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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aerosol optical properties in a rural environment near the mega-city Guangzhou, China: implications for regional air pollution and radiative forcing" *by* R. M. Garland et al.

R. M. Garland et al.

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We would like to thank Referee 1 for their careful reading of the manuscript and for their thoughtful comments. We have addressed their comments below; their original reviews are in italics with our responses following.

1) *This manuscript is well written and presents a wealth of valuable data combined with insightful analysis. I found the analysis of the diurnal variation of aerosol scattering coefficients and absorption coefficients (Figure 9) to be particularly interesting and important for understanding the total atmospheric column radiative effects from groundbased particle sampling measurements. However, I am somewhat surprised*

(given the comprehensive suite of measurements and the rigorous analysis) that there was no data or analysis presented on the aerosol humidification effects on aerosol optical properties. There is extensive analysis of the dry single scattering albedo, but what is really needed for radiative forcing calculations are the ambient aerosol properties at the high relative humidity which occurs in southern China in July. It is expected that there would be a significant sulfate component to the aerosol in China (due to sulfur dioxide emissions from coal combustion) that would result in significant particle humidification growth, which would yield increases in both scattering and single scattering albedo.

We have added a new section to the revised manuscript to discuss the possible impact of particle hygroscopicity on the particle's single scattering albedo (Section 3.1.4). The discussion in this section is below.

Aerosol optical properties depend on particle size and composition, which can be greatly influenced by hygroscopic growth (Mikhailov et al., 2006; Garland et al., 2007). Thus, it is critical to control the relative humidity when measuring aerosol optical parameters. In PRIDE-PRD2006, and most other earlier studies of aerosol optical properties with comparable instrumentation (Table 2), the aerosols were dried to ensure constant measurement conditions and comparability. Extrapolation of the parameters measured under dry conditions to varying atmospheric conditions is not trivial.

To investigate this aspect and better characterize the aerosol optical properties of the region, the ground-based PRIDE-PRD2006 data have been compared to AERONET remote sensing data retrieved for the Backgarden site (available for July 1,2,5,11-13,18-25,27). The AERONET single scattering albedo (SSA532) daily averaged values were +0-0.19 larger (on average +0.11) than for the dry ground-based SSA values. These AERONET data are for the whole column and at ambient conditions, so the difference between our SSA532 values and the AERONET values would be due to a combination of these effects.

ACPD

8, S4784–S4796, 2008

The impact of humidification on SSA532 can also be modeled, but the model results depend upon particle size and composition as well as the refractive index and mixing state of the aerosol particle may impact this calculation, and it is not clear how absorbing aerosols are impacted by humidification (Nessler et al., 2005; Mikhailov et al., 2006). The impact of humidification on the aerosol optical properties was modeled using the dry aerosol optical property measurements in PRIDE-PRD2004 in October 2004 at a site southeast of Guangzhou. In this study, Cheng et al., (2008), found a $<$10% increase in SSA532 from 30% RH to 80% RH, which are approximately the measurement and ambient RH for this current study, respectively. Additionally, the impact of hygroscopic growth on the aerosol scattering coefficient was measured for the urban site in downtown Guangzhou as part of PRIDE-PRD2006; the impact of RH on the absorption coefficient of the particles was neglected (Liu et al., 2008). Applying these hygroscopicity results to the Backgarden measurements, the SSA532 for the Backgarden site would increase by +0.01-0.23 (average of +0.10) from 40% RH to 80% RH. As can be seen from these two studies from the PRD region, the impact of relative humidity on the aerosol optical properties is highly variable and further investigations with improved techniques (simultaneous absorption and scattering measurements at different RH levels) will be required for a comprehensive and reliable characterization.

2) *On another issue, I am not completely convinced that the heavy pollution episode of July 23-25 is due to biomass burning. I did not find compelling evidence to determine whether meteorology (stagnation) or additional source strength (fires) were more important in elevating the aerosol concentrations and additionally there was no mention of the role of coagulation in increasing fine mode particle size which would also increase the scattering coefficient and single scattering albedo. The rate of coagulation increases as particle concentration increases, and therefore must have played some role in the heavy pollution event. The manuscript would be improved with the addition of some discussion of the dynamics of the particle size distributions (especially the fine mode) and their effects on optical properties. On page 7 you state: -a detailed discussion of the particle size distributions will be presented elsewhere. However some of this*

ACPD

8, S4784–S4796, 2008

Interactive Comment

information needs to be summarized in the current paper and applied to the analysis.

As described in the manuscript, the source of the pollution for 23-25 July was evident and unique: the burning of plant waste by local farmers was visible in the vicinity surrounding the measurement site, and it was the only time that such intense local biomass burning and pollution occurred during the campaign. The wind speeds during this period were below average (0.93± 0.64 m s-1), but similar and lower wind speeds (stagnation) occurred also during other times without leading to similar extremes in the extensive aerosol optical parameters. We cannot see how the local biomass burning could not have dominated the aerosol composition and properties on July 23-25.

A discussion on the size distribution and how it is related to the optical properties are related has been added (newly added Sections 3.4.1 and 3.4.2 and Figures 12, 13A and 14) and is also included in the discussion of the newly added Figure 18. In these newly added sections we discuss the relationship between the extensive properties and number concentration as well as the relationship between single scattering albedo and particle size. In the discussion of these new Figures we conclude that changes in the size distribution did not drive the changes in the single scattering albedo. Additionally, we have added Figures 18A-C to address this reviewer's comment below about the fine/coarse ratio in the Ångström curvature. In the discussion of these figures, we conclude again that "There is no strong relationship with this parameterization and single scattering albedo (not shown), thus suggesting that the changes in single scattering albedo are not only due to changes in aerosol size and size distributions, but are also driven by the addition of absorbing material as discussed above in Section 3.4.2."This full discussion can be found in Section 3.4.3.

3) *Page 2: -The daytime average single scattering albedo of 0.87 appears- should be -The daytime average mid-visible single scattering albedo of 0.87 appears-*

This has been changed in the manuscript.

4) *Page 9: -The overall accuracy of the PAS calibration in this study was within 10%,*

ACPD

8, S4784–S4796, 2008

thus the overall accuracy of the measured PAS absorption coefficients are also 10% (Schnaiter, 2005).- Please give an estimate of the uncertainty in the computed single scattering albedo based on all measurement uncertainties.

We did not estimate the uncertainty of our nephelometer during the field study; however we can assume it to be $\pm$ 8% as described below.

We have assumed that the instrument performed similarly (as it as the same make and model) as the nephelometer that was characterized in Anderson et al (1996); in this study they reported an error of $\sim$10%. We are confident that our instrument performed well as it was calibrated as stated in the TSI manual before leaving Germany, before the field mission began, during the field mission and after the field mission. These calibration constants were within 2%. During the campaign an auto-zero was automatically performed every two hours. These values were tracked manually throughout the campaign and no obvious problems were evident. Thus, the instrument performed at least as well as Anderson et al.(1996).

We have calculated our uncertainty more precisely though, using data collected in a field mission in Beijing (with an identical set-up for the nephelometer) directly after the PRIDE-PRD2006 campaign (Garland et al., submitted). The nephelometer performed similarly in both campaigns. Cheng et al. (submitted) has compared the Beijing nephelometer measurements to a Mie model and found them to agree within $\pm$ 8%. Thus, we will assume this to be the error for the nephelometer in PRIDE-PRD2006 as well. Using this error for the nephelometer and 10% for the PAS, Monte Carlo simulations were run and the uncertainty of the single scattering albedo was found to be $\pm$ 2%.

This discussion has been added to the revised manuscript (Section 2.2 and Section 2.3.2).

5) *Page 13: Can you present some additional data/ analysis to strengthen your claim that biomass burning was the principal reason for the heavy aerosol loading on July 23-25, possibly satellite hot spot images?*

ACPD

8, S4784–S4796, 2008

This time did have below average wind speeds (campaign average = 1.79 $\pm$ 1.15 m s-1 and during this event 0.93$\pm$ 0.64 m s-1), so stagnation most likely did contribute to this pollution event. However, this was not the only instance when slow wind speeds were present in the campaign (almost every day of the campaign had instances were the wind speed was $<$1 m/s). This was though, the only instance that we actually saw numerous fires at the farms in the vicinity of the measurement site. This event, as well as the criteria for excluding these data, has been clarified and an additional discussion has been added in the Results and Discussion Section (Section 3.1).

6) *Page 15: -The single scattering albedo increased during this time to 0.88, which is common in smoldering fires (Reid, 1998). The parameters determined during the smoky period can be considered to represent the optical properties of emissions from the burning of plant farming waste.- While it is true that the aerosol from smoldering combustion have less black carbon and therefore higher single scattering albedo (SSA), coagulation of fine mode particles under high concentrations (such as this pollution event) will also increase scattering and result in higher SSA. Some discussion of fine mode size distribution dynamics should be included here.*

We have only stated that the single scattering albedo is higher during this time, but did not attribute this change to particle composition nor size. We have added two new sections (3.4.1 and 3.4.2) to the revised manuscript, together with three new figures (Figure 12, 13A and 14) in order to address the reviewer's comments. In the discussion of these new Figures we conclude that changes in the size distribution did not drive the changes in the single scattering albedo. Additionally, we have added Figures 18A-C to address this reviewer's comment below about the fine/coarse ratio in the Ångström curvature. In the discussion of these figures, we conclude again that "There is no strong relationship with this parameterization and single scattering albedo (not shown), thus suggesting that the changes in single scattering albedo are not only due to changes in aerosol size and size distributions, but are also driven by the addition of absorbing material as discussed above in Section 3.4.2." This full discussion can be found in

ACPD

8, S4784–S4796, 2008

Section 3.4.3.

7) *Page 16: -In order to convert to atmospheric relevant conditions, the hygroscopic growth of these aerosol particles and its impact on their light scattering and absorption would need to be quantified, which is beyond the scope of this manuscript.- However this is what is needed for accurate radiative forcing studies, which you address in Section 3.4. If measurements of hygroscopic growth were not made during PRIDE, then I would argue that you should not attempt to make the radiative forcing calculations since the analysis would be biases towards low values of SSA that are representative of dry aerosol only, not ambient atmospheric conditions.*

We did not intend for the calculations in Section 3.6 (Section 3.4 in ACPD manuscript) to be detailed radiative forcing calculations. Rather, we only wanted to test the sensitivity of such calculations to the coupling of SSA and b. This has been clarified in the Results and Discussion Section (Section 3.6).

8) *Page 21: -Figure 10 shows the correlation of SIGMAs,550 and SSA532 to local wind direction and local wind speed.- Should be: -Figure 10 shows the relationship of SIGMAs, 550 and SSA532 to local wind direction and local wind speed.*

This is changed.

9) *-No strong correlation was seen between SIGMAs,550 (and SIGMAa,532, though not shown) and local wind direction.- Please give the r2 value here to quantify the level of correlation.*

We are not able to provide an R2 value because it is not clear which type of function would constitute a “well correlated“ relationship between sigma and wind direction, as well as SSA and wind direction. Thus we have changed the manuscript such that we do not talk of “correlations“ but rather “relationships“ . (Section 3.3)

10) *Page 22: -Average SSA532 values (0.8-0.9) are not correlated with wind direction.- Again please give the r2 value. Also the following 2 sentences after this suggest that*

ACPD

8, S4784–S4796, 2008

there is some correlation, making this paragraph confusing.

This statement meant that while the average SSA values of 0.8-0.9 were not related to a specific wind direction, the lower values of 0.6-0.8 were. An additional statement has been added to the manuscript to clarify this point (Section 3.3).

11) *Page 22, Figure 11A: It is not typical to compute 24-hour back trajectories. Usually 5 to 7 day back trajectories are presented since aerosol residence time in the troposphere averages about 1 week. Please explain why you chose to compute only 24-hour trajectories.*

We have included 4-day back trajectories as well (Figure 11C). A discussion of these back trajectories is now included in the Results and Discussion Section (Section 3.3).

12) *Page 24: -In contrast, the highest SSA532 values were measured on 12 and 20 July when the air masses were slowly moving and hence residing longer over local continental sources, which resulted in elevated aerosol concentration (high extensive properties) and photochemical aging (high single scattering albedo)- Again some discussion of coagulation causing larger size fine mode particles, and thus increased scattering (thereby increasing SSA), is needed here.*

We have added that this change is SSA532 may also be due to a change in particle size. Additionally, we have cited Wehner et al. (2008) who have seen an increase in accumulation mode particle size in slow moving and local air masses.

We have also added two new sections (3.4.1 and 3.4.2) to the revised manuscript, together with three new figures (Figures 12, 13A and 14) in order to address the reviewer's comments. In the discussion of these new Figures we conclude that changes in the size distribution did not drive the changes in the single scattering albedo.

Additionally, we have added Figures 18A-C to address this reviewer's comment below about the fine/coarse ratio in the Ångström curvature. In the discussion of these figures, we conclude again that "There is no strong relationship with this parameterization

ACPD

8, S4784–S4796, 2008

and single scattering albedo (not shown), thus suggesting that the changes in single scattering albedo are not only due to changes in aerosol size and size distributions, but are also driven by the addition of absorbing material as discussed above in Section 3.4.2." This full discussion can be found in Section 3.4.3.

13) *Page 26: -Many studies have used the wavelength dependence of alpha to gain information on the size distribution of the particles (e.g., Eck et al., 1999; 2001; Schuster et al., 2006; Gobbi et al., 2007).- Note these studies have computed curvature from extinction not scattering AOD. Also, please add the ONeill et al. (2001) references. ONeill, N. T., T. F. Eck, B. N. Holben, A. Smirnov, O. Dubovik, and A. Royer (2001), Bimodal size distribution influences on the variation of Angstrom derivatives in spectral and optical depth space, J. Geophys. Res., 106, 9787-9806.*

The reference has been added and the alpha has been changed to reflect that extinction values were used.

14) *Page 27: -To our knowledge, the second derivative observed on 25 July is the highest reported for atmospheric aerosols. It is substantially larger than the second derivative values reported for biomass burning aerosol in Bolivia (alphae 2.09; Eck et al., 1999) and in Zambia (alphae<2.2; Eck et al., 2001).- Be careful, the 2nd derivative for scattering coefficient would be expected to be greater than for the extinction coefficient (similarly as derived from extinction AOD). See Eck et al. (2001) Figure 13a that shows curvature decreasing with increasing absorption. Also, you should compute the theoretical limits of curvature with Mie code, since it seems that your high value of 3.44 may exceed what is physically possible (likely <2.5). Measurement uncertainty (bias) perhaps contributed to the very high values you have inferred from data acquired during PRIDE. -This suggests that the driving force for the curvature is not only the pollution level.- Eck et al. (2001) Figure 13b shows that the driving force behind the curvature is the radius of the fine mode size particles. -Using other ground based techniques (i.e., sun photometers) it has been suggested that the main driving force of the curvature is the fine/coarse ratio of the size distribution (e.g., Eck et al., 1999; Schuster et al.,*

ACPD

8, S4784–S4796, 2008

Interactive Comment

2006; Gobbi et al., 2007)- Although the fine/coarse ratio is important in determining the curvature, a factor that is even more important is the size of the fine mode particles.

We have estimated what the 2nd derivative for extinction would be in the Results and Discussion section. These values are smaller than those for scattering. The highest value that we approximated for the 2nd derivative for extinction was 2.56, which corresponds to the 2nd derivative for scattering of 3.44 on 25 July 2006, and is thus closer to those values measured by Eck et al. (1999).

Additionally, we have included an additional figure (Figure 18) and a discussion (in Section 3.4.3) on the impact that the fine mode size distribution has on the curvature. This analysis has been applied to various AERONET data sets in Gobbi et al. (2007). Our PRIDE-PRD2006 data set fit well within the same boundaries in this analysis that the AERONET data sets do, thus again indicating that our values for curvature are similar to what others have measured (Section 3.4.3).

15) *Page 31: -Figure 17 displays SSA532 versus b550 for this campaign (including 23-25 July) with the color scale as local time.- Should be: -Figure 17 displays SSA532 versus b550 for this campaign (including 23-25 July) with the color scale as local date.-*

This has been changed.

16) *Page 32: -Since SSA532 and b550 are negatively correlated (Fig. 17), they partially offset their respective radiative forcing as an increasing b550 indicates increased cooling while a decreasing SSA532 indicates increased warming.- Please be more specific: decreasing SSA results in increased warming of the aerosol layer, but increased cooling of the surface (due to decreased surface irradiance).*

The last half of this sentence was deleted and it was clarified in the text that these are “Top of the atmosphere“ calculations. As mentioned above, this calculation was only to show the sensitivity of the radiative forcing calculation to differing b and SSA relationships and should not be considered to predict warming or cooling. This has

ACPD

8, S4784–S4796, 2008

been clarified in the Results and Discussion Section (Section 3.6).

17) *Page 33: -Alternatively, as SSA532 decreases, at a fixed b550, the forcing efficiency increases, indicating increasing warming of the surface.- As SSA decreases the solar flux decreases rapidly, therefore resulting in surface cooling. Do you mean the aerosol layer warms as the SSA decreases?*

The last half of this sentence was deleted and it was clarified in the text that these are "Top of the atmosphere" calculations. As mentioned above, this calculation was only to show the sensitivity of the radiative forcing calculation to differing b and SSA relationships and should not be considered to predict warming or cooling. This has been clarified in the Results and Discussion Section (Section 3.6).

18) *Page 35: -Around periods of intense pollution there was curvature in the dependence of SIGMAs on wavelength, which caused a wavelength dependence of the Angstrom exponent. This curvature can be explained by the high proportion of aerosol volume in the fine fraction.- The large curvature is influenced even more by the size of the fine mode particle radius; the larger the submicron particle radius the larger the curvature.*

We have included an additional figure (Figure 18) and a discussion on the impact that the fine mode size distribution has on the curvature (Section 3.4.3).

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ACPD

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ACPD

8, S4784–S4796, 2008

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