Atmospheric
Chemistry
and Physics

Open Access

Discussions

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.

Anonymous Referee #2

Received and published: 7 June 2015

Konovalov et al. have performed simulations with the CHIMERE model to predict episode-specific impacts of wildfires on air quality over a portion of western Russian. Their effort on method development has focused on (a) building an emissions inventory for wildfires and (b) improving the treatment of organic aerosol (OA) through the implementation of the versatile volatility basis set framework. Their effort on model evaluation has focused on model-measurement comparison of (a) CO and PM10 at several ground sites and (b) aerosol optical depth (offline estimates against satellite-derived products).

The manuscript is very well written (definitely in the top quartile of papers I have reviewed). The scientific methods are sound and represent the current state-of-the-science (it is a separate matter that the science around organic aerosol chemistry and thermodynamics is still quite uncertain). The authors have done a great job to discuss the uncertainties that are propagated through their methods. The results are interesting (although not ground breaking) and the authors do a nice job of describing the results and their implications. Overall, I recommend publication in ACP. I have few comments to improve the discussion surrounding the treatment of organic aerosol and one clarification. Further, 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.

MAJOR COMMENTS

First versus Multi-generational Oxidation

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 semi-volatile behavior of POA and first-generation products of VOCs and un-speciated organics (and/or IVOCs?), although variable, have been somewhat con-strained 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.

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.

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.

C3300

Volatility Basis Set

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.

Scheme of Grieshop et al.

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 beyond 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.

CLARIFICATIONS

Fire Emissions

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.

MINOR COMMENTS

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.

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

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 large for number mean.

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).

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

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".

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".

REFERENCES

Donahue, N. M., Henry, K. M., Mentel, T. F., Kiendler-Scharr, A., Spindler, C., Bohn, B., Brauers, T., Dorn, H. P., Fuchs, H., and Tillmann, R.: Aging of biogenic secondary organic aerosol via gas-phase OH radical reactions, Proceedings of the National Academy of Sciences, 109, 13503-13508, 2012.

Grieshop, A., Donahue, N., and Robinson, A.: Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 2: analysis of aerosol mass spectrometer data, Atmospheric Chemistry and Physics, 9, 2227-2240, 2009a.

Grieshop, A. P., Logue, J. M., Donahue, N. M., and Robinson, A. L.: Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 1: measurement and simulation of organic aerosol evolution, Atmospheric Chemistry and Physics, 9, 1263-1277, 10.5194/acp-9-1263-2009, 2009b.

Hennigan, C. J., Miracolo, M. A., Engelhart, G. J., May, A. A., Presto, A. A., Lee, T., Sullivan, A. P., McMeeking, G. R., Coe, H., Wold, C. E., Hao, W. M., Gilman, J. B., Kuster, W. C., Gouw, J., Schichtel, B. A., Collett, J. L., Kreidenweis, S. M., and Robinson, A. L.: Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber, Atmospheric Chemistry and Physics, 11, 7669-7686, doi:10.5194/acp-11-7669-2011 2011.

Henry, K. M., and Donahue, N. M.: Photochemical aging of α-pinene secondary organic aerosol: effects of OH radical sources and photolysis, The Journal of Physical Chemistry A, 116, 5932-5940, 2012.

Heringa, M., DeCarlo, P., Chirico, R., Tritscher, T., Dommen, J., Weingartner, E.,

Richter, R., Wehrle, G., Prevot, A., and Baltensperger, U.: Investigations of primary and secondary particulate matter of different wood combustion appliances with a high-resolution time-of-flight aerosol mass spectrometer, Atmospheric Chemistry and Physics, 11, 5945-5957, 2011.

May, A. A., Levin, E. J. T., Hennigan, C. J., Riipinen, I., Lee, T., Collett, J. L., Jimenez, J. L., Kreidenweis, S. M., and Robinson, A. L.: Gas-particle partitioning of primary organic aerosol emissions: 3. Biomass burning, Journal of Geophysical Research: Atmospheres, 118, 2013JD020286, 10.1002/jgrd.50828, 2013.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 9107, 2015.