

Interactive comment on “Real-time observation of secondary aerosol formation during a fog event in London” by M. Dall’Osto et al.

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Received and published: 13 February 2009

Interactive comment on “Real-time observation of secondary aerosol formation during a fog event in London”; by M. Dall’Osto et al.

We thank the reviewers for their careful review of our manuscript. We have addressed each comment below in italics.

Anonymous Referee #2 Received and published: 13 January 2009

Dall’Osto and coauthors provided in this paper a discussion of time-resolved data on aerosol chemistry and mixing state during a fog event in London. Beside reporting the already-known production of particulate nitrate by liquid phase reactions, the Authors provide an interesting insight into the parallel changes in the composition of particulate organic substances. The use of ATOFMS data is not new, because Qi

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and Prather (2006) applied the same instrument for studying a fog event in California finding the same types of organic and inorganic particles observed by the Authors of the manuscript at issue. Although the study of Qi and Prather is already acknowledged in the manuscript, a more thorough comparison between the results of the two studies would benefit the discussion. The study of Qin and Prather (2006) has been now discussed more in detail. Not only has a summary of the two studies been presented, the discrepancies of the findings have been discussed.

During a study conducted in the Fresno Valley (California), Qin and Prather (2006) reported biomass particles with distinct diurnal variations, peaking at night and reaching a minimum during the day. In addition to biomass particles, a very similar particle type to our HMOC type was also detected. The temporal variations of HMOC and biomass counts tracked each other very well with a high correlation coefficient of 0.84. Although biomass and HMOC particle types had very similar temporal variations and many common peaks in their mass spectra, the particle size distributions of these two types differed from one another. The majority of the biomass particles were submicron ($Da < 1.0 \mu m$) with aerodynamic diameters peaking in the lowest detectable sizes ($0.5 \mu m$). Conversely, the HMOC and fog processed particles (fog processing marker peaks at m/z -81 [HSO_3^-] and m/z -111 [$HOCH_2SO_3^-$]; basically the main markers of our HMS particle type, Figure 4b) were primarily supermicron sized particles ($Da > 1.0 \mu m$) and had similar size distributions. From all the above evidence, Qin and Prather (2006) suggested that the HMOC particles mainly resulted from a combination of biomass emissions, gas/particle partitioning of semivolatile biomass precursors, followed by aqueous phase processing. However, they could not exclude the possibility that a small fraction of HMOC were HULIS directly emitted from biomass emissions, since HULIS has also been reported to be released from primary biomass combustion. They hypothesised that the observed diurnal variation was due to an increase in direct biomass emissions during night time, followed by gas/particle partitioning of semivolatile species which undergo aqueous phase processing at night. Our results show instead a much finer par-

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ticle size distribution for the HMOC particle type ($<300\text{nm}$) than the droplet mode (1-2 μm in their case). We believe that the peaks associated with HMOC detected by Qin and Prather (2006) are indeed due to fog processing. However, the fact they are found in both the fine biomass particles (freshly emitted) and the coarser HMOC particle type (more fog processed) probably indicates that the meteorological situation was rather stagnant throughout their field study. In other words, they did indeed detect HMOC particles linked with fog processing, but the mechanism of formation remains unclear. Our study suggest for the first time in real time that the formation of HULIS was observed on interstitial particles and not in evaporated fog droplets, suggesting heterogeneous formation mechanisms.

A major point concerns the production of humic-like materials, HULIS, seen by the ATOFMS as high-molecular weight oxidized organics, "HMOC". The appearance of HMOC has already been reported by Qi and Prather (2006) in connection with nocturnal fogs. Dall'Osto and coauthors showed that, contrary to the previous study, HMOC formed in London fog associated with interstitial aerosol not to evaporated droplets. It follows that HMOC was produced through different processes than liquid phase reactions in fog droplets, and the Authors conclude that the high-molecular weight organic compounds have to form in the gas phase. However, the gas-phase formation of HULIS implies gaseous precursors having a high O/C ratio and a MW of ca. 150 Da. Such precursors exhibit a strong partitioning coefficient towards the particulate phase amplified by the presence of fog. Therefore, such medium-MW oxidized VOCs are not expected to occur in the gas phase during fog and thus they do not allow the gas-phase formation of HULIS with fast kinetics. The heterogeneous formation of HULIS is still more likely even when it occurs on interstitial particles. At high relative humidities, the interstitial particles, which contain sulphate and other hygroscopic compounds, can absorb non-negligible amounts of water. The reason why HULIS formed in the interstitial particles and not in fog droplets, which have a much higher water content, could be due to pH effects, or to dilution effects on reactants in grown droplets. We accept that the high-molecular weight organic compounds are unlikely to be formed

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in the gas phase and a new explanation has been provided following that suggested by the referee. Contrary to previous studies, the formation of HULIS was observed on interstitial particles not in evaporated fog droplets, suggesting heterogeneous formation mechanisms depending on parameters other than the water content.

The lack of data on fog liquid water content and fog pH is a drawback of this study and limits the comparison with past experiments. Still, it is one of the few available studies providing time-resolved data on the formation of complex organic matter in the presence of fog. I also particularly appreciated the comparison between the ATOFMS and the AMS data, and the detailed analysis of the organic mass spectra. We thank the reviewer for appreciating the comparison between the ATOFMS and the AMS data.

In summary, the manuscript can be revised for publication on ACP with minor revisions, but the abstract must be rephrased, acknowledging that HMOC formation during fog has already been reported by a previous study. I contest the statement "Humic-like substances (HULIS) appear to be produced in the gas phase and condense into the interstitial aerosol" for the reasons above. Instead, I suggest a sentence like "Contrary to previous studies, the formation of HULIS was observed on interstitial particles not in evaporated fog droplets, suggesting heterogeneous formation mechanisms depending on parameters other than the water content and not fully understood". Modified accordingly

I report below my specific comments: Page 20020, lines 14 – 20. Rephrase the paragraph in clearer manner. Is the term "Oxidation" used here to indicate the initial steps leading to (non-volatile) particulate organic matter formation? Please, explain. Corrected

Page 20020, line 24. On the contrary, reaction pathways for cloud-phase formation of low-molecular weight organic compounds have been studied in details (e.g., Herrmann et al., J. Atmos. Chem. 2000; Herrmann, Chem. Rev. 2003). Corrected

Herrmann, H., B. Ervens, H. W. Jacobi, R. Wolke, P. Nowacki and R. Zellner (2000).

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"CAPRAM2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry." *Journal Of Atmospheric Chemistry* 36(3): 231-284. Herrmann, H. (2003). "Kinetics of aqueous phase reactions relevant for atmospheric chemistry." *Chemical Reviews* 103(12): 4691-4716.

Page 20023, line 5. Specify the meaning of "large" particles. Section now modified to accommodate the point raised by Reviewer # 1.

Page 20025, line 18. Why "chemico-physical"? I would rather say "chemical properties and mixing state of the chemical compounds". Corrected

Page 20027, line 26. BC not EC. Corrected

Page 20029, line 21. Please, use the original definition for HMOC as "high mass organic carbon" (Qi Prather 2006). Quote also the study by Moffet et al. (ACP 2008). Corrected and references added.

Page 20032, lines 21 - 25. Why nitrate was not detected in period 1 by ATOFMS? Some nitrate particles were detected by the ATOFMS in period 1, but the ATOFMS cannot provide quantitative temporal trends in the same way as the AMS. However a good correlation between nitrate detected by both the AMS and the ATOFMS can be seen in the current ACPD special issue (Dall'Osto, M., Harrison, R. M., Coe, H., Williams, P. I., and Allan, J. D.: Real time chemical characterization of local and regional nitrate aerosols, *Atmos. Chem. Phys. Discuss.*, 8, 19457-19486, 2008.)

Page 20034, line 15. If speculative, remove. Paragraph discussing particle number concentration has been removed.

Pages 20034-20035. The discussion about the minor cluster named Ca-SUL can be considerably shortened and simplified. Corrected

Anonymous Referee #1 Received and published: 22 January 2009

Review of Real-time observation of secondary aerosol formation during a fog event in

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London by Dall’Osto et al.

GENERAL COMMENTS: This paper reports measurements of 2 state-of-the art aerosol mass spectrometers during a fog event in London. The combination of data from these instruments provides an interesting look at changes in aerosol chemical composition before during and after this event. The fog event itself is interesting, however there are several instances of comparisons with other studies, and speculations about mechanisms, which go beyond what the available data can support. Either more supporting evidence needs to be added to the paper, to justify some of the conclusions, or the paper should report less of the speculations about mechanisms, and more on the observations. Either of these routes would require a major revision before subsequent publication in ACP.

MAJOR COMMENTS: The discussion of HULIS and high molecular weight organics (HMOC) are interesting and HMOC has been reported before in the literature, but does a maximum mass signal at m/z 289 justify a whole class of compounds being called HMOC? As an example Gross et al. (2006) saw peaks up to 700 amu in the negative signal of an ATOFMS during chamber experiments by averaging mass spectra over different time intervals. Can a similar analysis be done on this data set from before the fog event and at different points during the fog event be shown? This would be beneficial to show the chemical evolution of the m/z which make up this particular particle type. Unfortunately the mass spectrometer of the ATOFMS was not tuned in a way that m/z higher than 300 amu could be detected. We believe that a maximum mass signal at m/z 289 justifies a class of compounds being called HMOC following Qin and Prather (2006).

The study of Gross et al. (2006) is based on a laboratory study with specific compounds (the photooxidation products of 1,3,5- trimethylbenzene and NO_x were studied over a range of initial 1,3,5-trimethylbenzene concentrations 137-1180 ppb), lasting for about 9 hours. The time window within our study where we detect this fog event is much shorter and does not allow us to look at the intensity of specific peaks. However, it is

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important to remember that the particle classes detected (HMS, HMOC1 and HMOC2) are unique to this event, as clearly shown in Figure 1c.

In general, there does not appear to be enough comparison with time period prior to fog event and post fog event. Do the high MW disappear? Were they present before and just part of another cluster?

We present a real time case study with several state of the art instruments. We show about 10 hours (Figure 3) of almost continuous real time data before during and after the fog event. The temporal trend of cluster HMS is shown as example in Figure 1c, and it is clear this particle type appears only during the fog event throughout the whole field study. Clusters HMOC1 and HMOC2 are not included in the chart as they show similar trends. We believe those particle types are formed during the fog event and are likely to be dispersed once the fog conditions end.

The AMS data doesn't show much of a change in the OOA factor, nor does sulfate change appreciably during the event. This is something that is not discussed in detail in the paper. The AMS data shows no increase in Organic mass (OOA in particular), so the question becomes is there sufficient organic mass being produced (clearly nitrate levels are increasing), or are the HMOC particle types of the ATOFMS secondary processing of preexisting aerosol? This is an important question to address since both processes contribute to the physical and chemical properties of the aerosol, but are different pathways. If aerosol processing is indeed happening, then the authors should modify the title to include processing as well as formation. We address the issue of the constant mass loading of OOA extensively between line 27 pg 20031 and line 11 pg 20032. We do not know if the AMS was not able to detect this particle type due to its chemical composition or if the amount of organic mass being produced is sufficient for being detected by the AMS. However, the ATOFMS is showing some unique particle types produced via secondary processing on the interstitial aerosol. We also included some comments about the fact that sulfate did not change appreciably during the event.

Additionally on page 20031 lines 24-26 The statement: 'Moreover, the real-time single particle information obtained by the ATOFMS indicates that the formation of these high mass organic carbon species occurs during a fog event of only a few hours.' is not sufficiently proven by the paper, in the opinion of this reviewer. More explicitly this study uses the ART2a algorithm to cluster the single particle data of the ATOFMS into 306 unique clusters that were combined by hand into 20 particle types. The 2 particle types in question, HMOC 1 and 2, were present only during the fog event. It does not necessarily follow that the organic species that make up these particles are only present during the fog event. It simply means particles having this particular mix of organic species in the particle matrix only occur during this event. Do the m/z discussed in the HMOC data only occur during this event, or do they also occur during other points in the study? Again averaging mass spectra for longer periods of time in and outside of this fog event would present more evidence that these m/z are only present during this event. The temporal profiles are strongly suggestive of this particle type being formed during the fog event. We do not claim that it can only be formed during such an event.

20033/5-10. Regarding the mechanism of gas phase formation and subsequent condensation on interstitial aerosol I agree with the Referee 2 that there is insufficient evidence presented to prove that this is the mechanism of formation. Mechanism has been reinterpreted.

SPECIFIC COMMENTS: Comments below will have the following form. Page/Line: Comment

20022/20-26. The authors state that the flow of the subsample is laminar at Reynolds Number (Re) = 1400. However, the diameter of the larger sampling tube is 15cm as opposed to 4cm for the subsampling system. The Re for this is 15/4 times larger (5250) which is indicative of turbulent flow in the 10 meter sampling line. For this paper this particular point is not too much of an issue, but the authors made a point of calculating losses and describing the laminar flow of the subsystem, so do they have a comment

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on the losses and flow of the main sampling line? We have re-evaluated this point. The system was run with a reduced flow in the main draw to ensure it was laminar, meaning the sampling was slightly super iso-kinetic. Using the approximations in Baron and Willeke (2001), the theoretical losses down the pipe below $5 \mu\text{m}$ were negligible. We have replaced "in a iso-kinetic manner" (2002:23) with "under slightly super iso-kinetic conditions, which caused negligible losses below $5 \mu\text{m}$,"

20025/10-15 and Table 1. This discussion would benefit greatly from an additional column being added to Table 1, where the percent of particles on this particular day (or define a time period of interest and explicitly state what period that is). As the table gives statistics for the entire campaign, it is of little use to the reader who is told only about this particular day of the campaign. The reader is told that 80 percent of the particles on the morning (what time period?) are from the 6 groups listed, but they are not told the proportion of particles in the different groups. New column has been added to Table 1.

20026/9. m/z 57 is assumed to be mainly C_4H_9^+ in the custom PCA method used here, but the authors need to qualify this statement, since other potential ions (e.g. $\text{C}_3\text{H}_5\text{O}^+$) can also contribute to signal at this m/z . Amended accordingly.

20028/23-25. The scaling of ATOFMS distributions in the Qin et al. reference refers to a MOUDI and an APS, not a DMPS and APS as used here. MOUDIs measure aerodynamic diameter as does an ATOFMS. A DMPS measures mobility diameter, the difference being the influence of particle density on the diameter measurement. How was density taken into account in the scaling of the particle counts? More description is needed since this method differs from the method given in Qin et al. We apologize for the inaccuracy of the citation. The procedure for obtaining scaled size distributions with the ATOFMS is very much under constant debate. For example, a long discussion can be found in Moffet et al (2008) ACPD paper, where very detailed points were addressed by Jimenez and De Carlo (Measurement of ambient aerosols in northern Mexico City by single particle mass spectrometry - R. C. Moffet, B. de Foy, L. T. Molina,

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M. J. Molina, and K. Prather *Atmos. Chem. Phys. Discuss.*, 7, 6413-6457, 2007 SRefID: 1680-7375/acpd/2007-7-6413). We only use the scaled ATOFMS particle number size distributions as qualitative information, and the procedure for scaling counts with mobility diameter is described very well elsewhere (Reinard et al. 2007)

Reinard, M. S., K. Adoua, J. M. Martini and M. V. Johnston (2007). "Source characterization and identification by real-time single particle mass spectrometry." *Atmospheric Environment* 41(40): 9397-9409.

200229/3. Citations are needed for the statement "The formation and stability of HMS has been shown to be highly dependent on the pH of the particle or droplet, as well as the concentrations of other chemical species."; References (Kok et al. 1986; Lagrange et al. 1999) are added.

Kok, G. L., S. N. Gitlin and A. L. Lazrus (1986). "Kinetics Of The Formation And Decomposition Of Hydroxymethanesulfonate." *Journal Of Geophysical Research-Atmospheres* 91(D2): 2801-2804. Lagrange, J., G. Wenger and P. Lagrange (1999). "Kinetic study of HMSA formation and decomposition: Tropospheric relevance." *Journal De Chimie Physique Et De Physico-Chimie Biologique* 96(4): 610-633.

20030/6-8. I was unable to find in Qin and Prather (2006) where the ion formulas of $C_nH_n^+$ and C_n^+ were listed as indicative of HULIS. Additionally later in the paper carbon clusters C_n^+ ions were associated with EC (20032/19), and not HULIS. Regarding the $C_nH_n^+$ perhaps the authors mean $C_nH_m^+$ ions, which better fit the ions identities listed in the preceding lines. Corrected

20031/10-13. The statement that the results of this study "fully support"; the Feng and Moller (2004) study is flawed. The Feng and Muller study used HPLC coupled to ESI and determined a pattern of ions from the cluster analysis of negative ions which would corresponding to the formula given for the molecular mass of the parent species. The formula of $(282 \pm 2x) \pm 14y$ does not apply to the ions listed in this data set however. It is impossible to get a odd numbered mass based

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on the above formula, yet the ions listed have both odd and even values. For these reasons, one could argue that the results of the Feng and Muller (2004) study are NOT fully supported by the results here. The comparison with the work of Feng and Moller (2004) has been re-drafted to better describe the common features observed. The new text reads as follows:

Peaks at m/z at 141, 155, 282 and 286 were also reported by Feng and Moller (2004), in the analysis of m/z signals in WSOC from cloud water. One cluster was specifically attributed to polycarboxylic acids formed in an atmospheric polymerization process from low molecular weight organics of different origin in cloud water;

20033/1. The quoted size distribution (0.8-0.9 μm) for nitrate a little beyond the AMS transmission curve for the lens. It would be beneficial to show the AMS size distribution for nitrate in the paper, as it is cited as having the same size distribution. The quoted size distribution is in particle number concentration, seen by the APS (Figure 3c, aerodynamic diameter) and Figure 7 (qualitative scaled ATOFMS size distributions). The AMS saw a mode distributed in the accumulation mode at about 600nm (in the aerosol mass loading concentration). It is correct that the AMS transmission curve for the lens decreases markedly for particles at 800-900nm.

20033/19-20. Nitrate was present in the aerosol prior to the fog event. While it is clear that more nitrate made its way into the aerosol phase during the fog event, the initial separation of the modes between droplet and interstitial aerosol is due to activation. Particles containing significant inorganic species will activate over the particles with more organic character. So the finding of the HMOC in the smaller mode and nitrate in the larger mode is not necessarily indicative of chemical processes, but could be due to activation differences between particle populations. We agree with the point made by the reviewer and have amended accordingly.

20033/26-27. If this reaction is occurring in the interstitial air, and then products condensing onto un-activated interstitial particles, why does it only occur during the fog

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event, and not at other times or throughout the campaign? Water content must be the driving force, as this particle type occurs during the fog event and not at other times throughout the campaign. Perhaps surface reactions in the liquid droplets are taking place, and such conditions are only present at the humidity of the fog.

20034/11 and 13. The line 11 on this page states there is a decrease in particle concentration. Line 13 states there is a constant particle number concentration. Figure 3d indicates that line 11 is likely correct, so the speculation about new particle formation should be removed. Removed

20034/23-25. The sharp drop in the nitrate concentration can also be due to the decrease in the RH and the repartitioning of nitrate from the particle phase to the gas phase. See Seinfeld and Pandis (2006) figure 10.22. Corrected

20036/9-13. Based on previous comments, the statements about the formation mechanism should be removed from the conclusions. Removed

Figure 1. Similar to Figure 1c, it would be useful for the reader to see the temporal evolution of the different particle types on the morning in question. Showing the ATOFMS counts vs time for the 6 particle types in Table 1. Could be in supplementary information. We show in Figure 1c the hourly temporal series of ATOFMS particle type HMS, which is the unique marker for the fog event in consideration. As reported in the text, some of the 6 particle types were not unique to this event, including nitrate particle types and Ca-EC. The latter for example exhibits diurnal temporal trends typical of rush hours, whilst the former is associated with long range transport of pollutants. We will present an overview of these results in a separate paper, along with a full AMS data analysis. We prefer to keep Figure 1 clear and associated with the fog event.

Figure 4. Are there no signals at high m/z for the particle types shown in this figure? The following 2 figures show a zoom of the high m/z areas. If there are signals at high m/z for these particle types the reader would benefit from a figure similar to 5 and 6. There is a small signal in the spectra of the particle type Ca-EC, due to the

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presence of Polycyclic Aromatic Compounds as described elsewhere (Drewnick, F., Dall'Osto, M., Harrison, R.M.: Characterization of Aerosol Particles from Grass Mowing by Joint Deployment of ToF-AMS and ATOFMS Instruments; Atmospheric Environment 42, 3006-3017, 2008). We kept the structure of these ART-2a clusters simple as there was no need to describe these peaks.

TECHNICAL COMMENTS: 20022/21 and 23. Recommend that authors use the same unit of measure to describe the tubing diameters, currently listed as 150 mm and 4 cm. Corrected

200243/5. Suggest replacing 'approximately' with 'as such'. Corrected

20023/20. 'particle' should read 'particles'. Corrected

20023/27. To what does the 'high resolution' mass analysis refer to? The C-ToF-AMS can record data at high time resolution, but is not capable of high mass resolution. Please clarify the statement here. Corrected

20024/14. 'meteorology' should read 'meteorological parameters'; as described in the legend of Figure 2. Corrected

20027/13. ATOFMS and C-ToF-AMS should be switched in the sentence order since Fig 3a refers to the C-ToF-AMS data and Fig 3b. refers to the ATOFMS data Corrected

20027/12-18. Some of the details of sampling are redundant with the experimental section, and do not need to be repeated in this section (e.g. model numbers of instruments, and time resolution of sampling). Corrected

20027/17 and 26. Please be consistent with the use of BC and EC. The MAAP is an optical instrument so BC is appropriate which is used in line 17, but EC is used in line 26. Corrected

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20027/26. Fig. 3e; should read Fig. 3a,e; since the HOA data is given in Fig 3a. Corrected

20027/26. Recommend changing primary atmospheric pollutants; to primary vehicular atmospheric pollutants; or something similar. Corrected

20029/18. Figure 3a. refers to AMS data, perhaps the authors meant to write C-ToF AMS instead of ATOFMS. Corrected

20035/10-11. This line should be moved up before the discussion of nitrate particles, as it follows the previous statements. Moved

Table 1. It would be useful to indicate which particle types in table 1 are unique to the fog event. Indicated in the text

Figures 2 and 3. The time axis range is different for these 2 figures. Please make the the same for consistency. Figure 2 replaced

Figure 7. What are the units on this plot? The left axis is on the order of $1e9$. Number per what volume or time? N represents the scaled total ATOFMS particles belonging to the clusters described.

REFERENCES Gross, D. S., M. E. Galli, et al. (2006). Real-time measurement of oligomeric species in secondary organic aerosol with the aerosol time-of-flight mass spectrometer. *Anal. Chem.* 78: 2130-2137.

Seinfeld, J. H. and S. N. Pandis (2006). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. New York, Wiley.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 8, 20019, 2008.

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