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# *Interactive comment on* "Aerosol particle measurements at three stationary sites in the megacity of Paris during summer 2009: meteorology and air mass origin dominate aerosol particle composition and size distribution" *by* F. Freutel et al.

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*The paper by Freutel et al., titled Aerosol particle measurements at three stationary sites in the megacity of Paris during summer 2009: meteorology and air mass origin dominate aerosol particle composition and size distribution" is a well-written manuscript summarizing summertime observations of aerosol size and composition measurements in Paris and two suburban areas as well as from a mobile lab. Aerosol*

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*data interpretation was complemented by FLEXPART back trajectory analysis as well as measurements of O3 and NOx. Furthermore, PMF analysis has been performed on the AMS organic spectra. Although no significant new science regarding aerosol formation and evolution is presented in the paper, the results of the study are valuable for understanding summertime trends and characteristics of aerosols in Paris and the surrounding regions. Therefore, I recommend publishing the manuscript after the authors address the following comments:*

*1. Section 3.1: how do the O/C ratios of the OOA factors compare with other SVOOA and LV-OOA factors? I think it would be helpful to include a discussion based on the degree of aerosol oxidation level at the different sites (and a comparison to previous PMF factors) to gain more insight into OA evolution upon transport. It seems the distance between the suburban sites and downtown site is ~20 km. Assuming surface winds of say 1 m/s, it will take airmasses to travel this distance in ~5-6 hr, which is long enough for some local SOA formation from the primary emissions.*

This indeed would be an interesting additional discussion, and would gain useful information on the evolution of particulate organics. However, we unfortunately were not able to obtain robust results due to caveats for the application to this specific dataset:

- The commonly used approach of using f44 (the ratio of signal of organic m/z 44 to the total organic mass spectrum) as indication for O/C as proposed by Aiken et al. (2008) in our case is problematic: we found in the intercomparison measurements of the MoLa AMS at the different stationary sites that f44 between different instruments can vary a lot. We found in the intercomparison measurements the following average f44 values:

0.11 and 0.08 for Downtown resp. MoLa AMS

0.07 and 0.12 for Sub SW resp. MoLa AMS

0.11 and 0.10 for Sub NE resp. MoLa AMS.

Thus, it seems f44 (and therefore the inferred O/C) as measured by the AMS shows systematic differences (f44 Downtown > Sub NE >≈ MoLa > Sub SW). The uncertainty for f44 from these intercomparisons can be estimated to 0.05 (maximum discrepancy found).

The values of f44 for the PMF factors are as follows:

HOA: LHVP 0.06 > Sub NE 0.04 > MoLa 0.02 > Sub SW 0.01

OOA: LHVP 0.19 > Sub NE 0.18 ≈ MoLa 0.18 > Sub SW 0.13

This means that 1) the differences found in f44 are consistent throughout the campaign (since for the PMF-Factors which are obtained for the whole campaign, the same systematic biases as during the intercomparsion periods are found), and that 2) within the uncertainty of 0.05, no conclusion upon the difference of f44 between different sites can be drawn. Differences in f44 and therefore O/C would only be justified to analyze for one single instrument, which unfortunately isn't enough for the analysis suggested.

- To overcome the problems stated above, there would be needed routinely performed measurements of known organic substances with different O/C ratio throughout the campaign with each instrument, in order to calculate a calibration curve (f44 vs O/C) for each specific instrument following Aiken et al. (2008). Unfortunately such measurements were not performed during this campaign, therefore this is not possible for this dataset.

- A different approach would be the usage of HR analysis results instead of using the proxy of f44, in order to calculate directly the O/C ratio from the ions measured. For this dataset, these HR data however are only available for two of the instruments; the instrument at Sub NE was a C-ToF-AMS, where such an analysis is not possible. Therefore, although very interesting, this question unfortunately cannot be answered from the present dataset.

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*2. Section 3.1: It appears that the PMF analysis has been performed on the unit mass resolution Org spectra. Have you tried looking at the high resolution spectra to see what the contribution of oxygenated species to fragments commonly assigned to HOA (like 41, 55, 57, etc) are since recent lab and ambient measurements do report on 'intermediately oxidized' species with an HOA backbone (Kroll et al., Nature Chem, 2011 and Bahreini et al., EST, 2012)? If you see a significant contribution, have you tried running PMF on the HR spectra? Different degrees of oxygenation in HOA could be a reason of worse correlation between the 'split' HOA factor in this study and the reference HOA.*

The "split" HOA$_{traffic}$ correlates rather well with the reference HOA$_{traffic}$ mass spectrum (R2 of 0.93), so we do not think a significant contribution of intermediately oxidized species is present in this factor. For the "split" HOA$_{cooking}$ factor, we do observe only moderate correlations with the reference mass spectra (R2 0.6 to 0.8). However, as this high diversity of correlation factors already shows, the exact mass spectra of the cooking HOA seems to depend very much on the actual source, as cooking emissions can comprise much more diverse emitted substances than e.g. traffic. As also the diurnal cycle of this factor shows a very distinct pattern, we are rather confident that this factor is indeed dominated by cooking emissions; if there are other intermediately oxidized species mixed into this factor as well, this rather seems to be a minor contribution. A detailed HR-PMF analysis is available for the Sub SW site in (Crippa et al., 2012). The authors find two HOA-like factors (traffic- and cooking-related) as well from their HR analysis, but no significant contribution of oxidized species at m/z 41, which would indicate the presence of intermediately oxidized species as suggested. At m/z 55, large contributions also of oxidized species are present, which likely for the most part can be explained by the OOA factor extracted also from the UMR mass spectra.

*3. Pages 22227-22228 (and in the summary): as written, it appears that the authors*

*claim that organics were responsible for aerosol nucleation events. However, the measurements discussed here don't really include composition of the nucleation particles. Therefore, I suggest rewriting these sections to avoid drawing such conclusions.*

The reviewer is right, this section could be misleading. Therefore, we followed the reviewer's suggestion and deleted the sentence "New particle formation was observed in the diurnal cycles of EAS and CPC, which will be described below." in Section 3.3.1, and reworded the discussion of EAS diurnal cycle slightly (see reply to reviewer 3's comments). Furthermore, we changed the according sentence in the summary to:

"Furthermore, diurnal cycles of OOA mass concentrations and of particle number size distributions indicated a small local contribution of secondary organic aerosol formation (leading to condensation and particle growth) to the OOA mass concentration and possibly a small fraction of semi-volatile OOA partitioning between gas and particle phase."

*4. Page 22228 (and summary section): Decrease in OOA in the early mornings can also be due to an increase in the BL height. Therefore, I suggest normalizing the OOA mass with a non-reactive tracer (e.g., BC) to account for dilution differences before concluding if OOA is evaporating.*

This is a valuable point. Using BC as non-reactive tracer, however, is problematic due to the influence of local emissions at each site, which peak during the time period of breaking up of the boundary layer. We therefore used $SO_4$ as such a tracer, as it should not be influenced much by emissions of the city (see Section 3.3.1). We still found a diurnal cycle comparable to the one shown in Figure 7, thus the night time maximum in the OOA diurnal cycle does not seem to be only due to variation of boundary layer height. However, a small influence of boundary layer height possibly might be present; therefore, we have reformulated the conclusion of this section as follows to also include this possible influence:

"During the night, both ambient temperature and the boundary layer height are de-

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creasing, so more semi-volatile OOA is condensing onto existing particles and the particle number concentration is enhanced due to the shallower boundary layer. Rising boundary layer height and temperature in the morning lead to dilution of the particles and to re-evaporation of such semi-volatile species, similar to the temporal variation of $NO_3$ (see Fig. 7). However, in comparison with the advected, regionally distributed OOA (as discussed above), the possible contribution of such locally generated OOA is small."

We also changed the wording in the summary - see answer to comment #3.

*5. Figure 6: is there a reason for not showing 'central Europe' diurnal profiles?*

Yes, there is a reason for this: there were only about three days of measurement within this type of air mass, so only very few data points would be included for each hourly median value. Therefore we omitted it to not draw conclusions from statistically insufficient data points.

*6. Section 3.5: In my opinion this section is the most interesting contribution of the paper. However, I think comparing absolute concentrations is not useful because of the dilution that's imposed on the air masses as they travel from downtown to SW or NE. Similar to #4 above, I suggest considering enhancement ratios of these species against a non-reactive species (e.g., CO or BC). Also, how much NOx would react away through the transport from downtown? Would it be possible to estimate and add the amount of NOx that is reacted away back in?*

In principle, this is a good idea. However, when including uncertainties both due to the measurements themselves as well as to the unknown amount of local emissions at the two suburban sites, the comparison of ratios of NOx or HOA to BC between sites gets problematic. Therefore we did not include this discussion in the revised manuscript to avoid drawing conclusions from uncertain data.

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