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Atmospheric
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Discussions

# *Interactive comment on* "Urban organic aerosols measured by single particle mass spectrometry in the megacity of London" *by* M. Dall'Osto and R. M. Harrison

**Anonymous Referee #1**

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General Comments: In their manuscript DallOsto and Harrison describe the analysis of a sub-set of particle types measured in central London during the REPARTEE-I experiment using a single particle aerosol mass spectrometer (ATOFMS). During the REPARTEE-I experiment various aerosol properties were measured in central London in the Regent's Park using – among others – two aerosol mass spectrometers. After the same authors have presented nitrate-containing particles and secondary aerosol particles measured during this field campaign with the ATOFMS in previous manuscripts, this manuscript focuses on presumably locally generated particle types from the same data sets. In addition to a description of the typical mass spectra of the selected aerosol particle types the attempt is made to identify the sources or source processes and to

determine the nature of these particles. The manuscript is well written and the impression that the work was performed very thoroughly and self-critically is given. The individual mass spectra are extensively described and every effort was made to identify the nature of the particle types. In addition the limitations of the measurements and the associated analysis are clearly named, which supports the credibility of the analysis significantly. However, after reading both, the abstract as well as the whole manuscript the impression is left that a significant fraction of the source identification of the particle types and of the comparison of ATOFMS with AMS data is based on speculation and that no real conclusion about these sources can be made. Besides the Ca-EC particle type none of the particle types described here seems to be really identified and can be associated with any source with reasonable certainty. This becomes also clear when reading the conclusions of the manuscript, which mainly state that none of the instruments alone (AMS and ATOFMS) provide sufficient information for a reasonable explanation of the particle types, but also the combination of both does not really allow a reasonable identification of the nature and sources of the particles. It is unfortunate that already two papers have been published with the other fractions of the results of these measurements with this instrument. Otherwise the information within this paper could have well been added as a short paragraph to one of these papers to round up the information there. However, I do not think that the results presented here provide sufficient information to justify a whole paper.

Specific Comments: Abstract, Line 11: "... probably from condensation of semi-volatile species ...“: While this seems reasonable I wonder how you can be sure that these species are local in origin?

Abstract, Line 19: Do the particle types really correlate with the HOA fraction or with the absolute concentration of the HOA?

P3L3: "Primary particles“ are not defined as only particles from combustion sources. There are many other sources for primary particles (e.g. mineral dust, sea salt, pollens, plant debris, ...)

P3L10-12: Give a reference for this information.

P3L7-P5L7: There is an extensive description of secondary organic aerosol formation in this introduction. It is not really clear how this is related to the present manuscript, which does not focus on SOA.

P5L13: The description of the AMS used in this study is contradictory: Either it was a high-resolution ToF-AMS, then its name is HR-ToF-AMS or W-ToF-AMS, or it was a compact ToF-AMS, then its name is C-ToF-AMS.

P5L17: The claim that the AMS measures quantitatively 'precise' mass concentrations seems a bit exaggerated. Typically AMS precision is not better than 25-30%, especially when methods like PMF are used. I suggest deleting the word 'precise'.

P6L3-4: "In summary, three contributions were identified in REPARTEE I: . . ." – contributions to what? Write briefly how they were identified.

P6L7-18: This paragraph sounds a bit like cutting the whole ATOFMS data set into pieces for several papers. Make clear what the reasons for the presentation of individual subsets of data from the same instrument measured in the same field campaign in different manuscripts are.

P7L2: The measurement site was on an area reserved for parking. Was there local traffic which could have contaminated the measurements?

P7L20-22: Here it is claimed that the ATOFMS can provide quantitative information on particle number as a function of composition. It is not stated what kind of information this is (e.g. number concentration of such particles) and how it is related to real-world quantities. In addition according to DallOsto et al. 2006 (also stated further below) no quantitative information on particle concentrations can be provided by the ATOFMS since detection or analysis efficiencies depend on the particle type and composition.

P8L9: "In addition to the mass spectrometers . . ." – Only the ATOFMS was briefly described.

P8L10: The instruments described in this section do not measure physical but mainly chemical characteristics of the particles.

P9L11: Here it is stated that 'extensive calibrations' are needed to provide quantitative information on concentrations of particle types. Have these calibrations been performed?

P9L14-18: This section again sounds like the data set was cut in slices to be presented in different papers. Provide reasons for this division of the data.

P10L2: This seems like a very small diurnal variation of temperature and humidity.

P10L11-P11L4: Partially the description of the mass spectra (area matrices) is confusing. The shown AMs do not seem to reflect well what is described in these two paragraphs. For example in Ca-EC the EC intensity is much less than that of nitrate-related peaks, but EC is seen as a major component while nitrate is not. Sulfate has similar intensity as EC, but is seen as negligible. Cluster OC is claimed to be internally mixed with sulfate contrary to Ca-EC, however, in the latter the m/z 48 signal (SO) is more intense than in the OC cluster. What is the origin of signals at m/z 37, 39, 41, 55 which are more intense than several others which are mentioned? Also in the AM of cluster Na-EC-OC several peaks (e.g. 48, 97, sulfate, 46, 62, nitrate, 39, 41, potassium?) are not mentioned in the description at all.

P11L9-17: What is the point of showing this spectrum of a single particle? Is this spectrum typical for SOA-PAH? Then it should be reflected by the AM. If it is extraordinary, what is the point of showing it? The interpretation of this spectrum seems also a bit arbitrary. While some of the peaks are interpreted extensively using McLafferty (who describes electron impact mass spectra) others with similar intensity are simply neglected.

P11L19: Similar here: m/z -73 is not dominant as claimed in the text. The signals at m/z -33, -49, -57, -80, -81 and -97 are larger than that at -73.

P12L1: There is no “complete absence” of nitrate-related peaks as claimed. Signals at m/z -46 and -62 are clearly visible.

P12L24: Why are the size distributions of Ca-EC and OC indicative of a primary origin of these particles? How would be a secondary origin of these particles be in contradiction to those size distributions?

P13L1-2: Is there any interpretation for the second smaller mode in the size distribution of Na-EC-OC in the coarser region? In addition also for Ca-EC and OC hints of such a mode can be seen in the size distributions. Generally I doubt that these features in the size distribution are very significant. Taking into account the percentage of Na-EC-OC (1,7%) and the total number of particles analyzed (153595) only 2611 particles belong to the Na-EC-OC cluster. With the given range of the concentration of particles in Figure 3 it can be calculated that within this additional mode between 1 and 5 particles have been measured in the individual size bins. Add error bars to the size distributions to show whether such features are significant.

P13Chapter3.2.1: Since all four particle types together make up less than 12% of the total, correlations between bulk or ensemble measurements and time series of these types of particles can easily be by chance, especially when the correlation coefficients are so low.

P13L20: Average diurnal profiles are not necessarily very meaningful. They can easily be strongly biased by few extreme values accidentally occurring during a certain time of a day. Add either median and percentiles or error bars.

P15: How are all the uncertainties in this chapter calculated? How much of it is due to counting statistics? Within the uncertainties almost none of the differences are significant. How significant are these differences?

P16L6: The previous association of cluster Ca-EC with primary traffic-related combustion particles ‘is in agreement’ with the assumption that those particles here are also

from such sources, however, it does not ‘confirm’ this.

P16L6-13: Is it realistic that such different processes or sources generate the same type of particles? The explanation here sounds a bit like the desperate search for an explanation rather than that these measurements provide real insights into the processes occurring. Why is the small diameter of the particles an indication for organics condensing onto existing sulfate-rich particles? Also the following paragraphs – until the end of 4.1 – do not really provide a clear idea about the sources or nature of the particle types. All the attempts to explain them seem to be pretty speculative with some of the speculations being contradictory. Bottom line of this chapter is more or less that the sources and the nature of these particle types are not known – besides those for Ca-EC. For SOA-PAH the discussion even suggests that this particle type consists of different particle types mixed together in the analysis.

P19L17-19: The description of OOA that is provided here seems more like a description which is typically given for OOA-I and OOA-II. Is this meant here?

P20L1-4: “. . . as the qualitative temporal information of the ATOFMS particle number concentration of single particle mass spectral type does not allow a meaningful correlation with quantitative aerosol mass loading concentrations of organic components provided by the AMS.” If this does not allow a meaningful correlation, what is the point of doing it nevertheless?

P20L11-13: This statement suggests that there is no real ‘hard’ reason for the 4-factor solution in the AMS PMF analysis.

P20L14-P21L3: The conclusion of this paragraph is not very clear to me. There seems still no real explanation about the origin and nature of SOA-PAH.

P21L4-16: The discussion about the m/z 55 particles is a bit confusing. It suggests that this type is the sum of OC, Na-EC-OC and SOA-PAH types. However, it is not clear, whether this is really the case. Write clearly what is the case.

Conclusion: This work shows that not only AMS or ATOFMS alone are not able to give a comprehensive insight into aerosol composition and sources, but also the combination did not provide this insight – contrary to what is stated here.

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