

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 #3

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General comments:

This manuscript describes a comparison of ATOFMS and AMS measurements made in London as part of the REPARTEE-I campaign, 2006. The article focuses on single particle data for organic aerosol, but also describes two elemental carbon (EC) containing particle types. While the article contains some interesting results for polycyclic aromatic hydrocarbon (PAH) single particles, there is a lack of structure which obscures the main conclusions. The AMS results described herein have been previously reported (Allan et al. 2010). Two articles describing the ATOFMS results from this measurement campaign have also previously been reported (Dall’Osto et al, 2009a,b).

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A lot of effort and discussion involves the description of primary Ca-EC particles and comparison of these with the hydrocarbon-like organic aerosol (HOA) detected by the AMS. Both are tracers for vehicular traffic exhaust aerosol, and a comparison of these tracers is cited by the authors (Drewnick et al. 2008). However that article does not describe AMS HOA arising from PMF analysis but instead compares Ca-EC particles with PAH mass contribution estimates from the AMS. Nevertheless, both Ca-EC particles and AMS HOA are well-established tracers for vehicle exhaust and thus a reasonable correlation is expected, or even redundant. Another ATOFMS particle type containing sodium, EC and OC is identified, but a source for this particle type is not suggested, nor is there any correlation with the AMS OA types for this particle type. A third particle type “OC”, is also described, correlating weakly with AMS HOA, but possible sources of this particle type are discussed only briefly and are highly speculative.

The SOA-PAH particle class should be the focus of most of the discussion, exhibiting diurnal behaviour attributed to atmospheric oxidation of gas phase hydrocarbons arising from vehicular traffic emissions. ATOFMS analysis of ambient PAH-containing single particles arising from vehicular traffic has been previously reported (Gross et al. 2000). Thus, the main finding of this study is the previously unreported peaks in the ATOFMS data tentatively associated to oxygenated PAHs. The presence of oxygenated PAHs and quinones in urban aerosol is not a new finding and the authors' coverage of the scientific literature on this topic is inadequate. Previous studies involving off-line analysis of PAHs, oxygenated PAHs and quinones in ambient aerosol could have been cited, described, and compared with the ATOFMS dataset. Also, an effort to explore the AMS data for PAH contributions, as per the authors' previous work (Drewnick et al 2008), could have been carried out. Despite the author's best efforts, the source(s) of the SOA-PAH particle type remains elusive and the related discussion is at times confusing and speculative. Ultimately, this manuscript provides very little new information on the sources and composition of urban organic aerosols and is, in my opinion, not substantial enough to warrant publication in ACP.

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Specific Comments:

Abstract, line 5. "Some of which were accompanied by AMS measurements" is confusing. Please rephrase.

Abstract, line 21. Remove 2nd ":".

Page 5045, line 6/7. Modification of primary particles results in modified primary particles, not secondary particles

Page 5046, line 20. Sentence beginning "On the contrary" is confusing and should be rewritten

Page 5047, line 18. Remove "precise" and rephrase

Page 5048, lines 1-17. This section describes previous papers from the same measurement campaign and, in part, undermines the necessity of this study. This section could be condensed.

Page 5050, lines 1/2. Provide reference

Page 5050, line 21. Replace "hit" with "ionized"

Page 5051, lines 9-11. "no attempt was herein tried to scale ATOFMS measurements with other techniques". ATOFMS number size distributions are scaled in this study to corresponding particle sizing instrument data, as described in section 3.1.2. Furthermore, why not attempt quantitative scaling for each particle class for the whole campaign? Does it improve the correlations with the AMS OA data?

Page 5052, line 2. Why is the wind dependence not included? Was there no dependence upon wind direction for these particle types?

Page 5052, lines 9 and 17. The term "AMs" could be confused with "AMS". An alternative label could be used.

Page 5052, lines 23-25. A signal for m/z -26 is also clearly visible in the "SOA-PAH"

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mass spectral area matrix.

Page 5053, line 17. m/z -26 may also be due to CN-

Page 5054, line 4. The average mass spectra for the SOA-PAH particle class contain strong hydrocarbon peaks. It is therefore incorrect to say that the particles are "highly oxidized".

Page 5054, line 20. SOA may also exhibit such small diameters

Page 5054, line 26. OC is described as secondary here but described as primary in lines 20-21

Page 5054, lines 23 and 26. The use of the word "coarser" is a little confusing. Suggest rephrasing these sentences.

Page 5055, line 9. Should be "10-11" not "9-10"

Page 5055, line 16. COA is not described well and does not correlate with any of the ATOFMS particle classes.

Page 5055, line 23. Presumably m/z 55 is chosen in an effort to match ATOFMS data with the AMS COA factor. This is not explained.

Page 5056, line 13. Referring to diurnal trends as bimodal is confusing.

Page 5056, line 18. Again, the reason for examining m/z 55 is not clear.

Page 5057, lines 13-26. This part should be condensed significantly as it reports findings from a previous article. The pertinent findings, for example the correlations of the AMS OA factors with the ATOFMS particle types should suffice.

Page 5058. This discussion is at times speculative. The evidence for ATOFMS "OC" being exclusively primary is not provided. A source is not suggested. "The morning peak probably arises from condensation of semi-volatile organic compounds onto sulphate-rich particles". Is there any evidence for pre-existing sulfate particles? Or a

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mass loading for pre-existing sulfate in the AMS data?

Page 5058, lines 25-28. Highly speculative

Page 5059, line 1. State the city.

Page 5059, lines 6-8. This sentence is confusing

Page 5059, lines 24-25. The sentence beginning "The temporal trend..." is speculative

Page 5060, lines 4-6. Provide reference

Page 5060, lines 25-26. What evidence? Please clarify

Page 5061, line 3. m/z -81 is a marker for sulfite, not necessarily acidity

Page 5061, lines 17-29. This section should be condensed. Most of the findings are from another article.

Page 5062, line 4. R₂ = 0.50 should not be described as highly correlated.

Page 5062, line 4-5. HOA is not described in the Drewnick article, quantitative PAH estimates are compared with temporal trends of Ca-rich particles detected by ATOFMS

Page 5062, line 28- Page 5063, line 28. The correlations do not provide any conclusive answers. This section could be reduced. It is enough to state that a COA particle type may not absorb at the correct wavelength for ionization to occur.

Page 5064. The conclusions section is poorly written. The main conclusion is the on-line detection of oxygenated PAHs in ambient urban single particles. Also, why not use a similar AMS PAH estimation approach from the Drewnick article (2008). This may correlate with the ATOFMS PAH and SOA-PAH data.

Page 5064, line 1-2. Both instruments have been demonstrated to do both.

Page 5064, line 10. The ATOFMS has been successfully used for source identification and to investigate aerosol processing. Several demonstrations of this have already

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been published by the author.

Page 5064, line 20. The correlation for OC should not be described as strong. Also, the OC particle type is alternately referred to as primary and secondary throughout the manuscript.

Page 5064, lines 21-23. This is speculative.

Page 5064, lines 23-26. If SOA-PAH is attributed by the authors as arising through processing of local vehicular emissions, why is it expected to be correlated with AMS OOA, which has been described as the authors as being associated with continental air masses.

Table 1. Most of these particle types are not described in this article.

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