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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

Received and published: 22 January 2009

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

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Discussion Paper

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. 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? 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.

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

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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’s 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.

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.

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 on the losses and flow of the main sampling line?

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.

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20026/9: m/z 57 is assumed to be mainly C4H9+ in the custom PCA method used here, but the authors need to qualify this statement, since other potential ions (e.g. C3H5O+) can also contribute to signal at this m/z.

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.

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.”

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

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 +/- 2x) +/-14y does not apply to the ions listed in this data set however. It is impossible to get a odd numbered mass based 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.

20033/1: The quoted size distribution (0.8-0.9 um) for nitrate a little beyond the AMS

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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.

20033/19-20: Nitrate was present in the aerosol prior to the fog event. While it is clear that more nitrate made it’s way into the aerosol phase during the fog event, the initial separation of the modes between droplet and interstial 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.

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 event, and not at other times or throughout the campaign?

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.

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. There is also the

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

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.

Figure 4.: Are there no signals at high m/z for the particle types shown in this figure?

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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.

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.

200243/5: Suggest replacing ‘‘approximately” with ‘‘as such”.

20023/20: ‘‘particle” should read ‘‘particles”

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.

20024/14: ‘‘meteorology” should read ‘‘meteorological parameters” as described in the legend of Figure 2.

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

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).

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.

20027/26: ‘‘Fig. 3e” should read ‘‘Fig. 3a,e” since the HOA data is given in Fig 3a.

20027/26 Recommend changing ‘‘primary atmospheric pollutants” to ‘‘primary vehicular atmospheric pollutants” or something similar.

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

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AMS instead of ATOFMS.

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

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

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

Figure 7. What are the units on this plot? The left axis is on the order of 1e9. Number per what volume or time?

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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