

## ***Interactive comment on “Formation of secondary organic aerosol in the Paris pollution plume and its impact on surrounding regions” by Q. J. Zhang et al.***

**Anonymous Referee #2**

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Review of Zhang et al. “Formation of secondary organic aerosol in the Paris pollution plume and its impact on surrounding regions”

The authors present a model/measurement comparison based on aircraft data collected during the MEGAPOLI 2009 field study and the CHIMERE model. The species considered are NO<sub>x</sub>, black carbon (BC), organic aerosol (OA) and O<sub>3</sub>. The primary focus of the paper is on comparison of the observed and simulated slopes of OA vs. Ox (= O<sub>3</sub> + NO<sub>2</sub>). The simulations of OA (= SOA + POA) use one specific variant of the volatility basis set (VBS) approach using one specific emissions inventory. Specifically, they utilize a version in which (i) POA is treated as semi-volatile, such that semi- and

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intermediate-volatility VOCs (S/IVOCs) exist and are oxidized according to the scheme presented in Robinson et al. (2007), (ii) traditional VOCs are oxidized according to an entirely different scheme, based on that in Tsimpidi et al. and Lane et al. and (iii) the semi-volatile products from oxidation of traditional VOCs are allowed to continuously age. Within their VBS approach, they consider two variations, one in which “low NO<sub>x</sub>” relevant parameters for VOCs are used and one in which “high NO<sub>x</sub>” relevant parameters are used. They first find that the simulations do a generally poor job of reproducing the observed spatial distribution of NO<sub>x</sub> or BC for the three flights considered. Although unstated, since POA emissions are strongly linked to BC emissions since their POA emissions are assumed to come almost entirely from diesel vehicles, it is likely that the spatial distribution of POA is similarly poorly represented (although this is speculation on my part). Despite this poor agreement for BC and NO<sub>x</sub>, the authors go on to compare the OA and O<sub>3</sub> production, and more specifically the OA/Ox relationship. They find that the simulated slopes for their HNO<sub>x</sub> simulations are more similar to the observations than for their LNO<sub>x</sub> simulations. They further find that the contribution to the simulated OA/Ox relationship is dominated by formation of SOA from traditional anthropogenic VOCs (AVOCs, e.g. toluene), with smaller contributions from the S/IVOCs and from biogenic VOCs.

My major concern with this work is a complete lack of consideration of any model variations beyond the low/high-NO<sub>x</sub> distinction for the VOCs, or a real consideration of the inherent model uncertainties. In considering only the Robinson et al. (2007) scheme for S/IVOCs, they miss that there is at least one other commonly used “VBS” formulation, namely that of Grieshop et al. (2009). The Grieshop et al. (2009) model has the same basic formulation (continuous oxidation of S/IVOCs), but uses very different parameters to describe this oxidation. This is not to say that the Grieshop et al. formulation is better, only that there remain large uncertainties associated with even the fundamental model parameterization for S/IVOCs that have yet to be completely sorted out (see the papers by Dzepina et al. (2009, 2011) and Hayes et al. (2014), for examples). Additionally, the authors use an “ageing” scheme for the traditional VOCs that

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has not been experimentally justified. Yes, semi-volatile vapors can “age,” but it has not been established the extent to which such “ageing” is already inherently captured in the original VBS model parameters since in any photochemical oxidation experiment in the lab “ageing” occurs from the moment the lights are turned on. Recent efforts suggest that such simplistic inclusion of “ageing” is inconsistent with laboratory observations (Zhao et al., 2015). Again, this is not to say that the model formulation is necessarily incorrect, only that there remain many details to be sorted out such that better agreement of one particular variant over another when applied to the atmosphere cannot be taken as evidence that that variant is actually better, only that it happened to be given the current model inputs. As an example, had the authors used the Grieshop et al. (2009) parameterization, it is likely that the simulated amount of SI-SOA would have increased above what it was here (given the results in Dzepina et al. (2011) and Hayes et al. (2014)). This would have made the SI-SOA contribution increase, making the conclusion that these are “minor” contributors less robust. Similarly, had “ageing” of the traditional AVOCs been turned off, then there would have been less ASOA, which would have made the SI-SOA contribution appear even larger. Further, there is no NO<sub>x</sub> dependence assumed for the formation of SI-SOA while there is for ASOA, meaning that the differences found between the LNO<sub>x</sub> and HNO<sub>x</sub> simulations are not independent of these other issues. Overall, I find that this lack of consideration of other model variants greatly limits the conclusions that can be reached here. I strongly think that the authors need to rethink the robustness of the simulation results and associated conclusions. I think that this work would be much better if it were presented as a series of case-studies, such as was done in Dzepina et al. (2009, 2011) or Hayes et al. (2014), or even the authors own prior work looking at the Paris ground site data associated with this study (Zhang et al., 2013). (This is not to say that any of the cited studies have comprehensively assessed all possible model permutations, but they do at least consider how the inherent model formulation affects the results, and have shown that the model formulation, including the choice of emissions inventory, can have a large impact.) In its current form, I find that the conclusions regarding SOA formation in the

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atmosphere are strongly limited by the above limitations of the presented analysis, and I have additional concerns about the overall model results given the generally poor model/measurement agreement for NO<sub>x</sub> and BC. I think that this study would benefit from a more robust assessment of the uncertainty contributed by the fundamental model uncertainty.

Additional Major Comments:

The authors focus on the OA/O<sub>x</sub> relationship, rather than on any comparison with results from PMF analysis of the AMS data. It make sense to do so, since the PMF factors have some inherent uncertainty and may differently represent “background” or “fresh” SOA. Nonetheless, I am surprised that the authors don’t separately consider the relationship between the different factors (specifically the LV-OOA and SV-OOA factors and their sum) and O<sub>x</sub> to see how it compares with the overall OA/O<sub>x</sub> slopes.

Given the poor agreement between modeled/measured BC spatial profiles, I believe that taking advantage of the PMF analysis of the OA to consider the spatial distribution of the HOA factor as it compares with the simulated spatial distribution of POA would be useful. Again, I realize that this comparison may not be perfect due to differences in definition and identity (i.e. HOA may not exactly equal POA), but it would certainly help to give an order-of-magnitude idea of how well the model represents the spatial distribution of POA. This, in turn, has implications as to how well the model is/is not representing the spatial distribution of the SI-SOA precursors (which are co-emitted with POA).

According to the list of airborne chemical instruments deployed (Table 1) and the description of measurements only NO<sub>x</sub> was measured, not NO<sub>2</sub>. Only by reading the Freney et al. paper do I see that, in fact, NO and NO<sub>2</sub> were separately measured. This should be clarified.

P8079/L11: It would be helpful if the authors were to provide a time-series comparing the various pollutants to illustrate the “wider” OA plumes as well as the double

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maximum in the O<sub>3</sub> plumes. Additionally, since the focus of this manuscript is on relationships with O<sub>x</sub>, the authors should show a spatial distribution of O<sub>x</sub> for reference (similar to Figs. 2-5).

Fig. 6: It's overall a bit unclear that the authors are really focusing on the OA/O<sub>x</sub> relationship as determined by the increase from the outside-of-plume to inside-of-plume transition. They are not focusing on the formation within the plume itself by, for example, considering the OA/O<sub>x</sub> slopes only along the plume centerline. I believe that this is an important distinction that needs to be made, especially if one looks at Fig. 5 in detail. It seems that for both the plumes on the 16th and 29th the in-plume production is much greater in the model than it is in the observations. Regarding the observed OA/O<sub>x</sub> slopes (P8080), the authors should note that despite the similar slopes that the intercepts are very different.

Black Carbon: it is evident in looking at Fig. 3 that the BC concentrations in the plume are not accurately simulated. Even the precision is questionable. Given this very, very poor agreement for a non-reactive species, I have difficulty thinking that the emissions inventory in use here is appropriate. This leads me to question all subsequent simulations of OA (SOA + POA) given that the anthropogenic VOC and POA emissions (and associated IVOC emissions) will be highly uncertain. In my view, the authors need to provide much more extensive discussion regarding the poor agreement for this conserved tracer and what this implies for the simulation of reactive species (such as S/IVOCs).

Emissions Inventory: I find the discussion of the emissions to be confusing. From the reference they give and from what they state it seems as if they are using the inventory for BC and POA from Junker and Lousse (2008) (P8081, L9), referred to I think as the LA inventory in Zhang et al. (2013). However, the authors also state that their VBS-LNO<sub>x</sub> simulation is the same as the so-called "VBS-MPOLI" simulation in Zhang (2013), which seems to mean that they are using the MEGAPOLI specific inventory, not the LA inventory. This needs to be clarified. They previously seem to have found

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pretty big differences between these two inventories, which will be critical for their assessment here. Inventory uncertainty is not discussed, yet should be. Further, the authors talk about some other emission inventory of "both gas-phase and particulate phase" pollutants (P8081/L20), the meaning of which is unclear in the context of the LA and MPOLI inventories. I find this overall lack of clarity to be a major limitation.

Model evaluation: The authors interpolate their model results to "the exact flight location and time." (P8082/L4). The model resolution is 3 km. At 1 second temporal resolution, it might make more sense to average the observations over the appropriate domains.

P8082/L15: I disagree with the authors that "visual inspection" of the BC plumes shows that the direction is correctly simulated on the 21st and 29th. The plume direction on the 21st is also not correctly captured. It is also unclear what the authors mean when they say that not capturing the plume direction is "acceptable due to the rather circular structure of the agglomeration." What specifically is "acceptable?" The contributions of background (e.g. biogenics) may be spatially different, for example. And it is unclear what the authors mean by "most important concentrations." Do they mean "largest?"

In the BC and NO<sub>x</sub> model/measurement comparison, the authors report biases for the (i) maximum, (ii) average and (ii) 30th percentile, taken as background. However, the most notable thing that I see is the dramatic fall off in the concentrations in the model as the plume moves away from Paris, compared to the much more gentle fall off in the observed concentrations. As presented, I find that this fact is glossed over to a large extent. As I have already noted, I believe that the authors need to provide much more discussion of the model/measurement comparison for these species and how the observed differences might influence the SOA simulations. The authors seem to imply that by looking at the OA/O<sub>x</sub> slopes that such absolute model/measurement differences effectively cancel out. But this was not demonstrated and thus it is unclear how robust their conclusions are.

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Looking at Figures 2 and 4, it seems that the model NO<sub>x</sub> falls off faster than the observations while the model O<sub>3</sub> production is larger downwind. These two aspects will cancel out, to some extent, leading to potentially better agreement with modeled and measurement O<sub>x</sub>. However, I can't help but think that this cancellation of errors is indicating that with regards to O<sub>x</sub> that the authors might be getting a right answer for a wrong reason.

P8083: The authors note that the BC and OA plumes are "correlated" on the 16th and 21st, but "translated to the west" on the 29th. When I compare the figures, I see a "translation" on the 21st as well. Clearly, this is a qualitative assessment, but the authors can make this much more precise by, for example, including a line showing the maximum BC concentrations (i.e. the plume direction) on top of the OA figure.

P8085: The authors conclude "This overestimation can now be unambiguously related to the OA scheme: it is likely that the high SOA yields under low-NO<sub>x</sub> conditions are incorrect under plume conditions." I disagree that it is "unambiguous". It is also sensitive to the emissions of VOCs in the first place. Further, there is the additional "OA scheme" issue that the authors include "ageing" of SOA from VOCs, which has not been experimentally justified separate from the parameterized fits that were used. This is related to my main concern elucidated above.

P8085/L26: The authors conclude that the OA/O<sub>x</sub> slope overestimation in the last two plume legs is "related to relatively higher anthropogenic SOA formation due to continuous chemical aging when the flights are farther away from Paris fresh emissions." This is likely a correct statement, given the model scheme used. However, it does not address the question of whether this model scheme is appropriate in the first place. As already stated, the ultimate conclusions of this paper are currently limited by the particulars of the model formulation.

P8086: The authors conclude that SI-SOA is a minor contribution to the total SOA production. As noted above, I have concerns regarding the robustness of this conclusion

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given the limited assessment of emissions and model formulation uncertainties.

The authors don't consider emissions of cooking related OA, which can potentially contribute S/IVOCs in addition to POA. Is this known to not be important in Paris?

Minor concerns:

P8075/L2: The IPCC reference is insufficient, as it does not capture the "human health" and "ecosystem" concerns, only the climate concerns.

P8075/L3: "Long time time" seems a bit out of place. . .these pollutants, especially PM, are often considered short-lived in the atmosphere, certainly relative to pollutants such as CH<sub>4</sub> and CO<sub>2</sub>, but even pollutants such as CO.

P8076/L6: the meaning of "post-industrial" is unclear. Do the authors mean "industrialized"

There are numerous grammatical errors, awkward statements and run-on sentences that I found made this paper very difficult to read. I strongly suggest that this manuscript could benefit from editing by a native English speaker. One particular example early on in the manuscript is the sentence on P8075/L23-26, but there are numerous examples throughout the entire manuscript.

References

Grieshop, A. P., Logue, J. M., Donahue, N. M., and Robinson, A. L.: Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 1: measurement and simulation of organic aerosol evolution, *Atmos. Chem. Phys.*, 9, 1263-1277, 2009,

Dzepina, K., Cappa, C. D., Volkamer, R. M., Madronich, S., DeCarlo, P. F., Zaveri, R. A., and Jimenez, J. L.: Modeling the Multiday Evolution and Aging of Secondary Organic Aerosol During MILAGRO 2006, *Environ. Sci. Technol.*, 45, 3496-3503, 2011, doi:10.1021/es103186f.

Dzepina, K., Volkamer, R. M., Madronich, S., Tulet, P., Ulbrich, I. M., Zhang, Q., Cappa,

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C. D., Ziemann, P. J., and Jimenez, J. L.: Evaluation of recently-proposed secondary organic aerosol models for a case study in Mexico City, *Atmos. Chem. Phys.*, 9, 5681-5709, 2009, doi:10.5194/acp-9-5681-2009.

Hayes, P. L., Carlton, A. G., Baker, K. R., Ahmadov, R., Washenfelder, R. A., Alvarez, S., Rappenglück, B., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Zotter, P., Prévôt, A. S. H., Szidat, S., Kleindienst, T. E., Offenberg, J. H., and Jimenez, J. L.: Modeling the formation and aging of secondary organic aerosols in Los Angeles during CalNex 2010, *Atmos. Chem. Phys. Discuss.*, 14, 32325-32391, 2014, doi:10.5194/acpd-14-32325-2014.

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic aerosols: Semivolatile emissions and photochemical aging, *Science*, 315, 1259-1262, 2007, doi:10.1126/science.1133061. Zhao, B., Wang, S., Donahue, N. M., Chuang, W., Hildebrandt Ruiz, L., Ng, N. L., Wang, Y., and Hao, J.: Evaluation of One-Dimensional and Two-Dimensional Volatility Basis Sets in Simulating the Aging of Secondary Organic Aerosol with Smog-Chamber Experiments, *Environmental Science & Technology*, 49, 2245-2254, 2015, doi:10.1021/es5048914.

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