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

Anonymous Referee #2

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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 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 through comparison between the results of the two studies would benefit the discussion. A major point concerns the production of humic-like materials, HULIS, seen by the ATOFMS as high-molecular weight oxidized organics,

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"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. Why this happened differently from the Qi and Prather study cannot be clarified based on the available data. 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. 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 heteroge-

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neous formation mechanisms depending on parameters other than the water content and not fully understood". 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.

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).

Page 20023, line 5: specify the meaning of "large" particles.

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

Page 20027, line 26: BC not EC.

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).

Page 20032, lines 21 - 25. Why nitrate was not detected in period 1 by ATOFMS?

Page 20034, line 15. If speculative, remove.

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

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

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