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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Simulating the formation of carbonaceous aerosol in a European Megacity (Paris) during the MEGAPOLI summer and winter campaigns" *by* C. Fountoukis et al.

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*The manuscript presents simulations of black carbon (BC) and organic aerosol (OA) components (e.g. POA, SOA, and cooking OA) from the PMCAMx model for Paris and compares these results against measurement taken at three ground sites during the MEGAPOLI summer and winter campaigns. It is found that the model provides reasonably good predictions of BC, with some discrepancies during the morning rush hour. In addition, model-measurement agreement is achieved for the summertime SOA concentrations. On the other hand, for the base case, there are significant differences between the model and the measurements for POA and for SOA during the wintertime.*



*The manuscript concludes that the substantial discrepancy in the POA concentrations is due to the lack of cooking emissions in the base case. When a cooking emissions inventory based on field observations is implemented in the model, much better model-measurement agreement is found, which supports the importance of including this source category in chemical transport models. For SOA during the wintertime, the reason for the discrepancy is unclear, although it is speculated that missing SOA formation pathways or inaccurate biomass burning emissions may be responsible.*

*Overall this is an interesting manuscript that is well within the scope of ACP, and the work certainly has the potential to be of high quality. However, there are a number of points in the manuscript where the inclusion of additional data, information, or sensitivity studies is needed and the current discussion lacks sufficient depth. This additional work will need to be included before final publication. The terminology used in the manuscript should be clarified as well, as discussed in the general comment below.*

*General comment*

**(1)** *If I understand correctly, the authors are using the term "anthropogenic SOA" to refer to SOA formed from anthropogenic VOCs. This makes the manuscript confusing, since one could have anthropogenic SOA formed from SVOCs and IVOCs as well. This confusion is particularly problematic in the discussion of aging in Section 2 as well as in the conclusions. In Section 2, does the rate constant of* $1 \times 10^{-11}$ *cm*$^3$ *molec*$^{-1}$ *s*$^{-1}$ *apply to anthropogenic SOA from only VOCs or to all anthropogenic SOA including SOA-iv and SOA-sv? In the conclusions, the authors state that 13 percent of summertime SOA "consists of anthropogenic SOA". This is a very dangerous statement as it gives the reader the impression that 87 percent of SOA is biogenic. I believe the correct conclusion is that 87 percent of summertime SOA comes from biogenic VOCs or primary SVOCs and IVOCs that are either biogenic or anthropogenic.*

We agree that this terminology issue requires further clarification. When we refer to anthropogenic SOA (aSOA-v) we mean SOA from anthropogenic VOCs only. We use the

notation SOA-iv for SOA formed during the oxidation of intermediate volatility organic compounds (IVOCs) and SOA-sv for the SOA from semi-volatile organic compounds (SVOCs). The aging rate coefficient of 1 $\times$ $10^{-11}$ $cm^3$ $molec^{-1}$ $s^{-1}$ is applied to aSOA, and the 4 $\times$ $10^{-11}$ $cm^3$ $molec^{-1}$ $s^{-1}$ coefficient is applied to SOA-sv and SOA-iv. We have made changes throughout the text to make this clearer. In the conclusions we have revised the above statement mentioned by the reviewer to avoid any misunderstandings.

**(2)** *There is a similar problem with the alternating use of HOA and POA in the manuscript. Is there a difference between "predicted HOA" and "predicted POA"? This distinction is important because in older work HOA was used as a term to identify a product from component analysis of AMS data that was strongly associated with POA. However, with the improvement of AMS and PMF analysis, HOA has morphed into a quantity that is no longer equivalent to total POA, but instead it is more associated with only the vehicular component of POA. In the specific comments below some instances of this problem are noted. I recommend that the authors use terms such as "predicted total POA" and "predicted vehicular POA" rather than "predicted HOA" to avoid confusion.*

We have made changes throughout the text following the reviewer's suggestion. We now use the term "predicted total POA" instead of "predicted POA" and the term "predicted vehicular POA" instead of "predicted HOA" throughout the manuscript.

*Specific Comments:*

**(3)** *Page 25551, Lines 3 - 6: I realize this sentence is not based on the authors' own work, but it would be helpful if "larger geographic area" was better defined. Would this larger area be continental-scale versus local/city-scale or something else?*

We have revised this sentence accordingly.



**(4)** *Pages 25554 – 25555, Lines 23 – 7: This paragraph and the discussion of the percentages of OA and BC from various sources should be summarized in a table. Currently, the paragraph is difficult to read and it's hard to compare the different percentages, which would be of interest.*

We have added a table in the supplement summarizing these percentages and changed this part of text to make it easier to read.

**(5)** *Page 25556, Lines: Lines 26 – 28: Additional information should be provided regarding the instruments used to measure black carbon. For example, what wavelengths were used for the absorption measurement, what are the instrument model numbers, what was the absorption coefficient used to determine the BC concentration, and were possible artifacts such as shadowing corrected? This information is critical for evaluating the model/measurement comparisons with respect to BC and needs to be included in the manuscript directly or via the appropriate references. Similarly, an uncertainty for the BC measurement should be reported in Figure 6.*

We have added a reference (Freutel et al., 2013) that includes all the information regarding the instruments used and the corresponding analysis of their measurements. We also added information about the BC measurement uncertainty.

**(6)** *Page 25557, Line 23: Is there an explanation for why a west to east gradient is predicted?*

A west to east gradient is predicted during summer due to the regional source distribution and the corresponding evolution of photochemistry. We have added this explanation in the revised manuscript.

**(7)** *Page 25557, Line 24: The terminology is confusing here. It seems like "OOA" is being used interchangeably with "SOA" in this paragraph. These aren't exactly the*

*same thing – OOA is used to identify a component from factor analysis. Practically there is little difference, but only one name should be used, unless the authors are trying to distinguish between two different predicted quantities. This comment applies to the panel labels in Figure 2 as well.*

This particular line includes a typo which we have now corrected. The revised text in now reads: "OOA is predicted to account for approximately 90 percent of $PM_1$ OA at ground level over the Paris greater area (domain-average) during summer and 50 percent during winter." The original calculation was actually for the whole European domain. To avoid any confusion we have now made changes throughout the manuscript and use only the term "OOA" instead of "SOA" when referring to the total oxygenated OA. As explained in Section 5.3, the modeled OOA is defined as the sum of SOA from anthropogenic VOCs (aSOA-v), SOA from biogenic VOCs (bSOA-v), SOA from IVOCs (SOA-iv) and SOA from SVOCs (SOA-sv).

**(8)** *Page 25558, Line 20: Similar to the previous comment, the previous two paragraphs discuss POA concentration predictions by PMCAMx, and starting with this line PMCAMx predictions of HOA are described. Is this really a different quantity in the model? As the authors already mentioned, the baseline emissions inventory used in this work does not include cooking, so that means HOA and POA are the same quantity in the model. For the purpose of clarity, it is critical that the same name is used for the same quantity predicted by the model. Again, phrases such as "the model predicts low concentrations of HOA" are problematic since HOA is a term that is specific to factor analysis, whereas terms such as "vehicular POA" would be more accurate for describing model output.*

We have revised this as mentioned in our reply to Comment 2 above and use the term "predicted vehicular POA" instead of "predicted HOA" throughout the manuscript as suggested.



**(9)** *Page 25559, Lines 25 – 29: The authors should provide the prediction skill metrics of PMCAMx for BBOA in table format; similar to what has already been provided in the supporting information for HOA.*

We have added a new table in the supplementary information (Table S3) with the corresponding BBOA skill metrics.

**(9)** *Section 5.3: I agree with the first referee that the discussion of OOA in this section seems incomplete. An important shortcoming in the model predictions has been identified, but then there is no rigorous follow-up such as sensitivity studies. The article is not particularly long, so there seems to be a missed opportunity to explore the origin of this discrepancy. Since it is stated in the manuscript that there are large uncertainties in BBOA emissions, could the authors run a sensitivity study where the emissions of BBOA and the associated SVOCs and IVOCs are increased or modified in some other fashion? Alternatively, could a different parameterization be used for the formation of OBBOA?*

To provide additional information about the characteristics of this underestimation we have now added a new figure in the supplement showing the time series analysis of observed and predicted concentrations of OOA in Paris during winter. This analysis shows that the OOA underprediction is persistent throughout the whole simulation period. However, there are certain days with extreme underestimation (24 and 27 January and 4 and 7 February) and a couple of other days during which the model performance is reasonable, at least during certain hours of the day (29 January and 3 February). A back-trajectory analysis (also added in the supplement) shows that during the days with the extreme underestimation, air masses originate from continental Europe, either within France or from the northeast (mostly Germany) while during the days with reasonable model performance the air masses were mostly clean coming from the Atlantic and western France. This further supports our hypothesis in the manuscript regarding the missing process forming SOA in the model.

We have performed a series of sensitivity tests but we could not reproduce these high OOA levels in the Paris area without increasing dramatically the OOA over the rest of Europe. It should be noted that the same model did not show any major underprediction of wintertime OOA over Europe in other sites (Fountoukis et al. 2014b). For example it did not show any bias in Cabauw, NL. A simple sensitivity test where the BBOA emissions (and the associated SVOCs and IVOCs) are modified would not add any value to the manuscript since the errors are not systematic and uniform throughout the domain and also seem to be related to a mechanism forming OOA during the periods of low photochemical activity. The sensitivity of the model's predictions to the uncertain IVOC emissions has been analyzed by Tsimpidi et al. (2010). Other possible sources of uncertainty that have been investigated in past applications of PMCAMx include uncertainties in the aging scheme, aqueous secondary OA formation and others. For example, in Murphy et al. (2011) we explored a two-bin reduction in volatility upon one oxidation step with a simultaneous decrease (by a factor of 2) in the aging rate constants. A slight underprediction of the OA mass was found in Finokalia during May 2008 compared to the base-case one-bin shift. Hodzic et al. (2010) and Grieshop et al. (2009) investigated a two-bin reduction (in addition to the one-bin base-case saturation concentration reduction) with a reduced OH reaction rate constant and found both to perform adequately. In Murphy et al. (2012) we added a detailed functionalization scheme to approximate the effect on volatility of adding relevant functional groups to the carbon backbone (Donahue et al., 2011). This approach alone resulted in a significant increase of the OA mass. Adding fragmentation to the detailed functionalization scenario decreased OA mass concentrations to the approximate magnitude predicted by the base case (which employs a simplified scheme that is currently used in PMCAMx) and brought the model into reasonable agreement with the OA mass concentration measurements. In our base case aging scheme we use this simplified scenario that tries to describe the net effect of the chemical aging reactions (both functionalization and fragmentation) without treating any of the two types explicitly. An additional SOA formation pathway that is not simulated here is the in-cloud SOA formation from glyoxal



and methylglyoxal. In Murphy et al. (2012) we explored the contribution of this pathway to OOA concentrations at several European sites during both a summer and a winter period. Small enhancements to both average OA mass loadings (< 3 percent) and O:C (< 10 percent) at the surface were found. Their contribution to total SOA formed was low (0–4 percent). We have added text in the revised manuscript summarizing the above issues.

**(10)** *Supporting information, S3: All the figures showing model-measurements comparisons are diurnal averages except for this figure. In order to facilitate comparison the comparison of BBOA should be shown as a diurnal average as well.*

We have made the recommended change.

**(11)** *Page 25561, Lines 19 – 21: Wouldn't the SOA-iv concentrations also be underestimated and not just the SOA-sv concentrations? Based on the model description, it seems that there would be primary IVOCs emitted with the BBOA that has SOA forming potential.*

True. We have now corrected this statement in the revised manuscript.

**(12)** *Page 25562 – 25563, Line 27 – 9: The discussion in this paragraph of the possible reasons for the BC model-measurements discrepancy should be expanded; otherwise the conclusions are too weak. Firstly, the variability of the BC and mixing height measurements during the two campaigns needs to be presented in some fashion in the manuscript. (In fact, it seems that mixing height data is not shown anywhere in the manuscript.) For example, time series for the model and measurement results could be given in the supporting information, or the diurnal plots could use a box-and-whiskers format. Presenting only a diurnal average of the BC concentration and then mentioning only in the text the mixing layer heights for three specific days out of the entire campaign period is not sufficient for evaluating why the model has difficulty reproducing the*

*BC concentration during the morning.*

We have now expanded this part. Figure 6 now includes the variability (25th and 75th percentiles) of both the modeled and observed values for BC. We have also added a figure in the supplementary information showing the diurnal average plots of mixing height for both seasons and expanded the discussion related to that.

**(13)** *In addition, it would be a simple sensitivity study to correct the predicted BC concentration for the underestimated mixing height using the LIDAR observations. I agree that there is a significant uncertainty in the observations, but such a comparison would still be interesting. If the corrected model prediction of BC still does not match the observation, despite a potential positive bias of the LIDAR, then that would strongly indicate that there are other reasons for the model-measurement discrepancy besides an inaccurate representation of the mixing layer height. (In other words a positive LIDAR bias would lead to an over correction of the model, which is currently overestimating the BC measurement.)*

We thank the reviewer for pointing this out. We have added this correction of the predicted BC based on the mixing height underestimation and expanded this part of the discussion.

**(14)** *Section 5.5: Given that the inclusion of cooking emissions substantially improves the model predictions, the authors should summarize the prediction skill metrics of PMCAMx for this sensitivity study in a table. In other words, create a third table that is analogous to Table 2, but for the results with cooking.*

We have added the corresponding information to the revised paper with an additional figure and table.

**(16)** *Page 25563, Lines 19 – 20: What was the temporal profile of the added cooking*



*emissions during the winter period? Was it the same as during the summer period? If not, why is the temporal profile different?*

The wintertime temporal profile of cooking emissions was slightly different than the summertime one because these are based on the observed diurnal pattern of COA concentrations during the two periods. We have now added this in the revised paper.

**(17)** *Page 25563, Lines 24 – 26: The manuscript should also include a comparison of the modeled and measured COA for the SIRTA site. As described in Section 4, a COA factor was identified at the SIRTA site for both summertime and wintertime. So, it is not clear why this comparison is shown currently in the manuscript for only LHVP. This omission is conspicuous.*

We focused our original analysis in the city center because its concentrations were relatively high. For completeness we have now added the comparison for SIRTA as suggested by the reviewer.

**(18)** *Figure 7: Similar to a previous comment, showing only the diurnal average of the COA measurement does not give the reader sufficient information to interpret the results. A box-and-whisker plot would be strongly preferable or the corresponding time series should be included in the supporting information.*

We have now added the variability (25th and 75th percentiles) of the reported averages with boxes. We would rather exclude the whiskers (min and max values) as the figures are already busy with modeled and observed values on the same plots.

**(19)** *Page 25564, Lines 11 – 13: This sentence is confusing and its grammar/syntax should be verified. If the cooking OA can undergo aging in the model, does that mean cooking SOA is formed? Is the cooking OA assumed to be semi-volatile? Are IVOCs emitted with the cooking OA similar to other POA sources? More information is needed*

*for a reader to evaluate this sensitivity test. While reading the previous paragraph, one is given the impression that the cooking OA is inert, but now that seems to not be the case.*

We have checked and corrected this sentence. The VBS approach implemented in PMCAMx considers both primary and secondary OA as semi-volatile and photochemically reactive. This includes COA as well. As explained in the beginning of Section 5.5, COA was added in the sensitivity test by assuming an increase of the primary OA emissions. Since IVOCs are assumed proportional to the emitted primary OA mass, the addition of COA came with an increase of the IVOCs emissions. We have now clarified this point in the revised version of the paper.

**(20)** *Pages 25565 – 25566, Lines 25 – 37: How much is the contribution of COA to the total OA during summertime? It seems like the importance of COA for the total OA would be much smaller than the 70 percent figure given for the fraction of POA contributed by cooking.*

This is correct. The contribution of COA to the total OA during summertime is 20 percent. We have revised this sentence to make it clearer to the reader that this refers to the primary OA, not the total OA.

*Technical Comments:*

**(21)** *Introduction: At several points in the text the term "Megacities" is capitalized, but it seems that lowercase should be used as this word is just an ordinary noun (e.g. Cities versus cities).*

Corrected.

**(22)** *Page 25551, Line 14: air massES*

Corrected.



**(23)** *Page 25553, Line 18: generation reactions*

Corrected.

**(24)** *Page 25556, Line 6: It appears that the acronym "GOLF" is not defined.*

The definition has been added.

**(25)** *Page 25560, Lines 5 – 6: The acronyms SOA-iv and SOA-sv have already been defined.*

Corrected.

**(26)** *Page 25560, Line 11: Should this be aSOA-v?*

This is mostly transported OA from the boundaries and is considered to be part of bSOA-v.

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