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Atmospheric Chemistry and Physics Discussions

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 #2 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 of all we want to thank the Referee for the constructive and general feedback on the manuscript which helped to improve the manuscript. All the comments have been taken into consideration.

The major changes in the revised manuscript based on Referee #2 comments are to be found in the results section. To better connect the different observations the

diurnal analysis was gathered under two subsections. The first section "Diurnal cycle of aerosol number concentrations" discusses the aerosol number concentration and the atmospheric condition affecting these. Based on the general comments, air mass trend analysis and modelled planetary boundary layer (PBL) depth were added to the results and how they affect the reported ground level concentrations. The following subsection "Diurnal cycles of aerosol optical properties" is a continuation on how the air mass movement and secondary aerosol formation affect the observations.

Furthermore, a subsection in the results and discussion section was added on secondary aerosol formation. Since secondary organic aerosol remains a significant uncertainty in atmospheric modelling, the added subsection focuses on the degradation initiating processes (initiating oxidants). These are of profound importance of how the gas-phase pollutants chemically evolve. A more comprehensive approach would be outside the scope of this manuscript, especially since no chemical data exists. To aid the interpretation of additional secondary aerosol mass due to photochemistry, and how they affect the modal concentrations of the size distribution, Fig. (2b) was split into clear-sky days and days with cloud cover.

Based on the other referee's comments the emphasis of the analysis was shifted to weekdays to better isolate the traffic associated aerosol pollution. Furthermore, the text was copy edited to improve the grammar.

Answers to general comments:

1. Title: The different parts of the title seem disconnected from the conclusions of the text. What do new particle formation events have to do with optical properties? What is actually the message of the paper?

As was kindly pointed out by the referee, part of the title was disconnected from the conclusions section of the manuscript. The title was changed to "On the diurnal cycle of urban aerosols, black carbon and the occurrence of new particle formation events in springtime São Paulo - Brazil" which better reflects the scope of the revised manuscript.

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The message in the introduction and the conclusions section of the paper was matched with the title.

New particle formation events and analysis of the growth rates during the events provide an insight into the levels of condensable vapours, which grow particles once they are formed. Secondary aerosol mass in an urban environment, mainly consists of sulphates, nitrates, and organics. Secondary aerosol mass scatters light. Thus, optical properties facilitate the understanding of aerosol growth in terms of secondary aerosol mass gain. The revised manuscript will address the contribution of secondary aerosol mass and its implications on the optical properties.

The message of the manuscript is to describe the diurnal cycle and characteristics of the submicron aerosol in São Paulo. To date, submicron aerosol measurements within the megacity are scarce. Every megacity has its own characteristic, although it covers a small area of land it enforces a significant amount of air pollution with wide spread implications. The metropolitan area of São Paulo (MASP) represents one fifth of the Brazilian vehicular fleet and is, therefore, of climatological significance.

2. Abstract: The work is motivated by the use of bio-ethanol (a large fraction of the abstract is dedicated to this), but it is unclear how the particle concentrations, new particle formation event characteristics, sulphuric acid concentrations etc. presented in the abstract later are linked to this. What do the results tell about the bioethanol use (or something else that is new, or is the purpose of the paper to simply present size distribution observations from a new site)?

As pointed out, a misleadingly large proportion of the abstract and the introduction was dedicated to ethanol use. As previously mentioned, megacities impose a significant pollution burden on a regional scale. To date, submicron aerosol measurements were scarce within the MASP and were a major motivation for this study. This message was clarified in the abstract of the revised manuscript. Furthermore, a unique feature of the site is the high ethanol use, which is known to result in smog and elevated ozone

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concentrations. Eventually, this will have implications on the submicron aerosol due to the increase of the overall reactivity of the atmosphere. The formation of secondary aerosol mass, which is to be found in the submicron regime, will result in photochemical smog. In the revised manuscript, under the new title, both the abstract and the introduction were rewritten to match the content of the manuscript.

3. Introduction: It is not clear what the scientific objectives of this paper are - and why the particular approach has be chosen to address e.g. the haze problem. It might help if the authors would list the scientific questions that are studied in this paper and then make sure these questions are concretely addressed in the conclusion section.

The scientific objectives of the study are now explicitly stated in the introduction section of the revised manuscript. These objectives are exhaustively addressed in the conclusions section of the paper and discussed in the results section. On the approach, in general, coarse mode particles mainly originate from crustal material (with elements of silicon compounds, iron, and aluminium), sea salt, pollen etc. Fine mode particles (i.e. submicron) are known to consist of, soot, sulphates, nitrates, and a plethora of organic species. These are the constituents that make up the urban haze (smog). They do so through both the primary soot aerosols, trough photochemical degradation of precursor vapours through heterogeneous and photochemistry, all of which affect gas-particle partitioning of the air pollution. The occurrence of new particle formation and the sub sequential growth to cloud condensation nuclei (CCN) sizes in the area are unknown. The basis of the approach was included in the significantly rewritten introduction of the manuscript.

Initially, the study would have included aerosol mass-spectrometer (AMS) measurements but were for logistical reasons impossible to carryout. Hence, we had to rely on aerosol optical properties as an indicator of secondary aerosol formation.

4. Based on the results it looks like the analysis of particle formation events

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on this site are among the main contents of this paper. If the authors choose to concentrate on this as their main message, more work on the implications of the results is needed. Can the authors say something about the chemistry influencing the particle formation and growth?

The introduction, which originally was too focused on bio-ethanol, was rewritten to match the results section of the significantly revised paper. All the diurnal analyses were gathered under the two subsection "Diurnal cycle of aerosol number concentrations" and "Diurnal cycle of aerosol optical properties" to better carry the message of the manuscript. Based on the referee comments the analysis of the new particle formation events is no longer among the main contents of the revised manuscript.

A subsection discussing the chemistry associated with the high level of bio-ethanol use was added to the discussion section of the paper. Since no chemical data, such as aerosol mass-spectrometry or filter samples, were available, their influence on the observations remains to be quantified. The revised manuscript will address the importance of initiating oxidants and photochemistry for secondary aerosol formation. The secondary aerosols forming potential depend on these and are reflected in the aerosol optical properties of the aerosol. Any other approach would be outside the scope of the manuscript.

We point out heterogeneous chemistry involving organic carbon aerosols as a sink for ozone and the role of acid catalysts for aldehyde functional groups in the aerosol-phase. The reactions could be specific for secondary aerosol formation from ethanol combustion by-products.

How about the air masses that are predominant then? I am a little concerned whether the "new particle formation happens on the site" is enough of a conclusion for a scientific paper.

The revised manuscript discusses the role of PBL growth and air mass stagnation which undoubtedly play a crucial role in the ground level pollution at the site. PBL

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growth is based on NOAA - CIRES 20th century reanalysis version 2 data at the nearest grid point in the data set. Furthermore, a rose plot was included showing the origin of sulphur dioxide to be from the centre of the city. Diurnal wind directions were included in the revised manuscript along with discussion regarding the behaviour and references to other relevant meteorological studies in the area. The revised manuscript makes the case that there is a heat island effect affecting the observations at the site.

A comparison to other urban sites is presented, but with the current amount of literature on this subject is would be nice if the authors could discuss a little bit more extensively what the results of the comparisons imply.

A more detailed comparison to other urban cities was included in the revised manuscript (Table 1 in the revised manuscript). Discussion on the implications was added to the results and conclusions section of the revised manuscript.

5. It would be interesting to see a little more discussion on e.g. the different sources affecting the measurement site, even if no quantitative chemical data exists. I would thus suggest the authors to dig a little deeper in the analysis of their data set.

A subsection was added to the revised manuscript which discusses the chemistry associated with ethanol combustion and its implication on particulate matter levels. Since SOA formation of even a single precursor is not a stoichiometric quantity, but rather increases with organic aerosol loading the SOA forming potential is discussed with respect to the VOC degradation initiating oxidants from an ethanol-combustion point of view. Since no quantitative chemical data exists, we restricted Fig. 2b into weekdays only and split the data into clear-sky and cloud cover conditions. The differences revealed were added to the discussion in the results section of the manuscript.

As also pointed out by the other referee, the supporting measurement stations and their surroundings will be discussed in more detail. By splitting the optical properties tracked into weekday and weekend data sets, we could tell that there are differences

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in the single-scattering albedo of the aerosol. In the results section, we partly attribute the difference to a change in the sources associated with traffic.

The revised manuscript will include a rose plot of SO_2 and wind pattern analysis to aid the interpretation of the observations and the sources affecting the measurement site. In the revised manuscript, we argue there is a heat-island effect affecting the measurement station during clear sky conditions, which show up as low level horizontal southwesterly winds. This is argued to be a clean sector and will, therefore, affect the ground level aerosol concentrations at the site.

6. The manuscript seems to be carelessly written and the English language is poor in parts of the manuscript. I am convinced that this set of authors can improve the quality of the language and presentation significantly, and strongly encourage them to do so.

The manuscript was copy edited to improve grammar. We sincerely hope the grammar is to the liking of both referees in the revised manuscript. The presentation of the manuscript was also significantly changed, especially in results section, to carry the massage of the manuscript.

Answers to the specific comments:

7. p. 30433, line 24 on: Please explain what class Ia, Ib and II etc. events are.

The classifications are explained in the revised manuscript.

8. p. 30425, line 6 on: The authors are referring to a rose plot. Why is this plot (and other plots relevant for e.g. airmass analysis or source sector analysis) not shown?

The source sector plot we are referring to will be included in the revised manuscript. Diurnal wind direction patterns showing signs of a heat island effect affecting the measurements were also added to the revised manuscript. Furthermore, of PBL depth, air mass stagnation plots were included in the revised manuscript. These will all be

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addressed in the significantly revised manuscript, as suggested by the referee.

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