the basis of the RH recorded inside the Nephelometer, which will be compared with the scattering coefficient measured by the Nephelometer.

9. Seasonality is the highlight of this manuscript. I suggest the authors discuss more about the seasonal variations in chemical composition, hygroscopicity, and optical properties.

Reply: We agree with the reviewer. As ISORROPIA II was used to determine the associations among ions, the EORI and EGF were re-calculated and the seasonal variation of chemical composition, hygroscopicity and optical properties has been assessed accordingly.

10. After getting the reconstructed compositions, the authors could use the AIM model (http://www.aim.env.uea.ac.uk/aim/aim.php) to calculate the corresponding ions (ionsAIM). Comparison between ionsAIM and measured ions can be used to validate the reconstructed chemical compositions.

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)

11. Most of the data reported in the manuscript are either standardized or as a proportion ratio (fraction). No real measurement data were presented (neither absolute concentration of different chemical species nor Nephelometer measured scattering and back scattering coefficients). I suggest presenting these data in tables or figures, which would be interesting and valuable for the community.

Reply: We have taken this suggestion and more measurement result including ambient RH, RH recorded in Nephelometer, absolute concentration of different chemical

species are presented for the revised manuscript.

12. The English in the manuscript is not satisfying and need to be carefully revised.

Reply: It will be carefully revised to meet the language standards of the journal

13. Please rephrase the sentence “Since socioeconomic developed in recent years,. . .” (Line 23 in page 15641).

Reply: The sentence was rephrased to “Pollution caused by fine aerosol particles in Guangzhou and its surrounding area has attracted more and more attention from the public and scientists in recent years”.

14. “Seinfeld and Pandis” instead of “Seinfeld and Spyros” (e.g., Line 3 in page 15641 and several other places).

Reply: We agree with the reviewer. It’s corrected for the revised manuscript

15. It is hard for me to distinguish the colors of Mg2+ and NO3- in figure 2.

Reply: The figure will be modified in the revised manuscript, which will have easily distinguishable colors for each ion.

References

Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K+ - Ca2+ - Mg2+ - NH4+ - Na+ - SO42- - NO3- - Cl- - H2O aerosols. Atmos. Chem. Phys., 7, 4639-4659, 2007.

Shen, Z.X., Cao, J.J. , Arimoto, R. , Han, Z.W. , Zhang, R.J. , Han, Y.M. , Liu, S.X., Okuda, T., Nakao, S., Tanaka, S.: Ionic composition of TSP and PM2.5 during dust storms and air pollution episodes at Xi’an, China. Atmos. Environ., 43, 2911-2918, 2009.

Wang, G., Li, J., Cheng, C., Hu, S., Xie, M., Gao, S., Zhou, B., Dai, W., Cao, J., An, Z.: Observation of atmospheric aerosols at Mt. Hua and Mt. Tai in central and east

China during spring 2009-Part 1: EC, OC and inorganic ions. Atmos. Chem. Phys., 11, 4221-4235, 2011.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C7556/2012/acpd-12-C7556-2012-supplement.pdf

---

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 15639, 2012.