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Interactive comment on “The role of semi-volatile organic compounds in the mesoscale evolution of biomass burning aerosol: a modelling case study of the 2010 mega-fire event in Russia” *by* I. B. Konovalov et al.

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We are grateful to the Referee for the overall positive evaluation of our paper, for the useful discussion, and for the critical comments which were carefully addressed in the revised manuscript. Below we describe our point-to-point responses to the referee’s comments.

Referee’s comment: …while it might be hard to resolve, I found the paper to be too long and want the authors to think about (a) shortening some sections to avoid reader *fatigue and (b) breaking the summary and discussion to provide a focused summary of their work and a discussion section that highlights implications (what does this all mean) and future work.*

Indeed, shortening of this paper was not an easy task, especially taking into account that the referee suggested adding a new discussion section, and that we had to provide additional descriptions and explanations in response to the referees' comments. Unfortunately, we did not get any hints that would allow us to see where the text was too long and could be shortened. Nonetheless, we once again critically evaluated the content of our paper and removed some less important notes. A long section (Sect. 2.4.2) providing the description of the VBS framework in the reviewed manuscript has been split into four different sections (Sect. 2.4.1-2.4.4) in the revised manuscript to improve readability. The concluding section has also been split into two sections, following the recommendation by the referee. The new discussion section focuses on summarizing the major findings of our study and on a discussion of their implications.

Referee's comment: My biggest concern are the methods used to model first- versus multi-generational oxidation (or "ageing") of OA vapors and what it means for the findings from this work. Before I explain what I mean here, it would be nice if the authors clarified if they are ageing POA only or both POA and SOA produced from VOC/unspeciated organics? The text suggests that they are ageing POA only. Is there a reason why they think SOA vapors might not participate in ageing? There is ample evidence that SOA vapors could add or remove OA mass from ageing (Donahue et al., 2012;Henry and Donahue, 2012).If they did, how would it affect the OA composition results?

The multi-generation oxidation scheme was assumed to age both POA and SOA explicitly ("Evolution of oxygenated POA (OPOA) produced in the reaction of POA with OH was simulated in the same way as that of POA (that is, OPOA were governed by partitioning theory and experienced successive oxidation at the same rate and mass increment as POA)"). A multi-stage mechanism, which had earlier been implemented in Zhang et al. (2013), was used to simulate aging of "traditional" VOC precursors (and corresponding SOA products). By definition, a single-generation scheme (based on Jathar et al. (2014)) explicitly aged only POA; however, as it is noted in Jathar et al. (2014), "this scheme should account for some multi-generational aging" implicitly. In the revised version of our manuscript, the text describing the oxidation schemes has been, to a great extent, re-written by taking into account this and other comments of the referee.

R*eferee's comment: The semi-volatile behavior of POA and first-generation products of VOCs and unspeciated organics (and/or IVOCs?), although variable, have been somewhat constrained for biomass burning emissions using laboratory experiments (Hennigan et al., 2011;Grieshop et al., 2009a;Grieshop et al., 2009b; May et al., 2013; Heringa et al., 2011). In contrast, the parameterization for ageing of the SVOCs produced from POA partitioning/oxidation and oxidation of VOC/unspeciated organics remains relatively unconstrained (One can debate about what "first" versus "multi" means but in this case, by "first", I loosely mean what is produced in a smog chamber and by "multi" I loosely mean the extended aging in the atmosphere). The final OA produced in the model is a sum of the constrained first-generation products and the unconstrained future-generations of products. The distribution of first versus future generations will determine how constrained the final predictions of OA are with respect to the laboratory experiments. In the simplest sense, if the first generation products dominate, the predictions are more constrained and if the future generations dominate, the predictions are unconstrained. The authors have not described how important ageing is with respect to this distinction between first and future generations of products.*

To address the referee's question about the importance of ageing with respect to the distinction between the first and future generations of products, we performed a supplementary model run under the VBS-2 scenario, but without ageing of SVOCs produced from POA oxidation (that is, only the first stage of POA oxidation was assumed to take place). We found that, as could be expected, such a modified scheme produced considerably less SOA and PM_{10}. In particular, the maximum concentration of particle-phase SOA produced from oxidation of POA (S-SOA(p)) was almost a factor of two smaller in the modified simulation in Kuopio than in the original one (44 vs.76 $\mu\mathrm{g\ m}^{-3}$), and the normalized excess mixing ratio (that is, the ratio of enhancements caused by fires in PM_{10} and CO concentrations) value was evaluated to be about 30 percent lower (0.11 vs. 0.15). This result (mentioned in Sect. 3.1 of the revised manuscript) shows that, on the one hand, the second and further stages of oxidation were important in our simulations, but, on the other hand, the products of those stages did not provide a clearly dominating contribution to S-SOA(p).

Referee's comment: Related to the point above, I suspect, given the transport times between Moscow and Kuopio, that the OA in Kuopio is mostly produced from ageing and the results would be relatively insensitive to assumptions about POA volatility and surrogates used to model the unspeciated organics (the authors already see this with their sensitivity simulation with a slightly different k_{OH} *to model ageing). If that were indeed the case, the empirically-constrained improvements in the treatment of OA would not be responsible for better model-measurement comparison.*

Our results mentioned above indicate that our simulations are constrained by laboratory measurements to some degree. This point is mentioned in Sect. 3.1 of the revised manuscript. In regard to the referee's comment, we would also like to note that, in modeling of real-world cases in which aerosol is subject to atmospheric processing on time scales significantly exceeding those of typical smog chamber experiments, we obviously cannot rely exclusively on results of laboratory measurements. Rather, the outcomes of such modeling exercises evaluated against atmospheric measurements, can, in our opinion, be used to validate and advance the current understanding of aerosol processes. In this respect, our study demonstrated (as far as we know, for the first time for real atmospheric conditions) (1) that the "conventional" method of OA modeling can be clearly deficient in a situation where aerosol originates from wildfires and (2) that application of the advanced OA modeling approach based on the absorptive partitioning theory and taking into account oxidation of semi-volatile POA species is advantageous and yields sufficiently robust results in spite of the large uncertainties associated with the representation of the absorption/desorption and oxidation processes in a model.

Referee's comment: The authors state that they have not taken into account fragmentation reactions. But based on the above discussion, there results may be very sensitive to the inclusion of fragmentation reactions. There is evidence that multi-generational oxidation is potentially more susceptible to fragmentation than first-generation oxidation. So if the OA in this work (especially the transported and aged OA over Kuopio) is mostly a result of multi-generational oxidation then the model predictions are more sensitive to the fragmentation assumption and may be over-predicting the OA with photochemical age since the scheme used in this work continues to push more and more mass into the particle-phase with time.

We agree that disregarding fragmentation reactions could lead to over-predicting the increase of OA with photochemical age. To address this point, we have considered a new simulation scenario (named as "VBS-3" in the revised manuscript), in which fragmentation reactions are taken into account following Shrivastava et al. (2013; 2015) in the framework of a simple 2D-VBS scheme. As expected, the new scenario has produced less SOA than the original scenario "VBS-2", but it still has allowed us to achieve considerably better agreement with both ground- based and satellite measurements, compared to the scenario "STN" based on a "conventional" approach to OA modeling. We would like to note that the modeling representation of fragmentation processes is inevitably associated with large uncertainties; this is the main reason why such processes were not taken into account in the simulations presented in the reviewed manuscript.

Referee's comment: The volatility basis set (1D and 2D VBS) is a very convenient and efficient framework to represent the thermodynamics and chemistry of organic gases and particles. However, the framework is separate from the processes it has been used to represent (semi-volatile behavior of POA, multi-generational aging, dependence of *fragmentation with oxygenation and such). In other words, the VBS is just a framework to model processes and is separate from the scientific understanding/theory that the community has developed. That POA is semi-volatile and evaporates with dilution or heating is a theory and has nothing to do with the VBS. There are several instances in the paper that makes it sound like VBS and the process parameterizations are one and the same thing. For example, line 11 on page 9912: "Several studies applied this approach for modeling the evolution of OA from anthropogenic (fossil fuel burning) and (in some cases) biogenic emissions and found that it provides reasonable agreement between simulations and measurements". The VBS does not represent any approach; it merely represents a framework to model a particular approach, whatever that might be. If one desired, one could represent POA as non-volatile in the VBS. I would recommend the authors to revise the manuscript to address this distinction.*

We used the expression "the VBS approach" following some other papers, but we agree with the referee on this. The manuscript has been corrected accordingly.

Referee's comment: It appears that the "best" model performance is achieved by using the Grieshop et al. scheme. While this finding offers some insight, I would like to remind the authors that the Grieshop scheme is only constrained to a few hours of photochemical ageing and might not be representative of the longer ageing times simulated in this study. Let me make my point using an example; caveat: the idea is not to be precise. Let's say that the organic compound in the C=10000 μg/m3 bin is a C12O2.4 molecule with an O:C of 0.2 and a molecular weight of 182.4 (ignoring hydrogen and other species). As per the scheme, a single reaction results in a 40% mass increase and a product that has a C* of 100 μg/m3. Assuming that the entire mass increase comes through the addition of oxygen atoms (new molecular weight of 255.4), one would need to add approximately 4.5 oxygens. Following that same logic, the next reaction from a C*=100 μg/m3 precursor to a C*=1 μg/m3 product would require the addition of another 6.3 oxygens. There are problems with this scheme for two reasons. One, in two reactions the O:C of the product would be 1.1, which is far be-*

yond what has been seen in smog chamber experiments. And two, the above addition of oxygens does not account for fragmentation of the carbon backbone and hence the above predicted O:C is a lower bound estimate. These two manifestations in O:C make this scheme quite unrealistic for atmospheric ageing. While the use of this parameterization might yield good results, I do not think it is the right parameterization to use for ageing at regional and global scales. I understand that I am offering a criticism of the parameterization and not of its use in this work. However, I would like the authors to critically think about what the parameterization means and discuss their results in light of my example. I would also ask the authors to reconsider their emphasis on the VBS-2 model while presenting their results.

We thank the referee for this useful and stimulating analysis! We agree that the infinite chain of oxidation assumed in the Grieshop et al. (2009) scheme would eventually produce compounds with unrealistically high O:C ratio. It is, perhaps, less certain (at least for the special case of aging of biomass burning aerosol) whether the oxidation of SOA at the second and next stages would proceed with the same rate or whether it would slow down considerably and be associated with adding less oxygen atoms (and thus less fragmentation). It seems also not quite clear to what extent the oxidation and fragmentation rates may be different for compounds with significantly different volatility (C*). The last issue may be especially relevant for our study, since we consider a case where OA concentrations were typically much higher than those in ageing experiments in laboratories. Taking into account all these unknowns, it seems not at all easy to assess to what extent the evolution of real aerosol in the case addressed in our study would be different from that predicted by the Grieshop et al. (2009) scheme. By comparing our simulations with available measurements, we did not find any obvious indications that the Grieshop scheme is unrealistic. Nonetheless, realizing its potential shortcomings, we have tried to modify it. As stated above, the modified scheme presented in the revised manuscript takes into account fragmentation as well as condensed-phase transformation processes and has been used in a new scenario which is named "VBS-3" (instead of the former VBS-3 scenario which replaced the VBS-4 scenario). The focus of our discussion has been shifted to the new scenario. This update has not resulted in changes of any of the main conclusions of our study. Therefore, taking into account the robustness of our results, we believe that in spite of considerable uncertainties in the modeling representation of OA processes, the publication of our manuscript in ACP would be beneficial for advancing the modeling of biomass burning aerosol, as well as for reducing the gap between the rapid advances in laboratory studies of OA processes and their representations in 3D chemistry transport models.

Referee's comment: It seems to be like the authors are independently adjusting the fire emissions (using Fα) for each simulation to match CO and PM measurements while simultaneously changing the chemistry for OA. Clearly, this is not how one would probe the change in OA model chemistry to investigate improvements in model performance. I have several questions. Are the Fα computed for each site and for each simulation? Are both the gas and particle emissions adjusted? I am assuming that the authors only used the Fα for CO from the Moscow site to adjust gas emissions since those would be least affected by ageing. Was the PM adjusted too? If they did, why? What do the model predictions look like for unadjusted emissions? Regardless of the answers to the questions above, I would like the authors to be a little more clear about the total adjustment to emissions in the Methods section (may be in Section 2.3) and justify how the simulation-resolved adjustment has little influence on the inter-comparison of model-predicted PM from different simulations.

The simulations that took into account the emissions from fires were made using the optimal estimate of the correction factor, $F\alpha$, for BB emissions. Values of $F\alpha$ applied to emissions of all gaseous species were derived from CO measurements in Moscow combined with the simulations under the "standard" scenario. However, values of $F\alpha$ for aerosol species were indeed optimized using PM_{10} measurements in Moscow for each scenario independently. In doing so, we tried to isolate the effects associated with uncertainties in the fire emissions from those due to inaccuracies in the representation of aerosol processes. Indeed, if the emissions were, for example, systematically overestimated, a simulation with a "perfect" aerosol module would be positively biased; on the contrary, a simulation where actual SOA sources were missing could yield (at least, on average) nearly perfect agreement with the aerosol mass concentration measurements. Therefore, evaluation of different simulations against measurements could easily prompt a wrong conclusion regarding the model performance, unless the emissions were known to be sufficiently accurate. The idea of our analysis was to adjust the BB emissions to PM_{10} measurements in Moscow and then to test whether the simulations can reproduce the observed differences between PM_{10} concentrations in Moscow and Kuopio (see Section 3.1). A perfect simulation would be expected to yield good agreement with the measurements in both cities, while an imperfect one would likely be biased in Kuopio. Note, however, that this kind of analysis does not allow us to recognize a hypothetical situation (which is, in our opinion, rather unlikely) where the biases in the simulated aerosol evolution on its way from sources to Moscow and from Moscow to Kuopio would completely compensate each other. To reduce the risk of an incorrect conclusion, we evaluated our simulations against satellite AOD measurements (see Sect. 3.2). This explanation was added into Sect. 2.8 of the revised manuscript.

Referee's comment: 1.The scientific format for numbers in Tables 4 and 5 and Figures 3, 4, 5 and 7 are hard to compare across the simulations. I would recommend using a float format since the numbers are roughly of the same magnitude.

We changed the format for the numbers in all Tables and Figures as recommended by the referee.

Referee's comment: 2. The font sizes on all the figures might be too small for the final print edition. They can definitely be enlarged.

The font sizes have been enlarged in most figure labels and legends.

Referee's comment: 3. In Section 2.4.1, the authors discuss size distribution inputs using the mean diameter. Are those mass mean or number mean? They seemed too

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large for number mean.

We have specified that we discuss the parameters for the mass size distribution.

Referee's comment: 4. While I have seen myself and many of my colleagues struggle with this, the use of uniform terminology cannot be stressed enough. The one that I have a problem with is, SVOC. Robinson et al. defined SVOC as vapors partitioned from POA after atmospheric mixing. Here the authors have used it to mean POA vapors and oxidation products of VOCs. I would recommend the authors call the oxidation products of VOCs something else, may be just use V-SOA? (although, there is the concern of calling both the gas and the particle phase components as SOA).

We have tried to make our notations more consistent with other studies following the recommendations by the referee. Specifically, in the revised manuscript, we refer to oxidation products of VOCs as V-SOA and oxidation products of POA as S-SOA.

Referee's comment: 5. It might be worthwhile to mention that the unspeciated emissions from Jathar et al. (2014) also include IVOCs.

Unfortunately, we could not find any mention of "IVOCs" or "intermediate volatility" compounds in Jathar et al. (2014), except in the title of one reference in Supporting Information. We understand that, implicitly, the IVOC emissions were indeed taken into account in the analysis by Jathar et al. However, we are not sure that it would be appropriate for us to make that claim.

Referee's comments: 6. Page 9130, line 28: "ensure" not "insure". 7. Page 9123, line 25: "n-alkane" not "n-alcane". 8. Page 9235, line 3: "artifact" not "artefact". 9. Page 9136, line 9: "OA" not "AO".

The typos have been corrected.

Referee's comments: 10. Page 9136, line 23: "not only are our simulations imperfect" not "not only our simulations are imperfect". 11. Page 9142, line 5: "a factor of two relative to the simulations" not "a factor of two relative the simulations".

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The suggested corrections were done.

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