Response to the reviewers for the paper "Formation of secondary organic aerosol in the Paris pollution plume and its impact on surrounding regions."
Zhang et al.

The authors thank the referees for their useful comments on our paper. We carefully took them into account, and we think they substantially improved the paper. In our point-by-point response we have copied the referees' comments in black text. Our responses are in regular blue font. The according modifications in the revised manuscript are indicated **in bold text**.

Anonymous Referee #1

This article uses the regional model CHIMERE to understand sources of organic aerosol downwind of Paris during the MEGAPOLI project. The aircraft data set provides a valuable opportunity to evaluate the model as it captures processing of the Paris plume. The paper should be published after addressing a few items. In contrast to other work (such as Hayes et al. 2014 ACPD for Los Angeles or Hodzic et al. 2010 for Mexico City) the authors find that traditional SOA precursors (biogenic and anthropogenic) contribute more to SOA than S/IVOCs. It would be useful if the authors could present more discussion on why the results are different in this study.

Would the conclusions be different if traditional SOA systems were not aged?

Yes, they would be substantially different. If the traditional SOA systems were not aged and only the aging of S/IVOC was taken into account, the simulated photochemical productivities would be underestimated in the plume and the background concentrations which are dominated by BSOA would be reduced to 1 µg m^{-3}, thus largely underestimated with respect to the observations. In order to address this question, a new simulation VBS-LA is added, in which only S/IVOC undergo chemical aging, and not traditional SVOC. The important impact of traditional SOA aging is also studied with ground based observations in Zhang et al. 2013, in which the concentrations of ASOA and BSOA are lower than 1 µg m^{-3} without the aging system, but BSOA formation under assumption of aging system correlates well with observations.

How confidant are the authors in the estimate of S/IVOC emissions?

Uncertainties in these emissions are discussed in Zhang et al. (2013), who compare POA emissions to HOA obtained from a three factor PMF analysis at an urban background site in Paris (obtained from Freutel et al., 2013). POA emissions from a specific emission cadaster built for the Paris agglomeration described in Timmermans et al. (2013) are judged a priori as the most appropriate ones. This is why they have been used in this work. However, Zhang et al. (2013) show that POA simulations in the VBS framework (configuration VBS-MPOLI in Zhang et al., 2013) clearly underestimate HOA observations by about a factor of three, as do POA/BC and HOA/BC ratios. On the contrary, POA and the POA/BC ratio from the so called LA (Laboratoire d'Aérologie) emissions (Junker and Liousse, 2008) show much better agreement with observations with nearly no bias, even if they are a priori more crude since they have been obtained by spatial downscaling. From the differences in both of these inventories, uncertainty in POA emissions is estimated at least as a factor of three. To take this uncertainty into account, we decided to include the VBS-T1 configuration in Zhang et al.

2013 (hereby called VBS-LA), which allows comparing simulations with two different emission inputs.

Following Robinson et al., 2007 and Shrivastava et al. 2008, we put IVOC emissions as 1.5 times of POA/SVOC emissions. This factor is obtained from a limited set of measurements, and its uncertainty is difficult to estimate.

One simulation VBS-LA (so-called VBS-T1 in Zhang et al. 2013) is added to discuss the emission uncertainties. It is described in the following sentence in section 3.2 on p8081:

"The VBS-LA simulation (same as VBS-T1 simulation in Zhang et al., 2013) in which a single step oxidation scheme (Pun et al. 2007) is used for traditional ASOA and BSOA formation, and the VBS scheme for SI-SOA formation as for the other two configurations. The EMEP-LA emission inventory with three times larger BC and POA/SI-VOC emissions is used for the inner MEG3 domain. The fact that POA/SI-VOC emissions are three times larger and the absence of chemical aging for ASOA will favor SI-SOA with respect to ASOA formation."

Is the O/C ratio faithfully reproduced?

The O/C ratio is not addressed within this paper. This ratio is not given in the AMS data set in Freney et al. 2014 obtained with a "low resolution" C-ToF-AMS instrument.

Other comments:

1. Reword last sentence of abstract for greater clarity.

It (on p2 L41) is modified to:

"For the average of the month of July 2009, maximum OA increases due to emissions from the Paris agglomeration are noticed close to the agglomeration at various length scales: several tens (for primary OA) to hundred (for SI-SOA and ASOA) kilometers of distance from the Paris agglomeration."

2. In abstract, more clearly state the predicted role of VOC vs. S-IVOC precursors. "anthropogenic precursors" encompasses both. Also highlight that biogenic SOA is predicted to be the largest contributor.

The abstract is modified according to modification related to the comments and a new simulation is introduced following other comments. The biogenic SOA is an important contributor for regional air quality and to Paris as already concluded in Zhang et al. 2013. In this work, the impact of anthropogenic pollution from Paris is focused.

It is modified in the abstract:

"Two mechanisms of secondary OA (SOA) formation are used, both including SOA formation from oxidation and chemical aging of primary semi-volatile and intermediate volatile VOCs (SI-SOA) in the volatility basis (VBS) framework. As for SOA formed from traditional VOC precursors (traditional SOA), one applied chemical aging in the

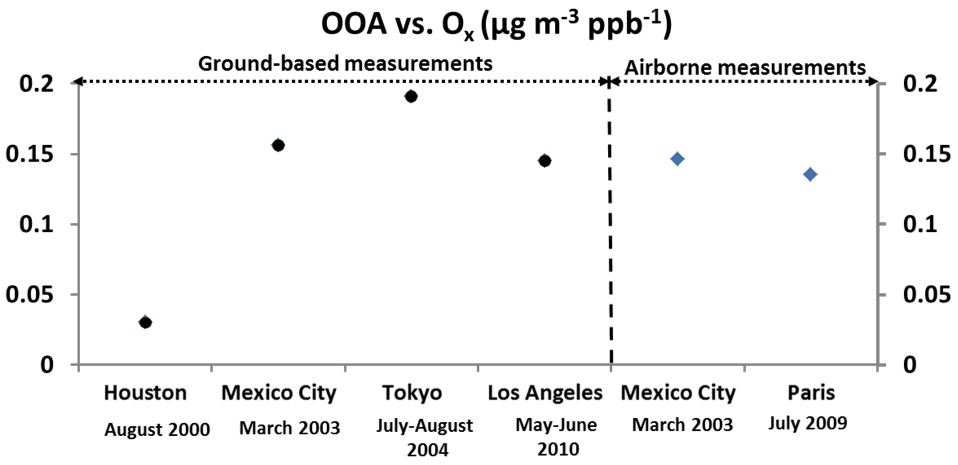
VBS framework adopting different SOA yields for high and low NOx environment while another applies a single step oxidation scheme without chemical aging."

and

"Also BSOA (SOA formed from biogenic VOC precursors) is an important contributor to regional OA levels (inside and outside the Paris plume)."

3. Figure 1: why are aircraft data shown as more of a "point" or range while the ground data is shown as a bar?

Figure 1 is modified to:



4. Table 4: Indicate that the correlations are with the OA,Ox pairs listed at the top. (It reads like the correlations are for OA/Ox and some other quantity). Relabel OPOA SI-SOA. Could POA be added for reference?

OPOA has been relabeled as SI-SOA and the text on p8099 has been modified to:

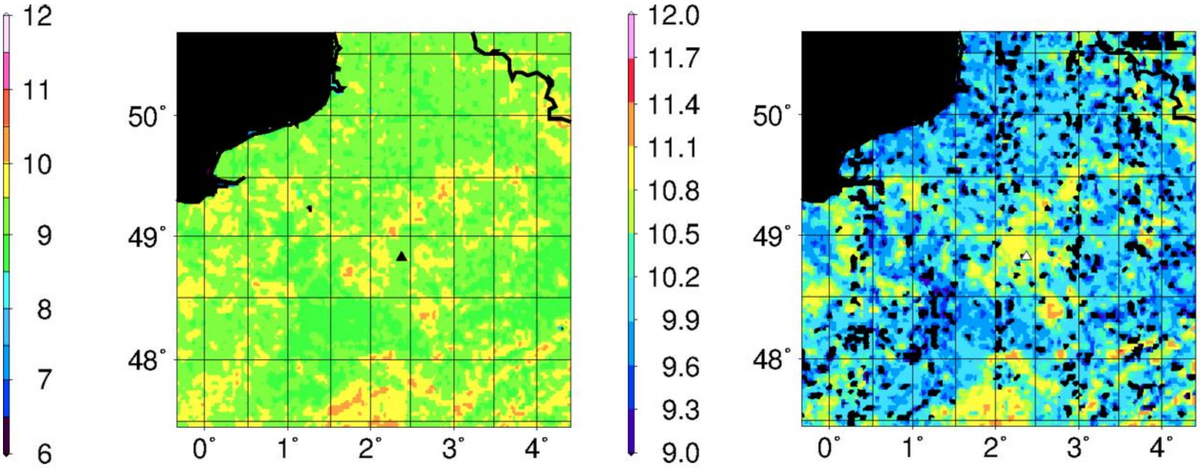
"Correlation coefficients between OA and O_x, SI-SOA and O_x, ASOA and O_x and BSOA and O_x for the flights on 16, 21 and 29 July, both from the measurements (AMS) and simulations with VBS-LNOX, VBS-HNOX and VBS-LA"

5. Figure 6: ASOA (and BSOA) seems to have two OA/Ox regimes. Is there a reason?

Indeed, the ASOA/Ox slopes are smaller for low Ox values and larger for larger Ox values.

Detailed analysis of this feature is beyond the scope of our paper. Only a tentative explanation is given here. Lower ASOA/Ox and Ox values appear at the edge of the plume, while larger values appear closer to its center. Differences in these slopes can in principle be due to the VOC split (Wood et al., 2010). In the center of the plume, reactive primary VOCs (hereby including SI-VOCs) emitted in the Paris agglomeration should be relatively more concentrated, while outside the plume more aged secondary VOC's should be relatively more predominant. The SOA formation potential is larger for the first ones, which indeed could explain the larger OA/Ox ratios inside the plume. In addition, high OA load in the plume increases the SOA production in the plume. Again, a thorough analysis of these problems is beyond the scope of this paper.

BSOA is predominated by regional production which leads to clear BSOA/Ox slopes for low Ox outside the plume. Inside the plume, BSOA production competes with others by oxidation with OH but with lower BVOC emissions from Paris. We show here for information a figure with hourly average emission of α-pinene (on the left) and isoprene (on the right) in log10, molecule cm^{-2} s^{-1}). They are indeed significant around the Paris agglomeration (its center being marked as a black or a white triangle)



6. Page 8075, line3, indicate “they” more clearly

The sentence on p8075 L3 is modified to

“Due to their long life time, PM2.5 and ozone have impacts at both the local and regional scale.”

7. Why was the 30th percentile chosen for background (vs. 5th or some other value)?

As the background values are variable, we intended to choose a median percentile as a representative value. The 30th percentile was chosen as a close to median given that roughly 20-40% of the largest values are belonging to the Paris plume (see for example figure 1 for NOx). Choosing for example a 20% or 40% percentile would only cause small differences in background values.

It is added on p8078 L19:

“The 30th percentile concentration of a pollutant on the flight legs downwind of Paris is close to the median concentration outside the Paris plume and represents its background level.”

8. What is the observed contribution of HOA to total OA? How does including HOA/POA influence the OA/Ox slopes compared to looking at only SOA or OOA/Ox?

The HOA derived from PMF analysis is in average about 20% to the total OA. However, the interpretation of PMF factors for our study is not straightforward, so we prefer compare observed and simulated OA vs. Ox slopes. This is made clear in the following revised sentence on p8079 L21:

“These LV-OOA and SV-OOA factors made up for by average about 65% of resolved OA factors and 37% of the total OA during these three MEGAPOLI flights. HOA (hydrocarbon like OA) make up for the remaining 35% of resolved OA factors and 20% of the total OA. While the HOA factor is generally attributed to POA, it might partly also correspond to oxidized POA, considered as SOA (Aumont et al., 2012, Cappa and Wilson, 2012), and to cooking-related OA (Freutel et al. 2013). Using total OA avoids these problems arising from the interpretation of PMF derived factors.”

9. Page 8081, give a few brief details on the S/IVOC implementation (such as how emissions were determined).

To explain the details, the following sentence is in section 3.1:

“As explained in more detail in Zhang et al. (2013), POA/SVOC emission factors for the main source in summer, traffic, are obtained from laboratory measurements under low level of dilution (with OA loading of 1000 μg m^{-3}). Under these conditions, the POA/SVOC emissions are emitted mostly in the particle phase. A volatility distribution following Robinson et al. (2007) was affected to these emissions. Additional IVOC emissions (factor 1.5 of POA/SVOC) were also considered following Robinson et al. (2007).”

10. Page 8083, the LNOX simulation underestimates background OA to a greater degree than HNOx despite having higher yields. Why does that occur?

Thank you for pointing out this inconsistency, which was due to an error. The sentence on p8083 L1 is corrected for the VBS-HNOX values:

“The modeled OA background concentrations are underestimated both on 16th and on 29th by VBS-LNOX, by respectively -1.6 (-41%) and -1.0 μg m^{-3} (-25%), and VBS-HNOX, by respectively -1.9 (-50%) and -1.4 μg m^{-3} (-33%).”

11. Page 8084, line 9, I don’t think you mean you will “investigate the relative contribution of OA to Ox.”

We intended to say that further analysis will be based on the OA versus Ox slopes. We modified the sentence on p8084 L9 to:

“In a later section (4.3), we will thus rely on OA versus O$_x$ slopes in the Paris plume for further analysis.”

12. Figure 6, In all cases, the model overestimates the observed OA/Ox slope. On the 21st and to a lesser degree on the 29th, that result seems to be driven by a large contribution of biogenic SOA. Is biogenic SOA enhanced in the plume?

Biogenic SOA is enhanced at a regional level, inside and outside the plume, but the ratio of BSOA/Ox is the largest on 21st (Fig. 5 and S6).

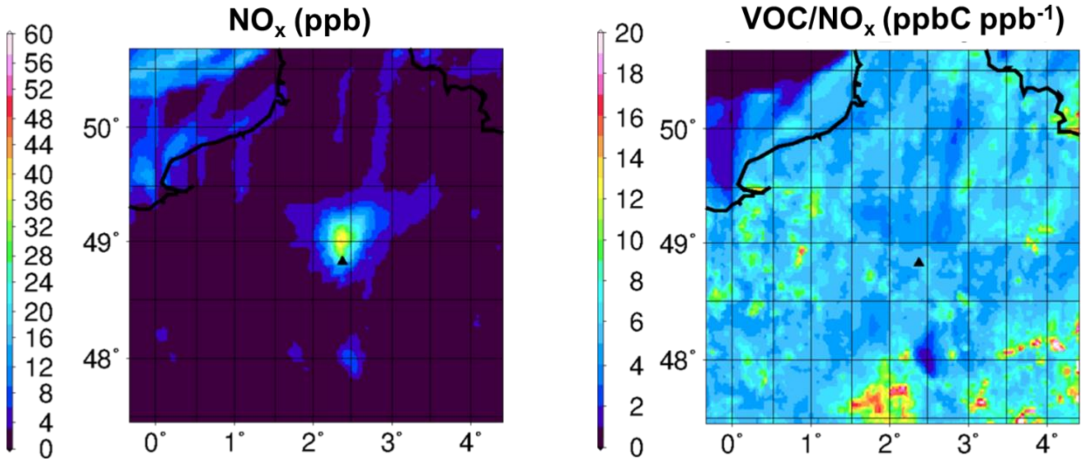
13. Can you calculate the RO2 radical fate to determine the relative importance of high vs low-NOx pathways in the observations?

In principle, this would be possible, but would require specific tagging during the simulations. In this work, this was not done.

14. Why wasn't the RO2 radical fate diagnosed in the model and the appropriate high or low NOx yield used? Even if the plume is dominated by RO2+NO, the background aerosol may not be.

Although the RO_2 + NO vs. RO_2 +HO_2 and RO_2 fate could in principle be used to determine when high or low NOx yield are appropriate, in this work a simpler criterion is chosen based on the VOC/NOx ratio, as also proposed in Lane et al. (2008b), high-NOx and low-NOx condition with the VOC/NOx ratio <3 ppbC/ppb and >10 ppbC/ppb, respectively. This leads to the choice of a high NOx regime in the MEG3 domain where we focus on the Paris agglomeration plume and a low NOx regime in the continental domain for background aerosol.

The figure below is added in the Supplementary Material to show the Paris plume from NOx concentrations and the corresponding VOC/NOx ratio at 10h on 16th. The black triangle represents the location of Paris. Within the Paris plume and especially close to Paris, it is close to or below the limit VOC/NOx ration of 3 ppbC/ppb, while values in the surrounding areas are generally above. As we are focusing on OA formation inside a plume, we choose to apply directly high NOx yield with the low VBS yields in the inner domain and a low NOx condition with high yield in the continental domain for background OA formation. Intermediate regimes between low-NOx and high-NOx are not used in this work.



To make this point clear, we added the following sentences on p 8081 L20 in section 3.2:

"Usually, a limiting VOC/NOx ratio of 3 and 10 ppbC ppb-1 is used to discern a high and a low NOx regime, respectively (Lane et al., 2008b). While the ratio of 10 ppbC ppb-1 is close or above the value for most of Northern France, indicating that it is close to a low-NOx regime, it is close to or below the ratio of 3 ppbC ppb-1 on the north of Paris in the plume region (Fig. S1). This low-NOx configuration is thus expected to overestimate ASOA formation in the Paris pollution plume under high NOx conditions around Paris. The emission inventory for the MEG3 domain is the specific MEGAPOLI inventory. "

15. Page 8085, lines 21-25 sentence could be clearer.

This sentence is modified to:

"The modeled slopes of OA vs. O_x, 0.12, 0.23 and 0.17 µg m^{-3} ppb^{-1} (for the 3 flights) are close to the measured ones (0.12, 0.18 and 0.16 µg m^{-3} ppb^{-1}) during the first two flight legs. On the contrary, these slopes, 0.17, 0.25 and 0.21 µg m^{-3} ppb^{-1} are overestimated by a factor of 1.3, 1.9, and 1.3 with respect to the measured ones during the last two flight legs."

16. Figure 7,8: captions indicate LNOx results are also shown, but are not included.

The figure captions are corrected to make clear that LNOX is not shown.

17. Are the intercepts of the OA/Ox regressions fixed?

No, these intercepts should not be fixed, because this would alter the slopes with respect to the measured or simulated points. The origin would correspond to continental background values, which are non-zero for both species.

18. Did the authors look at OA/CO ratios for additional insight?

No, we did not. The idea was to use the OA vs. Ox plot, to "normalize out" both the effect of precursor and oxidant (mainly OH) levels. OA/CO ratios only normalize with respect to precursor concentrations.

References:

1. Hayes et al. 2014 ACPD: http://www.atmos-chem-physdiscuss.net/14/32325/2014/acpd-14-32325-2014.html

2. Hodzic et al. 2010 ACP: http://www.atmos-chem-phys.net/10/5491/2010/acp-10- 5491-2010.html

Anonymous Referee #2

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 NOx, black carbon (BC), organic aerosol (OA) and O3. The primary focus of the paper is on comparison of the observed and simulated slopes of OA vs. Ox (= O3 + NO2). The simulations of OA (= SOA + POA) use one specific variant of the volatility basis set (VBS) approach using one specific emissions inventory. Specifically, the utilize a version in which (i) POA is treated as semi-volatile, such that semi- and 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, the consider two variations, one in which "low NOx" relevant parameters for VOCs are used and one in which "high NOx" relevant parameters are used. They first find that the simulations do a generally poor job of reproducing the observed spatial distribution of NOx 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 NOx, the authors go on to compare the OA and O3 production, and more specifically the OA/Ox relationship. They find that the simulated slopes for their HNOX simulations are more similar to the observations than for their LNOX 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-NOx distinction for the VOCs, or a real consideration of the inherent model uncertainties. In considering only the Robinson et al. (2007) scheme for I/SVOCs, 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).

We agree that uncertainties related to different formulations of SOA formation within the VBS scheme is an important topic in the community. There are different schemes based on the VBS theory for organic aerosol simulations in 3D CTM, including Grieshop et al. (2009), Donahue et al. 2006/Robinson et al. 2007, Lane et al. 2008a, Pye et al. 2010, Shrivastava et al. 2011 and 2013, Couvidat et al. 2013 and others which are under development. In this work, we are in a 3D modelling perspective with a well resolved grid over a large domain (3km, Northern France). Thus it is more difficult to test a large series of different VBS formulations than it would be for a box model study. To take into account the referees remark, we added results from another VBS configuration, in which traditional VOC aging is not considered, and in which uncertainty in POA emissions is taken into account (three times larger POA emissions). Thus this latter configuration (named VBS-LA using the EMEP-LA inventory, because of the focus on uncertainties of the emission inventory, named VBS-T1 in Zhang et al., 2013) favors SI-SOA formation. On the contrary, the initial VBS-LNOX and VBS-HNOX configurations might favor traditional ASOA and BSOA formation, as the referee points out based on the Zhao et al. (2015) paper. In addition, also the more aggressive Grishop et al. (2009) scheme is included in the discussion. The interest is to see to which extent both very different configurations reproduce observations, and to address uncertainty in the SOA product contribution. In this way we hope being able to respond to the referees concern about better including uncertainty in SOA simulations.

The following text is added to introduce this strategy in the section 1 on p8077 L2:

“Among the various formulations that have been derived in the frame of the VBS scheme (for example, Lane et al., 2008, Murphy and Pandis., 2009, Dzepina et al., 2011, Shrivastava et al., 2013, Zhao et al., 2015), specifically two are chosen for this paper (as already for Zhang et al., 2013), because they either favor large ASOA or large SI-SOA build-up in the plume. In this way, we intend to address uncertainty spanned by

the co-existence of different VBS schemes in the formulation of different SOA types within the plume.”

It is added in section 5.1:

“The larger SI-SOA vs. Ox slopes in the VBS-LA simulation are easily explained by the larger POA emissions in this configuration. The range of SI-SOA vs. Ox slopes between the VBS-HNOX and the VBS-LA configuration thus represents uncertainty due to POA emissions (Table 5). Even larger SI-SOA vs. Ox slopes during these flights would be expected also if the more aggressive SI-SOA formation scheme by Grieshop et al. (2009) had been used. With the Grieshop et al. (2009) formulation, SVOC species have a reaction rate constant two times lower than in this study with Robinson et al. (2007), but are shifted to two orders of magnitude lower volatility (instead of one), with a mass increase by 40% for each oxidation step (instead of 7.5%). Box simulations by Dzepina et al. (2011) for Mexico City and by Hayes et al. (2015) for Los Angeles yield about two times larger SI-SOA yields with the Grishop et al. (2009) than with the Robinson et al. (2007) scheme. These results suggest an additional possibility to increase SI-SOA contributions to plume SOA.”

Additionally, the authors use an “ageing” scheme for the traditional VOCs that 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).

The aging scheme for the traditional VOCs from Lane et al. 2008a is used in this paper. Our study is similar to what is called “empirical chamber fits plus aging within VBS” in Zhao et al. (2015). Zhao et al. (2015) suggests indeed lower yields for first-generation products which better fit to laboratory experiments.

It is added in section 5.1 on p8087 L8:

“Recently, the comparison of different VBS based SOA schemes to chamber measurements in Zhao et al. (2015) suggests lower SOA formation from traditional VOC precursors (ASOA), by explicitly simulating the first generation products, than when using the parametrization from Lane et al. (2008a) as in our study. In addition, Lane et al. (2008a) do not account for BSOA chemical aging, while we do based on the results of Zhang et al. (2013). Thus, the relative contributions of ASOA and BSOA to plume SOA build-up in the VBS-LNOX and VBS-HNOX configurations used in this paper are considered as an upper limit, while the primary SI-VOC emissions for SI-SOA formation are considered as a lower limit. Others studies taking into account fragmentation reactions (Jimenez et al. 2009; Shrivastava et al. 2011; Murphy et al. 2012) reduces OA formation.”

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.

As mentioned above, the SOA modelling uncertainty is now better taken into account in the revised paper by introduction the VBS-LA simulation.

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.

Yes, indeed, aging of traditional AVOC’s is switched off in the newly added VBS-LA configuration. The relative SI-SOA contribution is much larger then.

It is added in section 3.2 on p8081:

“The VBS-LA simulation (same as VBS-T1 simulation in Zhang et al., 2013) in which a single step oxidation scheme (Pun et al. 2007) is used for traditional ASOA and BSOA formation, and the VBS scheme for SI-SOA formation as for the other two configurations. The EMEP-LA emission inventory with three times larger POA/SI-VOC emissions is used for the inner MEG3 domain. The fact that POA/SI-VOC emissions are three times larger and the absence of chemical aging for ASOA will favor SI-SOA with respect to ASOA formation.”

Further, there is no NOx dependence assumed for the formation of SI-SOA while there is for ASOA, meaning that the differences found between the LNOX and HNOX simulations are not independent of these other issues.

We used the existing VBS scheme (Robinson et al. 2007) to simulate the formation of SI-SOA, in which shifts in volatility and increase in mass per oxidation step are independent pof NOx. To our knowledge, there is yet no NOx dependent VBS scheme for the formation of SI-SOA available for use in CTM simulations.

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.

As stated above, in the revised version, different model variants are taken into account and uncertainties are discussed.

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.)

Again, to address this concern, a new simulation VBS-LA (VBS-T1 in Zhang et al. 2013) is added in the revised version.

In its current form, I find that the conclusions regarding SOA formation in the 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 NOx and BC. I think that this study would bene- fit from a more robust assessment of the uncertainty contributed by the fundamental model uncertainty.

Again, the uncertainty in our results and especially in the simulated ASOA vs. SI-SOA is now emphasized.

Additional Major Comments:

The authors focus on the OA/Ox 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 Ox to see how it compares with the overall OA/Ox slopes.

Our choice to directly use the OA/Ox relationship and not PMF output is motivated by the fact that the attribution to "unknown" in the PMF analysis was relatively high, up to 25-50% of the total OA concentrations. In addition, uncertainties related to the PMF study with low resolution C-ToF-AMS measurement are high. HOA is ~20% of the total OA concentrations. Note, that there is probably a fraction of cooking related HOA included in this amount. Thus, the OA/Ox is studied instead of the sum of LV-OOA and SV-OOA.

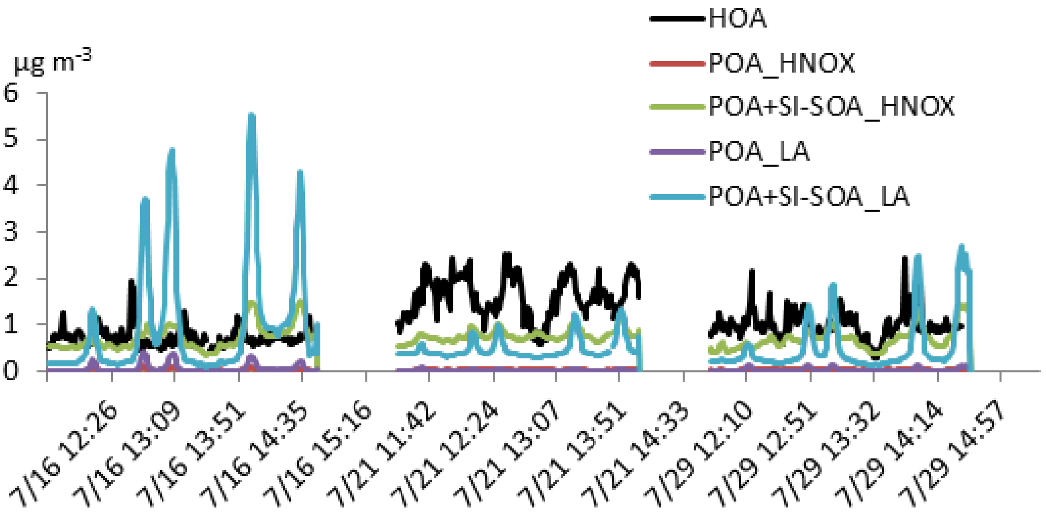
We modify the sentence on p8079 L21 to:

"These LV-OOA and SV-OOA factors made up for by average about 65% of resolved OA factors and 37% of the total OA during these three MEGAPOLI flights. HOA (hydrocarbon like OA) make up for the remaining 35% of resolved OA factors and 20% of the total OA. While the HOA factor is generally attributed to POA, it might partly also correspond to oxidized POA, considered as SOA (Aumont et al., 2012, Cappa and Wilson, 2012), and to cooking-related OA (Freutel et al. 2013). Using total OA avoids these problems arising from the interpretation of PMF derived factors."

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).

BC evaluation is studied in detail in Petetin et al. (2015). They have suggested that the bias in the model could not be attributed to errors in emission inventories only, because of uncertainty in measurement and in the choice of the mass specific absorption coefficient.

A figure comparing HOA against POA and the sum of POA and SI-SOA for both MPOLI (VBS-HNOX simulation) and LA emissions is presented below in order to illustrate the uncertainties related to HOA comparison with simulations and emissions. HOA (in black) is derived from the AMS measurements. POA_HNOX (in red) and the sum of POA and SI-SOA (POA+SI-SOA_HNOX in green) are from VBS_HNOX simulation. POA_LA (in purple) and the sum of POA and SI-SOA (POA+SI-SOA_LA in blue) are from VBS_LA simulation. The HOA plume (difference between the maximum in a flight transect crossing the plume and the 30th percentile) concentration is 1.34, 1.18 and 1.60 µg m^{-3}, on 16th, 21st and 29th, respectively. It is respectively 0.4, 0.06 and 0.12 µg m^{-3} for POA and 5.35, 0.98 and 2.3 µg m^{-3} for the sum of POA and SI-SOA from the VBS-LA simulation. Indeed, as said above, it is not clear whether HOA should be compared to POA alone or the sum of POA and SI-SOA It is respectively 0.09, 0.02 and 0.04 µg m^{-3} for POA and 0.96, 0.46 and 0.79 µg m^{-3} for the sum of POA and SI-SOA from the VBS-HNOX simulation. The plume concentration of the sum of POA and SI-SOA from VBS-HNOX simulation is closest to the HOA measurement with -28% of underestimation on 16th while those from VBS-LA are closest on 21st with -17% of underestimation and on 29th with 44% of overestimation. As a conclusion, due to uncertainties in the emission inventories and due to differences between the VBS-LA and VBS-HNOX, both overestimations and underestimations with respect to observations have been obtained, a no significant bias is made evident. In addition, another difficulty in simulation is due to weak winds in the morning of the flight days. For 21st and 29th, winds are overestimated in the simulations , which leads to underestimations of the primary pollutants concentrations (Petetin et al. 2015). A simulated wind direction bias is found in this latter work, but it doesn't affect much on the conclusion of the OA/Ox ratio and the OA impact from Paris emissions.



It is added on p8282 L26:

"Our study focusses on three days with particularly low wind speeds with variable wind direction during morning hours in the Paris agglomeration, allowing for primary pollution build-up and subsequent secondary pollution build-up in the plume. As shown in figure 2 of Petetin et al. (2015), it turns out that the meteorological model (MM5, but similar results are obtained for WRF) forcing the CTM simulations is not capable to simulate these wind direction variations for two of the three flight days, on 21st and 29th of July, thus underestimating the pollution accumulation in the Paris region, and subsequently in the plume."

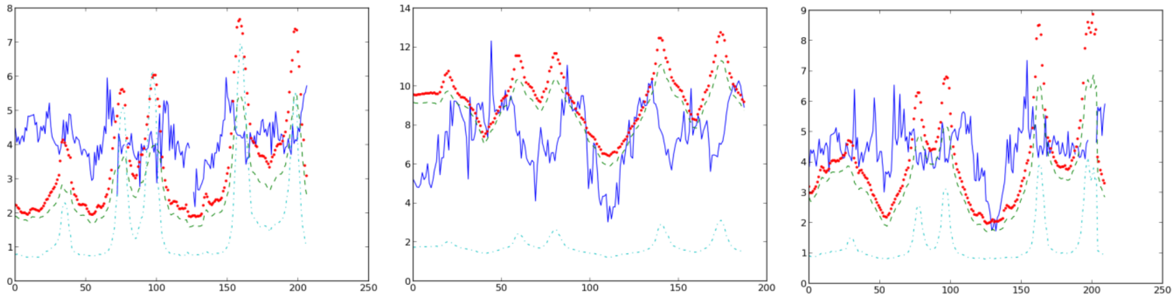
According to the list of airborne chemical instruments deployed (Table 1) and the description of measurements only NOx was measured, not NO2. Only by reading the Freney et al. paper do I see that, in fact, NO and NO2 were separately measured. This should be clarified.

We add in the caption on p8096:

“NO, NO_2 and NOy are measured (Freney et al. 2014, Supplementary Material).”

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 maximum in the O3 plumes. Additionally, since the focus of this manuscript is on relationships with Ox, the authors should show a spatial distribution of Ox for reference (similar to Figs. 2-5).

The times series for OA comparison (in µg m^{-3}) on the three flights are presented as below (blue line: measurements; red and green dotted line: VBS-LNOX and VBS-HNOX simulations; light blue dotted line from VBS-LA simulation).



The spatial distribution of Ox plume figure (Fig. S2) is added in Supplementary Material.

Fig. 6: It’s overall a bit unclear that the authors are really focusing on the OA/Ox 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/Ox 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/Ox slopes (P8080), the authors should note that despite the similar slopes that the intercepts are very different.

Maybe the reviewer wants to point out that plume formation is not necessarily well represented by the slopes, as the slopes cover the whole transect. We have chosen to use all points over the while transect, because this would use the largest number of observations and yield the most robust results, while using only the centerline would drastically restrict the number of points. However, when using all points different slope regimes (also mentioned by another reviewer) can occur. Indeed, this can cause some uncertainty in the slopes. Some sentences are added in section 5.1 to address this point.

It was presented in section 5.1 in discussion with the VBS-LA simulation:

“If the slope was only taken for points with larger SI-SOA and Ox values, which are closer to the plume, a larger slope would have been determined. To a lesser extent this feature also appears for VBS-LNOX simulations. “

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).

Uncertainties in these emissions are discussed in Zhang et al. (2013), who compare POA emissions to HOA obtained from a three factor PMF analysis at an urban background site in Paris (Freutel et al., 2013). POA emissions from a specific emission cadaster for the Paris agglomeration described in Timmermans et al. (2013) are judged a priori as the most appropriate ones. This is why they have been used in this work. However, Zhang et al.(2013) show that POA simulations in the VBS framework (VBS-MPOLI in Zhang et al., 2013) clearly underestimate HOA observations by about a factor of three, as do POA/BC and HOA/BC ratios. On the contrary, POA from the so-called LA emissions (Junker and Liousse, 2008) show much better agreement with nearly no bias (similar for the POA/BC ratio) for its VBS application, even if they are a priori more crude as obtained by spatial downscaling. Thus uncertainty in POA emissions is estimated at least as a factor of three. To take this uncertainty into account, we decided to include the VBS-LA configuration with the larger LA emission in the revised version of this paper as replied above.

The consequence of underestimation of primary pollutant is discussed on p8083 L15:

“Direct comparisons for POA are not shown here because of the uncertainty in HOA factors from the PMF analysis, and because of the incomplete match between HOA and POA. However, the BC underestimation in simulations lets us also expect a POA underestimation.

Consequences of these underestimations in primary pollutants for the build-up of secondary pollutants are briefly discussed here:

- **First, as shown above for BC, the underestimation is alleviated in the alternative VBS-LA simulation with larger BC (and POA) emissions. Thus unexpressed uncertainty in meteorological data is partly taken into account by that in emissions.**
- **Second, the use of OA vs Ox slopes for evaluation of the SOA production efficiency normalizes out the effect of errors in primary pollutants, as equation (1), it merely depends on the ratio of the product yields. This is why the use of this ratio is important for this study.**
- **Third, in a VOC limited regime as characteristic for the Paris region (e.g. Deguillaume, et al, 2008), the rate of secondary pollutant build-up is far from proportional to the primary precursor concentration. On the contrary, in the extreme case that NOx compounds represent the only OH loss, NOx and OH concentrations are inversely proportional (e. g. Kleinman et al., 1997). When assuming a constant ratio in primary pollutants, the flux in equation (1) is then independent of VOC concentrations, and only depends on the production rate of odd hydrogen radicals (OH+HO2+RO2).”**

Equation (1) is added on p8075 L23:

“(1) $VOC + OH \rightarrow \cdots \rightarrow \cdots \rightarrow \alpha\, O_x + \beta\, SOA + \cdots$”

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 Louisse (2008) (P8081, L9), referred to I think as the LA inventory in Zhang et al. (2013). However, the authors also state that their VBS-LNOX 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 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.

The LA inventory is applied on the larger continental domain for all simulations. The MEGAPOLI inventory is applied on the smaller MEG3 domain covering Northern France for the VBS-HONX and –LNOX simulations. The uncertainties of the emissions inventory are discussed in detail in Zhang et al. 2013 and Timmermans et al. (2013). And the LA inventory is used on the MEG3 domain in the VBS-LA simulation for discussion about uncertainties of POA/SI-VOC emissions and SOA formation scheme without chemical aging.

It is modified on p8081 L5:

“For the large domain, anthropogenic gas phase emissions are calculated from EMEP annual totals (http://www.ceip.at/emission-data-webdab/), while black carbon (BC) and primary organic aerosol (POA) are prescribed from an emissions inventory prepared by Laboratoire d’Aérologie (LA) (Junker and Louisse, 2008). In the different simulation set-up’s in section 3.2, emissions for the inner domain MEG3 over Northern France are either taken from the same EMEP-LA inventory, or from an alternative inventory specifically designed for the MEGAPOLI project, the Airparif-TNO-MEGAPOLI inventory, in which the refined Paris emissions from Airparif with a resolution of 1 km are integrated into the European wide TNO inventory (Timmermans et al., 2013).”

The differences between the EMEP-LA and the MEGAPOLI emissions inventories are also added:

“In this latter inventory, BC and POA emissions for the Paris agglomeration are about two and three times lower than in the EMEP-LA inventory, respectively, and VOC emissions are about a third lower, while NOx emissions are similar. These differences are explained by use of spatial downscaling techniques in the EMEP-LA inventory using proxies that generally tend to overestimate megacity or urban emissions, while the Airparif-TNO-MEGAPOLI inventory is constructed following a bottom-up approach (Timmermans et al., 2013).”

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.

The temporal resolution of C-Tof-AMS used on the plane is 30s in Table 1. For a typical cruising speed during measurements of 360 km/h of the ATR-42 aircraft, this corresponds to a horizontal resolution of 3 km, thus compatible with that in simulations.

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?”

This is modified on p8082 p15:

“The qualitative inspection of simulated and observed BC plumes shows that the plume direction is correctly simulated on the 21st and 29th, while a difference of about 20° occurs on 16th (Fig. 2). This will little affect the study on OA impact from Paris to its surroundings due to the rather circular structure of the agglomeration (Shaiganfar et al., 2015). Both in the modeled fields and in observations, the largest concentrations appear close to the Paris agglomeration during these three flights.”

In the BC and NOx 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/Ox 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.

In Petetin et al. (2015), difficulty in simulation due to weak wind in the morning was pointed out. The simulation overestimates the wind and thus leads to underestimations of the primary pollutants concentrations. Simulated wind direction bias is found in this work, but it doesn’t affect much on the conclusion of the OA/Ox ratio and the OA impact from Paris emissions. The use of OA vs Ox slopes for evaluation of the SOA production efficiency normalizes out the effect of errors in primary pollutants. The consequence of underestimation of primary pollutant is discussed on p8083 L15:

“Direct comparisons for POA are not shown here because of the uncertainty in HOA factors from the PMF analysis, and because of the incomplete match between HOA and POA. However, the BC underestimation in simulations lets us also expect a POA underestimation.

Consequences of these underestimations in primary pollutants for the build-up of secondary pollutants are briefly discussed here:

- **First, as shown above for BC, the underestimation is alleviated in the alternative VBS-LA simulation with larger BC (and POA) emissions. Thus unexpressed uncertainty in meteorological data is partly taken into account by that in emissions.**
- **Second, the use of OA vs Ox slopes for evaluation of the SOA production efficiency normalizes out the effect of errors in primary pollutants, as equation (1), it merely depends on the ratio of the product yields. This is why the use of this ratio is important for this study.**
- **Third, in a VOC limited regime as characteristic for the Paris region (e.g. Deguillaume, et al, 2008), the rate of secondary pollutant build-up is far from proportional to the primary precursor concentration. On the contrary, in the extreme case that NOx compounds represent the only OH loss, NOx and OH concentrations are inversely proportional (e. g. Kleinman et al., 1997). When assuming a constant ratio in primary pollutants, the flux in equation (1) is then independent of VOC concentrations, and only depends on the production rate of odd hydrogen radicals (OH+HO2+RO2).”**

Equation (1) is added on p8075 L23:

“(1) $VOC + OH \rightarrow \cdots \rightarrow \cdots \rightarrow \alpha\, O_x + \beta\, SOA + \cdots$”

Looking at Figures 2 and 4, it seems that the model NOx falls off faster than the observations while the model O3 production is larger downwind. These two aspects will cancel out, to some extent, leading to potentially better agreement with modeled and measurement Ox. However, I can’t help but think that this cancellation of errors is indicating that with regards to Ox that the authors might be getting a right answer for a wrong reason.

Again, this fast fall off for primary pollutants is linked to the overestimation of wind speed. As the photochemical productivity rate is the focus of this work, the use of OA vs. Ox is expected to normalize out the effect of this error. Thus, following the given equation (1), the rate is adequate in any condition of primary pollution.

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.

It is modified on p8083 L15:

“The measured OA plume is correlated with the measured BC plume on 16th, while it appears translated to the west on 21st and 29th, as is also the ozone plume (Fig. 3, 4 and 5).”

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-NOx 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.

It is modified on p8085 L15:

“This overestimation can be related to the SOA formation scheme:…”

As replied above, the aging scheme for the traditional VOCs (Lane et al., 2008a) is used for the VBS-HNOX and –LNOX simulation. The VBS-LA simulations using a single step oxidation scheme (Pun et al., 2007) for traditional SOA formation with EMEP-La inventory are added for discussion on uncertainties related to the simulations. The important impact of traditional SOA aging is also studied with ground based observations in Zhang et al. 2013, in which the concentrations of ASOA and BSOA are lower than 1 µg m^{-3} without the aging system, but BSOA formation under assumption of aging system correlates well with observations.

P8085/L26: The authors conclude that the OA/Ox 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.

For analyses on the last two flight legs, the results from the VBS-HNOX simulation using the MEGAPOLI inventory and the VBS scheme for traditional SOA formation (Lane et al. 2008a) are focused.

Again, the VBS-LA simulation is added in order to take into account uncertainties related to the emissions and SOA formation schemes. Three times higher POA emissions from LA inventory is used and lower traditional SOA formation scheme from a single step oxidation method is used. The conclusion on OA formations in section 5.3 is modified:

“In conclusion, both the VBS-HNOX and VBS-LA simulations show different monthly average OA product distributions. As discussed above, the ASOA and BSOA contributions in VBS-HNOX present an upper limit for ASOA and BSOA produced in the plume (and in background airmasses). On the contrary the small plume and background values in VBS-LA simulated without any chemical aging are probably underestimated, in particular because they underestimate the SOA observations within the Paris agglomeration (Zhang et al., 2013). On the contrary, For SI-SOA, differences between both simulations are weak. However, alternative VBS schemes (Grishop et al., 2009) would simulate higher SI-SOA formation, as noted above (about a factor two from box model studies in other urban plumes).”

and the conclusion in section 6 are thus modified:

“However, an alternative scheme with three times larger POA emissions, and without ASOA and BSOA aging, also shows good agreement with observed OA vs O_x slopes, though it strongly underestimates background and urban Paris OA. This leads us to

the conclusion that due to uncertainties both in POA emissions and in the SOA formation formulations, uncertainly in the SOA product distribution remains large. The constraint of observed OA vs. O_x slopes on the SOA product distribution in the Paris plume is unfortunately weak, and does not reduce this uncertainty (while it does for anthropogenic OA yields). Both ASOA and SI-SOA could be the major anthropogenic SOA products for two flights. In the simulations anthropogenic SOA is the major contributor to plume SOA on two flight days, while BSOA is major or equivalent on the third day."

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 given the limited assessment of emissions and model formulation uncertainties.

Again, after adding the VBS-LA simulation, the impact of emission and SOA formation scheme uncertainties are discussed and added as above.

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?

Yes, it contributes to POA in Paris (Freutel et al. 2013), however, no cooking related POA emission inventory has been developed up to now to our best knowledge. .

It is modified in section 3.1:

"Cooking emissions, which have been shown significant for the Paris agglomeration (Freutel et al., 2013, Crippa et al., 2013) are not included in either of these emission inventories."

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

A reference (Seinfeld and Pandis, 2006) is added.

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 CH4 and CO2, but even pollutants such as CO.

It is modified:

"Due to their life time (several days to weeks),"

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

It is a tertiary oriented economy, not 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.

The manuscript has been carefully checked by a native English author.

Anonymous Referee #3

This study presents quite useful results from an excellent dataset. Overall the quality of the data and analysis is sufficient for eventual for publication in ACP, but several issues must be addressed.

Major comments:

1. There should be more discussion of the impact of using OA/Ox instead of OOA/Ox as done for the other studies quoted. By how much does OA/Ox exceed OOA/Ox? I am guessing about 50% based on the reported ~30% contribution of HOA to OA, but the comparison of the measured OA/Ox ratios to the modeled ratios and to other studies' measured ratios would be much clearer if OOA were also used. The rationale for not using LV-OOA and SV-OOA as stated is that HOA contains some oxidized POA, and as a result "Thus use of OA in this study avoids these attribution problems." – but it leads to the questions just listed above. How much is the comparison to modeled SOA/Ox affected when OOA vs. OA is used?

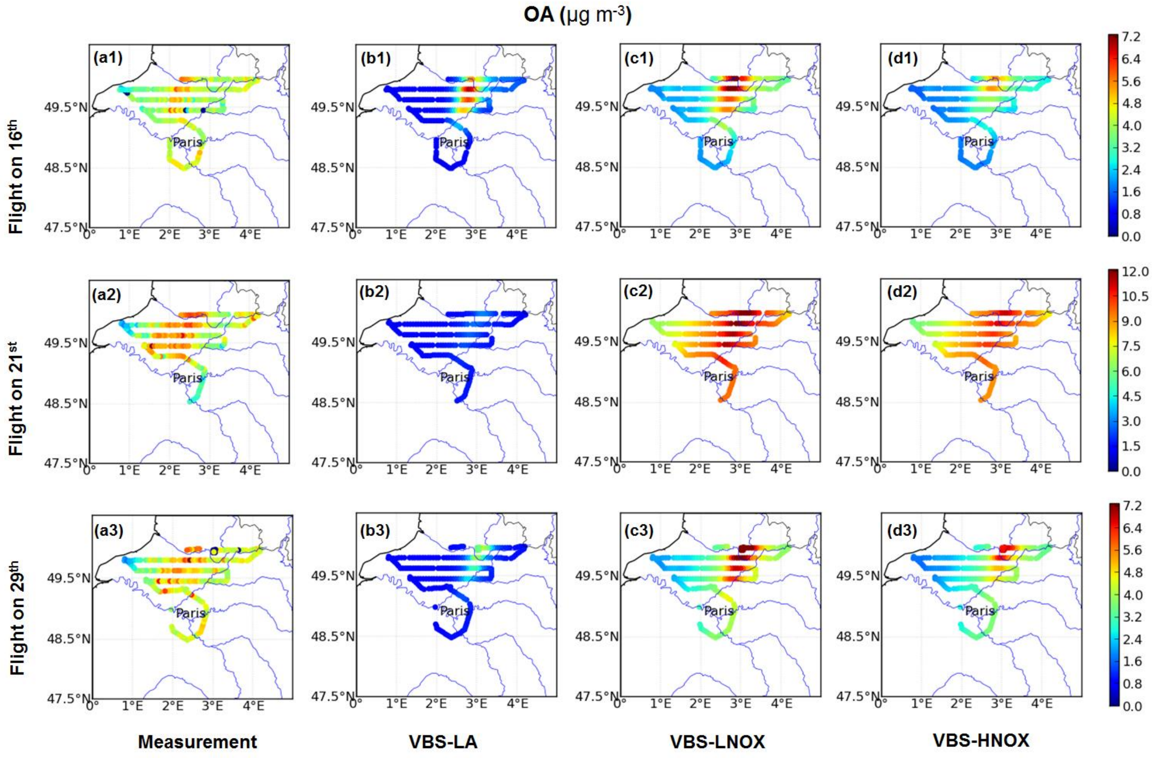
The modeled POA has little contribution to the total OA. The HOA derived from PMF analysis is on average about 20% to the total OA. However, HOA may include one part of oxidized OA fraction for which its quantity is not easily determined and cooking related OA for which there is no emission inventory for the model. To avoid these problems, we choose to compare use directly OA/Ox (see also answers to the referees 1 and 2).

To make this clearer, we added on p8079 L21:

"These LV-OOA and SV-OOA factors made up for by average about 65% of resolved OA factors and 37% of the total OA during these three MEGAPOLI flights. HOA (hydrocarbon like OA) make up for the remaining 35% of resolved OA factors and 20% of the total OA. While the HOA factor is generally attributed to POA, it might partly also correspond to oxidized POA, considered as SOA (Aumont et al., 2012, Cappa and Wilson, 2012), and to cooking-related OA (Freutel et al. 2013). Using total OA avoids these problems arising from the interpretation of PMF derived factors."

2. More discussion is needed regarding the (measured) NOx and BC plume not being spatially coincident with the (measured) secondary OA and Ox plume on the 29th. This seems to suggest that the origin of the Ox and OA on the 29th is not the Paris plume. What are the ramifications for the comparison of model vs. measured OA/Ox? Are the modeling inputs for this day simply not appropriate? On a similar note, are there problems the spatial distribution of emissions in the model?

In addition to emissions from the Paris agglomeration, regional and mainly biogenic formation transported to Paris by southerly winds contributes to both OA and Ox for the three flight days. The plume is wider than the primary pollutants are. OA is partially correlated with the BC/NOx plume while high concentrations are also found on the west probably due to regional biogenic contribution. The figure of OA comparison on 29th (Fig. 5 as shown below) is modified by a clearer color scale to show this. In addition, ozone is titrated by NO, thus the spatial structure of the ozone plume is expected to be different than that of primary pollutants. The OA and Ox well correlates with a coefficient R of 0.72 and the ratio is little affected by the introduction of this probable biogenic contribution (which also affects ozone). In addition, it seems that regional SOA formation has a similar level of importance as the anthropogenic emissions from Paris at least on this day. In the model simulations, the location of these secondary and primary plumes is better correlated.



Related comment: What is the ratio of gasoline to diesel consumption in the greater Paris region, especially compared to the other locations where the OOA/Ox method has been used? (Tokyo, Mexico City, etc.)? I do not suggest adding a detailed analysis of the differences in emissions, but a short discussion of the major differences in emissions between these locations would inform the comparison of the slopes and their modeled values, especially given the importance of aromatic VOCs in the modeled results How much of the overestimate of OOA/Ox by the model is explained by the SOA formulation in the model vs. the accuracy of the emissions (both quantity, speciation, and spatial distribution)? Is the ratio of aromatic VOC emissions to other Ox and SOA precursors particularly high in Paris?!

In France, only about 30 -40% of distributed fuel in 2009 was gasoline, the largest part was diesel. The diesel part is probably larger for France and the Paris agglomeration than for other megacities, but the authors lack detailed information on this point. On the other hand, Borbon et al. (2013) found emission ratios for C7–C9 aromatics in Paris higher than in Los Angeles and other French and European Union urban areas by a factor of 2–3. Accordingly, we added on p8087 L3 :

“Borbon et al. (2013) found emission ratios for C7–C9 aromatics in Paris which were by a factor of 2–3 higher than in Los Angeles and other French and European Union urban areas. This clearly could favor large anthropogenic SOA formation to OA in the Paris plume.”

In addition, in the revised paper uncertainties in SOA formation and in POA emissions are much more emphasized. The VBS-HNOX or –LNOX simulation is considered to favor the traditional ASOA formation by applying yields and chemical aging overestimating corresponding results from chamber experiments (Zhao et al., 2015). An additional VBS configuration is added (VBS-LA) in which the EMEP-LA inventory with three times larger POA emissions is used instead of the MEGAPOLI inventory and in which ASOA and BSOA aging is not considered. As a consequence, this configuration yields smaller ASOA formation, but larger SI-SOA formation in the plume. It reproduces observed OA/Ox slopes with about the same quality as does the VBS –HNOX configuration.

Accordingly the text is modified on p8089 L15:

"The ratio of the photochemical productivities of SOA and Ox (represented by the slope of OA vs. Ox) is well simulated (overestimation of less than 30% on the average of three days) for the Paris plume from VBS-HNOX when low SOA yields are applied on the SOA formation scheme. The overestimation might be related to too large yields of ASOA in the VBS scheme set-up in this work which was based on the parameters given in Lane et al. (2008a) and Murphy et al., (2009)."

3. Contrary to most other studies, this one has modeled OOA/Ox actually exceeding measured OA/Ox. More discussion is warranted. Is this due to the yields and version of the volatility basis set used, or does this model work better for the Paris region for some reason, and if so why? As presented it is difficult to assess why the model actually overstimates OOA/Ox- does this represent the "current" state of SOA modeling, or just one particular way of doing it?

OA simulations with the VBS scheme have generally good agreement against measurements from most of the studies in Paris (Zhang et al. 2013 and this study), in US (Murphy et al. 2009), in Mexico City (Hodzic et al. 2010) and in Tokyo (Morino et al. 2014). However, different SOA formation schemes based on the VBS setup have been used especially in more recent studies. In particular, Zhao et al, (2015) suggests lower yields for ASOA formation with respect to the scheme from Lane et al. (2008a) used in our study.

It is added in section 5.1 on p8087 L8:

"Recently, the comparison of different VBS based SOA schemes to chamber measurements in Zhao et al. (2015) suggests lower SOA formation from traditional VOC precursors (ASOA), by explicitly simulating the first generation products, than when using the parametrization from Lane et al. (2008a) as in our study. In addition, Lane et al. (2008a) do not account for BSOA chemical aging, while we do based on the results of Zhang et al. (2013). Thus, the relative contributions of ASOA and BSOA to plume SOA build-up in the VBS-LNOX and VBS-HNOX configurations used in this paper are considered as an upper limit, while the primary SI-VOC emissions for SI-SOA formation are considered as a lower limit."

In the revised version, emissions and SOA formation uncertainties are discussed by introducing the VBS-LA simulation using LA inventory with three times higher POA/SI-VOC emissions than the MEGAPOLI inventory and a traditional single step oxidation scheme for SOA formation.

It is added in section 3.2 on p8081:

"The VBS-LA simulation (same as VBS-T1 simulation in Zhang et al., 2013) in which a single step oxidation scheme (Pun et al. 2007) is used for traditional ASOA and BSOA formation, and the VBS scheme for SI-SOA formation as for the other two configurations. The EMEP-LA emission inventory with three times larger POA/SI-VOC emissions is used for the inner MEG3 domain. The fact that POA/SI-VOC emissions are three times larger and the absence of chemical aging for ASOA will favor SI-SOA with respect to ASOA formation."

and the conclusion in section 6 on p21 L667 are thus modified:

"However, an alternative scheme with three times larger POA emissions, and without ASOA and BSOA aging, also shows good agreement with observed OA vs O_x slopes, though it strongly underestimates background and urban Paris OA. This leads us to the conclusion that due to uncertainties both in POA emissions and in the SOA formation formulations, uncertainly in the SOA product distribution remains large. The constraint of observed OA vs. O_x slopes on the SOA product distribution in the Paris plume is unfortunately weak, and does not reduce this uncertainty (while it does for anthropogenic OA yields). Both ASOA and SI-SOA could be the major anthropogenic SOA products for two flights. In the simulations anthropogenic SOA is the major contributor to plume SOA on two flight days, while BSOA is major or equivalent on the third day."

Minor comments:

1. pg 8075 line 20 and several other locations: While this study is certainly not the first to use the term "Oxidant" to refer to Ox (= O3 + NO2), as in ". . .as a function of oxidant formation", it is very confusing, since the word oxidant also refers to OH, O3 and NO3. Indeed later in this manuscript the term "oxidant agents" are used, as well as "oxidant levels". I highly recommend simply referring to Ox as Ox and ozone as ozone but NOT as "oxidant". Note that the term Ox is not an abbreviation for "Oxidant"! Ox was initially defined as O3 + O for stratospheric chemistry...

The use of the term oxidant has been modified to avoid confusion on p8075 L18:

"Field data provide strong constraints on SOA related processes. In particular, the relation between SOA and Ox (O_3 + NO_2) has been used to express SOA formation as a function of photochemical products formation"

2. Abstract: Rather than state that there is "good agreement", state that the model actually overestimates the observations, by __%.

It is modified on p8074 L11:

"Simulated slopes slightly overestimated with respect to the observed one by a factor of 1.1, 1.7 and 1.3 for the three airborne measurements,"

3. Description of NOx measurements- very little info is given. I had to look in the Freney et al paper, and from there to the supplement to find adequate description of the measurements – important given the importance of NO2 to Ox in urban plumes.

Information about these measurements is added on on p8096 (Table 1).

“NO, NO_2 and NO_y are measured. (Freney et al. 2014, Supplementary Material)”

4. Figure 4 – would be better to plot Ox rather than O3

For comparison, a figure with O_x (Fig. S2) is added in the Supplementary Material.

5. pg 8077, line 16: “flight legs perpendicular to the plume time” – what does this mean?

It is modified on p8077 L16:

“Perpendicular flight legs to the plume axis were chosen ranging from 50 to 100 km in order to sample both the plume and rural background conditions at the lateral plume edges.”

Pg 8078, line 2, “. . . were priviliged” – please clarify/edit.

It is modified:

“**Because of a limited number of flight hours, and in line with the principal objective to document the photochemical production of pollutants, flights were performed on days with light wind (< 3 m s-1) and cloud free weather conditions”**

Anonymous Referee #4

Zhang et al. describe a study that compares airborne measurements taken during the MEGAPOLI campaign against the CHIMERE regional air quality forecasting model. In particular, the authors focus on SOA formation and evaluate the model performance with respect to OA and OA / Ox. Then the model is used to (1) evaluate the evolution of the Paris plume as it is transported from the city, and (2) attribute the total OA mass to different components: POA, biogenic SOA (BSOA), anthropogenic SOA from VOCs (ASOA), and SOA from primary SVOCs and IVOCs (SI-SOA). There are also comparisons for other atmospheric species such as BC and NOx.

This is an interesting analysis given the recent interest in SOA parameterizations for atmospheric chemistry models, as also noted by the other reviewers, and the airborne measurements represent a valuable opportunity to test these parameterizations. I think the use of OA / Ox is an interesting approach that allows the authors to compare a pseudo-intensive property rather than an extensive property. However, after reading the manuscript, I think that there are four major unresolved points, which should be addressed before publication.

BC Carbon and POA: The model does not accurately reproduce BC concentrations, which is acknowledged by the authors. However, given that BC and POA share sources and are often correlated, it is likely that POA is underestimated in the model as well. It is impossible to be certain if this is the case though, because no comparison of modeled and measured POA is performed. Given that the emissions of the SI-SOA precursors are calculated using the POA emissions, if the POA is underestimated in the model, then the SI-SOA will be underestimated as well. A comparison of modeled and measured POA concentrations is therefore necessary. This would require carrying out PMF analysis of the AMS data, which has its own uncertainties, as mentioned by the authors. However, I would point out that these uncertainties are most likely smaller than the underestimates of 70% and 74% for BC, and thus such a comparison would still be valuable. The authors could also estimate POA using the method of Ng et al. (2011).

BC evaluation is studied in detail in Petetin et al. (2015) who have suggested that the bias in the model could not be attributed to errors in emission inventories only, because of uncertainty in measurement and in the choice of the mass specific absorption coefficient.

Uncertainties in these emissions are discussed in Zhang et al. (2013), who compare POA emissions to HOA obtained from a three factor PMF analysis at an urban background site in Paris (Freutel et al., 2013). POA emissions from a specific emission cadaster for the Paris agglomeration described in Timmermans et al. (2013) are judged a priori as the most appropriate ones. This is why they have been used in this work. However, Zhang et al. (2013) show that POA simulations in the VBS framework (VBS-MPOLI in Zhang et al., 2013) clearly underestimate HOA observations by about a factor of three, as do POA/BC and HOA/BC ratios. On the contrary, POA from the so-called LA emissions (Junker and Liousse, 2008) show much better agreement with nearly no bias (similar for the POA/BC ratio) for its VBS application, even if they are a priori more crude as obtained by spatial downscaling. Thus uncertainty in POA emissions is estimated at least as a factor of three. To take this uncertainty into account, we decided to include the VBS-LA configuration with the larger LA emission in the revised version of this paper as replied above.

It is added in section 3.2 on p8081:

"The VBS-LA simulation (same as VBS-T1 simulation in Zhang et al., 2013) in which a single step oxidation scheme (Pun et al. 2007) is used for traditional ASOA and BSOA formation, and the VBS scheme for SI-SOA formation as for the other two configurations. The EMEP-LA emission inventory with three times larger POA/SI-VOC emissions is used for the inner MEG3 domain. The fact that POA/SI-VOC emissions are three times larger and the absence of chemical aging for ASOA will favor SI-SOA with respect to ASOA formation."

The consequence of underestimation of primary pollutant is discussed on p8083 L15:

"Direct comparisons for POA are not shown here because of the uncertainty in HOA factors from the PMF analysis, and because of the incomplete match between HOA and POA. However, the BC underestimation in simulations lets us also expect a POA underestimation.

Consequences of these underestimations in primary pollutants for the build-up of secondary pollutants are briefly discussed here:

- **First, as shown above for BC, the underestimation is alleviated in the alternative VBS-LA simulation with larger BC (and POA) emissions. Thus**

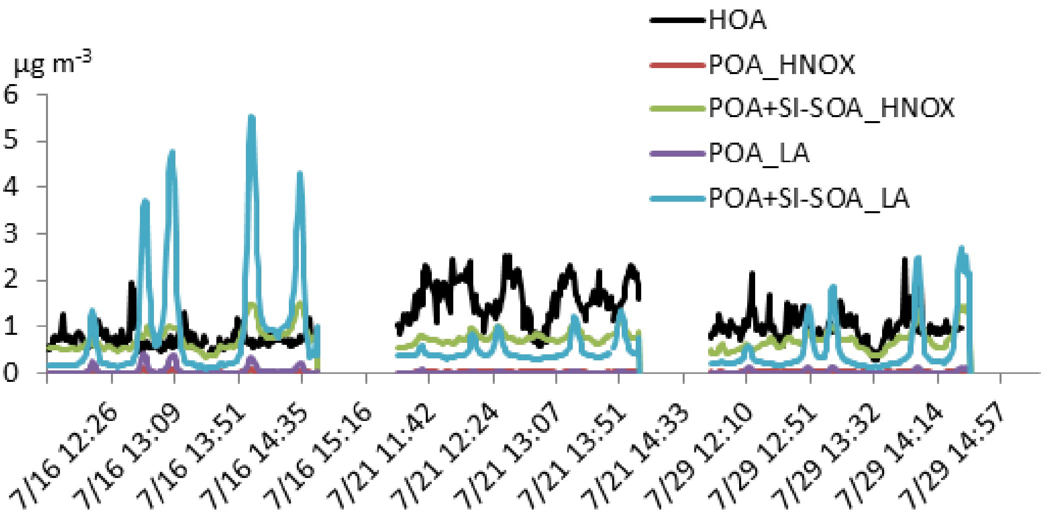
unexpressed uncertainty in meteorological data is partly taken into account by that in emissions.

- **Second, the use of OA vs Ox slopes for evaluation of the SOA production efficiency normalizes out the effect of errors in primary pollutants, as equation (1), it merely depends on the ratio of the product yields. This is why the use of this ratio is important for this study.**
- **Third, in a VOC limited regime as characteristic for the Paris region (e.g. Deguillaume, et al, 2008), the rate of secondary pollutant build-up is far from proportional to the primary precursor concentration. On the contrary, in the extreme case that NOx compounds represent the only OH loss, NOx and OH concentrations are inversely proportional (e. g. Kleinman et al., 1997). When assuming a constant ratio in primary pollutants, the flux in equation (1) is then independent of VOC concentrations, and only depends on the production rate of odd hydrogen radicals (OH+HO2+RO2).”**

Equation (1) is added on p8075 L23:

“(1) $VOC + OH \rightarrow \cdots \rightarrow \cdots \rightarrow \alpha\, O_x + \beta\, SOA + \cdots$”

A figure comparing HOA against POA and the sum of POA and SI-SOA for both MPOLI (VBS-HNOX simulation) and LA emissions is presented below in order to illustrate the uncertainties related to HOA comparison with simulations and emissions. HOA (in black) is derived from the AMS measurements. POA_HNOX (in red) and the sum of POA and SI-SOA (POA+SI-SOA_HNOX in green) are from VBS_HNOX simulation. POA_LA (in purple) and the sum of POA and SI-SOA (POA+SI-SOA_LA in blue) are from VBS_LA simulation. The HOA plume (difference between the maximum in a flight transect crossing the plume and the 30th percentile) concentration is 1.34, 1.18 and 1.60 µg m^{-3}, on 16th, 21st and 29th, respectively. It is respectively 0.4, 0.06 and 0.12 µg m^{-3} for POA and 5.35, 0.98 and 2.3 µg m^{-3} for the sum of POA and SI-SOA from the VBS-LA simulation. Indeed, as said above, it is not clear whether HOA should be compared to POA alone or the sum of POA and SI-SOA It is respectively 0.09, 0.02 and 0.04 µg m^{-3} for POA and 0.96, 0.46 and 0.79 µg m^{-3} for the sum of POA and SI-SOA from the VBS-HNOx simulation. The plume concentration of the sum of POA and SI-SOA from VBS-HNOX simulation is closest to the HOA measurement with -28% of underestimation on 16th while those from VBS-LA are closest on 21st with -17% of underestimation and on 29th with 44% of overestimation. As a conclusion, due to uncertainties in the emission inventories and due to differences between the VBS-LA and VBS-HNOX, both overestimations and underestimations with respect to observations have been obtained, a no significant bias is made evident. In addition, another difficulty in simulation is due to weak winds in the morning of the flight days. For 21st and 29th, winds are overestimated in the simulations , which leads to underestimations of the primary pollutants concentrations (Petetin et al. 2015). A simulated wind direction bias is found in this latter work, but it doesn’t affect much on the conclusion of the OA/Ox ratio and the OA impact from Paris emissions.



SI-SOA: Assuming that POA is underestimated by a similar percentage as BC, the authors should run a sensitivity study in which the concentrations for the precursors of SI-SOA are increased by a factor of 2 – 4, depending on the outcome of the POA comparison. This sensitivity study would allow the evaluation of how the model predictions depend on the emissions, which are highly uncertain.

As presented above, a new simulation VBS-LA is added in this work in order to take into account POA/SI-VOC emission uncertainties. In addition, chemical aging is not applied on traditional SOA formation. As a result, OA/Ox ratios with this configuration are relatively similar to those obtained with the VBS-LNOX configuration.

The conclusion on OA formations in section 5.3 is added:

"In conclusion, both the VBS-HNOX and VBS-LA simulations show different monthly average OA product distributions. … On the contrary, For SI-SOA, differences between both simulations are weak. However, alternative VBS schemes (Grishop et al., 2009) would simulate higher SI-SOA formation, as noted above (about a factor two from box model studies in other urban plumes)."

Background OA: The article should include a better explanation of why 30% of the maximum concentration was used as the threshold for identifying the background. At the moment there appears to be no explanation for the choice of this percentage, and so the division between background and non-background seems arbitrary.

As the background values are variable, we intended to choose a median percentile as a representative value. The 30th percentile (not 30% of the maximum concentration) was chosen as a nearly median given that roughly 20 – 40% of the largest values are belonging to the Paris plume (see for example figure 1 for NOx). Choosing for example a 20% or 40% percentile would only cause small differences in background values.

Model selection: It seems that this version of CHIMERE was run with parameterizations that will favor the production of ASOA relative to SI-SOA. The parameterization used for ASOA includes multi-generation oxidation that will result in quite high SOA yields. At the same time, the Robinson et al. mechanism produces less SI-SOA than the parameterization published by Grieshop et al. (2009). It is not discussed however in the manuscript how the selection of parameterizations used could potentially alter the results. Given the value of this data set, I encourage the authors to expand their analysis to include the Grieshop mechanism as well as the single-generation oxidation mechanism for VOCs, which I believe is already incorporated into CHIMERE (Zhang et al. 2013). At least, the authors should add caveats in the abstract and conclusions that their study is limited to only one specific parameterization, which is a major uncertainty in this study, and thus the relative importance of ASOA versus SI-SOA cannot be determined.

The SOA formation scheme used in VBS-HNOX and LNOX favors ASOA formation. The VBS-T1 simulation in Zhang et al. 2013 is added as VBS-LA in this study, which favors SI-SOA formation with respect to the traditional anthropogenic SOA. And the effect of the Grieshop mechanism as well as other schemes is discussed.

The conclusion on OA formations in section 5.3 is modified:

"In conclusion, both the VBS-HNOX and VBS-LA simulations show different monthly average OA product distributions. As discussed above, the ASOA and BSOA contributions in VBS-HNOX present an upper limit for ASOA and BSOA produced in the plume (and in background airmasses). On the contrary the small plume and background values in VBS-LA simulated without any chemical aging are probably underestimated, in particular because they underestimate the SOA observations within the Paris agglomeration (Zhang et al., 2013). On the contrary, for SI-SOA, differences between both simulations are weak. However, alternative VBS schemes (Grishop et al., 2009) would simulate higher SI-SOA formation, as noted above (about a factor two from box model studies in other urban plumes)."

The effect of other VBS schemes is added in section 5.1 on p8087 L8:

"Recently, the comparison of different VBS based SOA schemes to chamber measurements in Zhao et al. (2015) suggests lower SOA formation from traditional VOC precursors (ASOA), by explicitly simulating the first generation products, than when using the parametrization from Lane et al. (2008a) as in our study. In addition, Lane et al. (2008a) do not account for BSOA chemical aging, while we do based on the results of Zhang et al. (2013). Thus, the relative contributions of ASOA and BSOA to plume SOA build-up in the VBS-LNOX and VBS-HNOX configurations used in this paper are considered as an upper limit, while the primary SI-VOC emissions for SI-SOA formation are considered as a lower limit."

Additional Minor comments:

OOA versus Ox scatter plots: What is the significance of the x-intercept in these plots? Why does the x-intercept change so much, for example in Figure 7c, when comparing the measurements against the model?

These intercepts should not be fixed, because this would alter the slopes with respect to the measured or simulated points. The origin would correspond to continental background values, which are non-zero for both OA and Ox.

P8088/L15: Following my comment above, it seems likely that the average POA concentration of 0.15 ug m-3 for Paris is underestimated.

Uncertainties of POA emissions are discussed by comparing with VBS-LA simulation with three times higher emissions with respect to the VBS-HNOX simulation. The conclusion is modified as replied above.

A discussion on July 2009 average OA species distributions with the new VBS-LA configuration is added on p8089 L6:

"For the VBS-LA simulation, the larger primary S/IVOC emissions within the LA inventory lead to larger average POA concentration, up to 0.7 µg m^{-3} within the Paris agglomeration. Monthly maximum plume SI-SOA concentration is about 0.3 µg m^{-3} in VBS-LA (Fig. S12). The lower SI-SOA concentration albeit higher POA concentrations is due to lower OA load in the plume. Indeed, monthly average plume ASOA is small, below 0.05 µg m^{-3}, plume BSOA is below 0.3 µg m^{-3}. BSOA shows a similar spatial pattern in VBS-LA, but with lower absolute values than in VBS-HNOX."

P8089/L22: "It is likely that these values remain rather similar for a large range of emission and photochemical conditions" This phrase is very vague. What is meant mean by a "large range" or "rather similar"? It would be best if the authors could provide specific numbers. Otherwise, I would simply delete this sentence and note that similar OA to Ox (or SOA to Ox) ratios are observed for many, but not all, cities.

To make this point more precise, we added on p21 L674:

"**Observed OA vs Ox slopes of about 0.14 to 0.15 µg m^{-3} ppb^{-1} compare well to those observed in the Mexico City, the Los Angeles and the Tokyo plumes with different emissions and photochemical conditions during different seasons (Fig. 1).**"

Quality of writing: While the writing in the manuscript is acceptable. The presentation of the science would be clearer if the text was edited for the quality of the English. As an example, the last sentence of the abstract is very confusing.

It is modified in the abstract on p8074 L19 :

"For the average of the month of July 2009, maximum OA increases due to emissions from the Paris agglomeration are noticed close to the agglomeration at various length scales: several tens (for primary OA) to hundred (for SI-SOA and ASOA) kilometers of distance from the Paris agglomeration."

A native co-author has carefully reread the revised paper.

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