

## ***Interactive comment on “The variability of urban aerosol size distributions and optical properties in São Paulo – Brazil: new particle formation events occur at the site” by J. Backman et al.***

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**Answers to Interactive comment by Anonymous Referee #1 on “ The variability of urban aerosol size distributions and optical properties in São Paulo - Brazil: new particle formation events occur at the site” by J. Backman et al.**

First we want to thank the Referee for the constructive and detailed feedback which helped to improve the manuscript. All the comments have been taken into consideration.

We want to point out that the novelty of this study is not only the high ethanol, use but also the fact that the metropolitan area represents one fifth of the whole Brazilian

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vehicular fleet by numbers. To date, measurements on submicron aerosols within the metropolitan area of São Paulo are scarce. This was a prime motivation for the study. Initially, a misleadingly large proportion of the abstract and the introduction were dedicated to the ethanol use. The introduction of the manuscript was rewritten to match the scope of the revised manuscript and the new title "On the diurnal cycle of urban aerosols, black carbon and the occurrence of new particle formation events in spring-time São Paulo - Brazil". The high use of ethanol is known to deteriorate air quality through the accumulation of ozone and ultimately lead to photochemical smog. In particular, this leads to high aerosol concentrations in the submicron regime.

The major changes in the revised manuscript based on Referee #1 comments were that the emphasis of the diurnal cycle analysis was shifted to weekdays to better isolate the traffic effects, as suggested. The figures were split into weekday/weekend focusing on weekdays. As suggested the black carbon was included in the analysis and compared to the values reported by Baumgardner et al. (2007).

A comprehensive discussion on ethanol specific atmospheric chemistry would be outside the scope of the manuscript. Especially, since secondary organic aerosol (SOA) formation still remains a serious challenge for the scientific community (Kroll and Seinfeld 2008). However, a subsection discussing the oxidants which initiates the cascade of chemical processes, which form secondary aerosol was added to the manuscript.

In the results section the diurnal cycle of the urban aerosol number concentrations were gathered under two subsections, to meet the comments by the other referee. Air mass movement and modelled planetary boundary layer depth analysis were also included in the revised manuscript, as suggested by the other referee.

Furthermore, the text was copy edited to improve the grammar.

### Answers to general comments

***"Since the data indicates a weekday/weekend effect in Sao Paulo the diurnal***

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***patterns may be more clear by restricting the analysis to weekdays only to better isolate the traffic effects."***

This is a good comment. The revised manuscript will focus on weekdays in order to capture the traffic effects. The emphasis of Fig. (2) was changed to weekdays along with the text in the section discussing the matter. Additionally, the days were classified into sunny and cloudy days by comparing modelled and measured global solar radiation. Thus, better isolating the photochemical processes responsible for producing condensable species (Fig. 2b). Discussion on the Fig. (2b) was added to the results section. Furthermore, Fig. (4) and (5) were changed to emphasise on weekdays along with the discussion in the text.

***"It would also be interesting to see the analysis of the weekend/weekday pattern extended to additional observations besides number concentrations, most notably black carbon. Comparing black carbon observations to those reported for Mexico City (Baumgardner et al., ACP 7, 2517-2526, 2007) might be a useful exercise, particularly with respect to the higher ethanol use."***

This was a good and justified suggestion. An additional y-axis was added to the results section showing diurnal black carbon (BC) mass concentrations during weekdays and weekends along with discussion regarding the figure. Weekly BC trends were also added to Figure 3 as a subplot. A comparison to the light absorbing carbon (LAC) reported by Baumgartner et al., (2007), although the measurement techniques differ, was added to the revised manuscript. The Multi Angle Absorption Photometer (MAAP) used in the study is based on a technique where the sample air is drawn through a fibre-filter where the particles are deposited. By measuring the filter transmittance, filter reflectance, and volume of air, BC mass concentrations can be estimated. BC is defined using elemental carbon (EC) mass concentrations from which the mass absorption cross-section (MAC) is calculated (Bond and Bergstrom 2006). The MAC of the aerosol can then be used to calculate the BC mass concentration (Petzold et al. 2005).

The SP2 used by Baumgardner et al. (2007) uses a different technique. In the instrument, particles are suspended in the sample cavity which they pass through. In the cavity, they are subject to an infrared laser (1064 nm wavelength), which is absorbed by light absorbing carbon. Light absorbing carbon particles are heated by the laser to a temperature at which they incandescence. The intensity of the incandescence is proportional to the mass of the LAC. The scattered light is then used to calculate the particle size using Mie theory, assuming spherical particles. They report LAC mass concentrations measured with a SP2 in the size range of 150 - 600 nm. However, they also report values using a Particle Soot Absorption Photometer (PSAP) which measures light absorption by the aerosol with a filter based technique (Bond et al. 1999). Based on these arguments we chose to use this data for the comparison suggested by the referee. Unfortunately, they do not state the inlet they used.

***"The manuscript would also benefit from further copy editing to improve the grammar. Some examples are listed below, but it is not an exhaustive list."***

The manuscript was copy edited to improve the grammar. We sincerely hope the grammar of the revised manuscript is to the liking of both referees.

### Answers to specific comments

***P30422, L12-16: It would be useful to include here any references that discuss differences in particle and/or ozone yields of aldehydes to other VOCs to aid the interpretation of the observations in a region expected to have higher aldehyde emissions relative to other VOCs due to the very high use of ethanol in fuel.***

References discussing these will be provided. A more comprehensive discussion on the topic will also be included in an additional subsection in the discussion section revised manuscript. The subsection discusses how the degradation of ethanol (unburned fuel), acetaldehyde, and formaldehyde favours the accumulation of ozone ( $O_3$ ). The role of heterogeneous chemistry of  $O_3$  in the presence of organic carbon aerosol and acid catalysts is also discussed. The discussion focus on the initiating oxidants

responsible for the cascade of subsequent reactions, which ultimately produce secondary aerosol mass. As included in the discussion, SOA yield from even one given precursor is not a stoichiometric quantity but increases with the overall loading of organic aerosol. A more thorough discussion on SOA formation from VOCs would have been outside the scope of the manuscript.

***P30423, L15: Sample line lengths, material, internal dimensions and flow rates (or residence time) for the different systems should also be provided here.***

The sampling lines lengths, material, dimensions, and flow rates were written into the text as suggested.

***P30424, L10-13: The decision to omit the other two SO<sub>2</sub> monitoring sites needs to be supported in more detail. How far in km were the other sites and in what directions (could be referred to on the map). Were the stations in different surroundings (e.g., industrial)? What metrics were used in the authors' assessment?***

A just statement. Both the Congonhas and the Cerqueira Cesar stations were omitted because both stations are dominated by local heavy traffic, whereas the Osasco station and the campaign site are not (Gallardo et al. 2012). The reference was included in the manuscript, and both sites were added to Fig. 1 as suggested along with a more thorough explanation in the text to support the decision.

***P30425, L2-3: Might be better to move this paragraph to the instrument calibration section. Please also provide method used to calibrate flows.***

The paragraph was moved to the instrument calibration section as suggested. The flow rate calibration methods were also added to the subsection.

***P30425, L10: Should "ion" also be capitalized?***

Yes, it should. Corrections were made accordingly.

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***P30425, L28: Please provide a reference for the inversion method of the NAIS.***

At the time of submission to ACPD, no reference was available. The reference will be provided in the revised manuscript (Mirme and Mirme 2011).

***P30426, L3-4: "optical properties tracked: : black carbon mass" Suggest changing this to "optical properties tracked were light scattering coefficients measured by a nephelometer (Model 3563, TSI: : ) and light absorption coefficients converted from black carbon (BC) mass concentrations reported by a Multi Angle Absorption Photometer (MAAP, Model: : :)."***

The text was changed according to the suggestion.

***P30426, L11: ambient RH or RH measured in the instrument?***

We mean RH inside the instrument, and this was clarified in the text.

***P30426, L19: replace "nephelometer data" with "temperature and pressure measured in the nephelometer"***

Changes were made accordingly.

***P30427, L9: Reporting the diffusional losses in the driers as equivalent lengths of tubing suggests the authors applied a correction for losses, but this isn't explicitly stated in the manuscript. Was a loss correction applied to the reported size distributions?***

Corrections for diffusion losses in the sampling lines were applied to the reported size distributions. This should (and will) explicitly be stated in the revised manuscript as the referee kindly pointed out.

***P30429, L11-13: Was this for the study period or does it describe typical climate pattern?***

This describes a typical spring to summer transition. It is both representative of the

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measurement period and the typical climate pattern. This was clarified in the text.

***P30429, L15+: Number concentrations reported as  $20.1 \times 10^3$  and  $6.28 \times 10^4$  (and elsewhere) throughout these two paragraphs. Format should be the same unless significant digits change to reflect uncertainty in the values reported.***

Formats were changed to be the same. The accuracy of the reported values now matches the comparison values.

***P30430, L5: Change "edges" to the particular statistic being referred to (e.g., 5th and 95th percentiles, min/max).***

The edges were changed to 5th and 95th percentiles, which are now explicitly stated in the text and the figure caption.

***P30430, L23: Please define "median particle number size distribution". Is this the size distribution corresponding to the median number concentration, the distributions of the medians in each bin, or something else?***

We meant the median particle concentration in each size bin, in the particle number size distribution. This was clarified in the text.

***P30432, L12: "for carbonaceous aerosol" Does this refer to mass or number?***

The article cited reports black carbon mass concentrations and "for carbonaceous aerosol" was changed to "for BC mass concentrations".

***P30432, L13: Should this be "peak at the same time"?***

Yes, we meant "peak at the same time". The sentence is not included in the revised manuscript due to the revisions suggested by the other referee.

***The fact that both scattering and absorption have peaks does not necessarily mean that primary aerosols are driving them. For example, the reference cited describes observations in Mexico City that highlight the importance of sec-***

**ondary rather than primary aerosols for scattering properties (see their Figure 10). The statement is also contradicted by P30433, L1 "After the morning rush hour, when convectational mixing increases and photochemistry comes into play, SSA experiences a gradual increase: : :"**

In brief, the cited article makes a strong case that the primary aerosol (soot) is a vital contributor by mass during morning rush-hour and secondary aerosols during daylight hours. They determined a fixed SSA (0.54) for the primary aerosol using AMS data, which let them estimate that 35 % of the scattering during morning rush-hours is due to secondary aerosol mass and up to 75 % in the afternoon (their Figure 10). The figure describes the fraction of SOA that contributes to the total scattering and, therefore, not absolute values in the total light scattering by the aerosol (in  $Mm^{-1}$ ) on which we base our statement.

Aerosols emitted from combustion sources not only absorb but also scatter light (Bond and Bergstrom 2006, Sheridan et al. 2005). For example, using the primary aerosol SSA in the cited article (SSA = 0.54 at 532 nm), the fraction of light scattering to absorption is  $\sigma_{SP}/\sigma_{AP} = (1 - SSA)^{-1} = 2.2$ . Consequently, the primary aerosol scatters over twice as much light as it absorbs. SSA is a measure of light scattering to light extinction, which in turn depends on the aerosols chemical composition, mixing state, and the particle number size distribution. It is, therefore, not comparable with the total mass of the aerosol, nor the contribution by SOA to the total scattering, hence, not in contradiction with the statement as claimed. As was pointed out by the referee, this does not, however, exclusively mean primary aerosols are driving both and, therefore, the sentence was removed.

In the revised manuscript, Fig. (2b) is split into days with cloud cover and clear-sky condition days to seek the SOA contribution. During clear-sky mornings, there are more Aitken-mode particles than during cloudy days (precipitation omitted). Arguably, the higher concentrations of Aitken-mode particles during cloud free mornings result from the condensational growth of nucleation-mode particles. Therefore, nucleation-

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mode particles are less likely to coagulate thus explaining more Aitken-mode particles during clear-sky conditions.

Since no chemical data exist, the gain in secondary aerosol mass is further analysed in the following subsection discussing the aerosol optical properties. To aid the interpretation of secondary aerosol mass gain,  $O_3$  data was included in Fig. 5.  $O_3$  is a significant source of hydroxyl (OH) radical and play a crucial role in the formation of secondary aerosol mass (Jacobson 1999, Meng et al. 1997, Seinfeld 1989, Tanner et al. 1988). We also included discussion on the role of nighttime formed nitrous acid (HONO) as a source of early morning hydroxyl (OH) radical before  $O_3$  accumulates.

***P30432, L26-28: The reasoning here is difficult to follow. What exactly is meant by "small in size"? Smaller than the non-absorbing particles? What evidence supports the conclusion that soot aerosols in the primary fleet are dominant in number? Is there a strong correlation between absorption coefficients and aerosol number? Both have peaks in the morning, but by 12 LT the absorption coefficients have already returned to near "background" values (Figure 5a) while number concentrations are still considerably elevated (Fig. 2a).***

As was kindly pointed out by the referee, the message is ambiguous. By small in size we meant smaller than the non-absorbing particles.

Part of the statement is based on the minimums in first the count mean diameters (CMD, 10 - 11 LT) and later the surface mean diameters (SMD, 13 - 14 LT). Especially the later one is associated with the aerosols ability to scatter light, which, among other things, is dependent on the size. More importantly, they are indicative of the size distribution as a whole. These weighted means do not reflect concentrations and, therefore, not the amount of scattering and absorption (Fig. 5a).

During morning rush hour there is an increase in both Aitken mode and nucleation mode particles, not in the accumulation mode particles (Fig. 2b). At the same time, there is the morning rush hour characteristic peak in light absorption associated with

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soot. As pointed out, this does not unambiguously mean that soot aerosols are dominant in numbers, therefore, we understand that the statement is too strong, based on these facts. The statement was removed from the revised manuscript and, therefore, both the SMD and CMD plots.

***P30433, L8: "The low SSA values presented here indicate that the City of Sao Paulo has a direct net warming effect on a regional scale." This is a strong statement to make on the basis of a measurement at a single location for 3 months of the year. Additional SOA formation downwind of the city (either due to changes in gas-particle partitioning with changes in temperature and RH or additional photochemistry) could increase the SSA above the 0.85 critical value, which itself depends on a large number of factors including surface albedo, aerosol distribution and clouds. Also, what is meant by the "City of Sao Paulo"? The city also is responsible for other emissions, such as those needed to generate the electricity it consumes, that are not necessarily represented by the measurement location. Perhaps the statement could be changed to "aerosols emitted sources within the City of Sao Paulo have a direct net warming..."***

The referee is unquestionably right. By the City of São Paulo, we meant within the geographical metropolitan area of São Paulo and not the city as a whole system. As mistakenly written it was too strong of a statement and will, therefore, be changed.

As will be discussed, in brief, in the revised manuscript a  $NO_2$  reservoir associated with ethanol and aldehyde degradation can carry  $NO_2$  over long distances in the form of peroxyacetylene nitrate (PAN). Therefore, PAN can change the reactivity of the atmosphere far downwind (Tanner et al., 1988), thus presumably changing the optical properties of the aerosol, as well.

Furthermore, as was kindly pointed out by the referee, aerosol radiative forcing depends on the surface albedo, upscatter fraction and asymmetry of the aerosol and cloud cover conditions too. These additional clarifications were added to the text in the

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revised manuscript. Furthermore, the sentence should read as the referee suggests which was corrected in the revised manuscript. Unfortunately, the Nephelometer did record the back scattering fraction of the aerosol which could have led us to estimate the critical  $\omega_0$  of the aerosol were the radiative forcing change sign. However, this was added to the discussion in the revised the manuscript.

***P30433, L10-16: As written, it is not clear how the discussion of Angstrom exponents adds to the manuscript since size distributions were measured directly. Since the nephelometer was behind a 2.5  $\mu\text{m}$  size cut the reported values cannot fully capture the possible contributions of dust and sea salt regardless.***

We acknowledge the fact that, with the  $\text{PM}_{2.5}$  inlet, we cannot reflect upon the contributions by dust and sea salt. The Angstrom exponent subplot was removed from the figure.

***P30434, L25: Another possibility that should be stated here is that the conversion technique used to calculate the  $\text{H}_2\text{SO}_4$  proxy from  $\text{SO}_2$  measurements was off since it was based on a different site, as noted earlier in the manuscript.***

This is true and will be mentioned in the revised manuscript along with the discussion on the other uncertainties.

***P30435, L7: Suggest changing "As both the" to "As the timing of the : : :"***

Changed were made as suggested.

### **Answers to comments on the Figures and Tables**

***An additional table summarizing the study averages (for N, etc.) and comparisons to other locations might be useful.***

The suggested table summarizing the observations was added to the revised manuscript including discussion on what they imply.

***Fig 1: Suggesting shading roads a different color or grey to distinguish from***

**other labels.**

Changes were made according to the suggestion. Roads were shaded to grey to distinguish them from the labels.

**Fig 2: Write out abbreviations. Add x-axis label. State what the "statistical edges" of the data are (min/max?). What are the red points?**

The abbreviations were written out in the legend in the figure, and x-axis labels were added. Statistical edges were substituted with 95th and 5th percentiles in the text. The outliers (red points) were removed.

**Fig 3: Not sure why this needs to have a log-scaled y-axis.**

The Y-axis was changed back to linear scale. A BC mass concentration subplot was added to the figure with a linear Y-axis.

**Fig 5: panel label locations are too close to the data, move to top left and adjust axis scales if necessary.**

Corrections were made accordingly. The outliers in red were removed.

**Fig 6: Legend is covering some of the data. Suggest adding "black circles, which indicate peaks of the size distribution" to the caption.**

Legends now cover all of the data. The suggested insertion "black circles, which indicate peaks of the size distribution" was added to the caption of the figure. An X-axis label was added to the figure.

**Fig 7: Legend covering some of the data. X-axis label is missing.**

Legends now cover all of the data. The  $H_2SO_4$  proxy legend is inside the subplot to the right of the lower panel. X-axis label was added.

**Fig 9: X-axis label missing. Caption should describe data source for the number time series. Would be helpful to have size ranges for different N concentrations**

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**listed in legend or caption (e.g., DMPS ( $X < 800 \text{ nm}$ ), CPC 3022 ( $D > X \text{ nm}$ ), ...).**

X-axis label was added. The size ranges were added to the figure caption.

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