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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 #2

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This is an interesting paper representing a well executed study. However, there are weaknesses in the data analysis and interpretation and as a result the overall significance of the findings is unclear. The association of the Ca-EC particle type with vehicle emissions is well supported and consistent with work reported by others. Other findings, such as the preferential deposition of amines onto less acidic particles go counter to current thinking on this subject; this brings into question the use of m/z 81 as an indicator of particle acidity. It is not clear why the AMS factors were only compared to the four ATOFMS particle types described in this paper, rather than the entire set of 15. The comparison of m/z 55 time series from the ATOFMS and AMS requires substantial clarification or should be removed. Many of the issues raised below can presumably

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be addressed through revisions and perhaps some additional analysis. The conclusion section requires revisions so as to focus on what was determined through this study.

Detailed Comments

Abstract

P2-L5: weren't all particles that were classified accompanied by the AMS measurements?

P2-L7 We do not know that these four types are due to local particles. Perhaps you could revise to "postulated to be due to locally generated aerosol"

P2-L10-15 This is a difficult sentence that should be revised.

P2 L18 Secondary aerosol production

Introduction

P3-L10 Define VOC (not just in abstract)

P6-L9 The Harrison 2010 reference is missing

P6-L10 Introducing the summary table (Table 1) of the campaign at this point would help. If 15 particle types were classified, and only 4 are reported here, then what is the significance of the others? What were the key findings for the others? The summary table should be used to help clarify the objective of this work within the context of the previous papers. The acronyms used in Table 1 should also be defined, perhaps in the figure caption

Experimental

P8-L2-6 Aside from allowing for the detection of high molecular weight species, what are the potential consequences of this for particle classification and identification? Was the use of this low energy a deliberate choice or the result of an aging flash-lamp? Elaborate on the reasons for this choice as it is not common practice and it likely

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influenced your spectra.

P9-L2 What were the criteria for similarity? It is not elaborated on in detail in Dall'Osto and Harrison, 2006.

P9-L8 Sampling artifact may not be the correct terminology here. You are probably referring to transmission efficiency biases here.

P9-L11 Replace “techniques” with measurements or instruments?

Results

P9-L13 You should adhere to one term for particle types or clusters, or distinguish them if there is a difference for this study. It appears as though they are used interchangeably.

P9-L13 If 12 particle types were organic in nature, then shouldn't you consider the entirety of these for comparison with the AMS organic PMF factors? The 4 you have chosen represent a very small number concentration of all particles measured by ATOFMS, even for the organic particle types. Referring to the table containing a summary of all the particle types from REPARTEE-1 would be useful here.

P10-L11 The spectrum for Ca-EC only has very minor peaks at -36, -48 and -60. Why is EC being emphasized over OC as being characteristic of this particle type? State your naming criteria. The OC peaks (27, 43) seem to be more prevalent. Perhaps showing these spectra on a log scale would better illustrate the extent to which EC was present. Also peaks at 36.48 and 60 can arise from the fragmentation of organic compounds. Using a log scale might better indicate if higher mass peaks (72, 84 etc) were also present.

P10-L15 Is this low sulfur diesel fuel or gasoline?

P11-L13 Many of the listed peaks are not visible in these figures. Using a log scale might help

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P11-L20. The peaks listed are indicative of sulphate which may or may not be fully neutralized. They do not necessarily indicate acidic particles or compounds. m/z -195 is more commonly used as a marker of acidity (i.e., m/z -81 is very often present, while m/z -195 is much less often observed). From these mass spectra, m/z -195 is absent, or very low. Is there other evidence to suggest that these particles are acidic?

P12-L12 Qin et al. (2006) reported a scaling method using APS and MOUDI. The authors should discuss the scaling method using both DMPS and APS data in more detail.

P12- L28 These fragments may have been produced as a result of the decreased laser power used during this campaign.

P12:L15 Fig. 3 shows only up to just above 1 μ m. P12-L21 How do these size distributions show a primary source? This appears to be an overstatement. Perhaps replace indicative by suggestive? P12-L23 350 nm is not coarse Perhaps "larger" would avoid confusion P12-L26: The meaning of this statement is not clear as these are complex particles. The core may or may not have been primary. By definition the SOA coating is not primary. However, presumably the PAH compounds that deposited on the particles were primary with some degree of secondary processing. P13-L9 10th-11th (?) P13-L11 Consistent terminology will help readers. The AMS components are not clusters. Are the PMF factors, components, factors or something else? P13-L25 How did you determine this? Include the Pearson R correlation coefficient and indicate if it was statistically significant, and what do you define as a "strong correlation"? P14-L24 What are the +- here? Is it still mean +- 1 standard deviation?

Discussion

P16-L5 The meaning of "confirms its primary origin" is unclear and possibly an overstatement. Is the suggestion that this study confirms that at this site these particles only come from vehicles or mostly (primary) come from vehicles. Presumably the meaning is not intended to be broader and applicable to all sites. While the weight of evidence

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certainly points to vehicle emissions, it is not clear if this has been demonstrated conclusively, if this is the intended meaning of “confirm” Thus do your results really “confirm” that it’s vehicular emissions? You might summarize here why your results suggest vehicular emissions (i.e., reiterate that it “correlates strongly” with vehicular emissions tracers). Further, is it fair to compare these mass spectra to others that were generated using higher laser intensity? If so, justify why? If caution should be exercised when interpreting these mass spectra (and there should be), explain what parts of the interpretation should be performed more carefully. Some fragments will likely always appear (i.e., m/z +27/43), but others may never be observed under traditional ATOFMS operating conditions.

Pg 16 –L10 Does the sulfate or evening peak (or both) suggest an additional source in the evening? This is a bit confusing.

P16L12 Onto sulfate rich particles only in the morning? Clarify why you believe that particles are sulfate rich in the morning. For example, is the sulfate signal higher in this cluster in the morning?

P16 –L15 As shown in Fig3, the second mode of the cluster is ~ 0.9 μm . Is there any possibility that these larger particles are from misclassification of aged sea salt particles (NaNO_3 or Na_2SO_4)? It also would be useful to provide back-trajectory analysis to identify source regions for the Na-EC-OC cluster.

P17-L15 Refine the wording here (e.g. indicates and anthropogenic source). If there were multiple VOC sources contributing to this particle type, then this trend does not necessarily exclude a biogenic source. It could possibly be biogenic with another week-day influenced source added to it.

P17-L16 Again, you should justify that what you’ve measured can indeed be compared to previous measurements.

P19-L2 Can additional evidence be provided of particle acidity? The use of -81 peak

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alone is debatable. Does your observation hold true when you consider m/z -195 as a marker for acidity instead? The suggestion that amines are more prevalent on less acidic particles goes counter to most of the existing lab and field data or current understanding based on thermochemical modeling.

Further in what sense are these organo-nitrogen peaks secondary? They could be primary amines. Perhaps what you mean to say is that they promote uptake of gaseous amine precursor compounds. However, this uptake has previously been found to be promoted on acidic particles.

P20-L1: Were the AMS factors only compared with these four particle types or all 15? If it was only these four, why? If it was all 15 then these findings should be summarized.

P20- L10-14 This statement doesn't make sense when following the previous statement. Four factors were not chosen because it resulted in factor splitting. You need to develop this thought further.

P20-L21 What do you mean by "atmospheric chemistry" here? Do you mean oxidation of VOC precursor gases from sources other than food cooking?

P20-L25 Why do you focus on m/z 55 for both of these very different instruments? How can you be sure that this one ion fragment resulted from the fragmentation of the same type of compound. These two instruments rely on very different ionization principles, which inherently result in very different fragmentation patterns. More evidence is required to say that m/z 55 represents the same "parent compound". Were the 11500 particles with M/z drawn from the whole populations of 150,000 or only the four clusters discussed in this paper? If it is from the 150,000 then it is interesting that this 55 peak was only evident in three of the clusters, those discussed in this paper. If the 11,500 spectra were drawn only from the particles discussed in this paper than the meaning of this analysis is unclear. Since the basis for performing this comparison and the findings are very unclear I recommend deleting this section.

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Conclusions

Pg 22 L1-5 While these statements may be true, it's not clear how these conclusions arise from data presented here P20-L16. Didn't you compare a lab and ambient spectra to "confirm: that the Ca-EC particles came from vehicles?"

Figures and Tables

Table 1 define the acronyms, perhaps in the figure caption Table 2: Are any of these r^2 values statistically significant? Fig 4 caption: replace profiles with factors Fig 3-5: use same color scheme and markers for the four ATOFMS clusters Fig 6: Why are these axes in red? If these difference calculations were performed with absolute peak area as the unit, then why are the differences $E-02$? They should be much larger. Are these a fractional difference? The meaning of "and little content" in the caption is unclear

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 5043, 2011.

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