

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. Kononov et al.

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We thank the Referee for the evaluation of our manuscript and for the helpful suggestions. All of the referee's comments have been carefully addressed in the revised manuscript. Below we describe our point-to-point responses to the referee's comments.

Referee's comment: 1. Section 2.4.2 Suggest differentiating between POA in the gas phase and particle phase using different subscripts e.g. POA(g) and POA(a). This is

C5446

important to clarify that aging and oxidation in the VBS scheme implemented by the authors is done just in gas-phase.

The suggested clarification is done in the revised manuscript. Specifically, we have introduced different subscripts for indicating gas phase and particle phase species. Furthermore, we have clarified in the text of the revised manuscript (specifically in Sect. 2.4.3 and 2.4.4) that we mean gas-phase oxidation.

Referee's comment: 2. Page 9123: Line 20: The authors say that they use the same mass yields as given in Table S3 of Jathar et al. But Table S3 of Jathar et al. has yields for $C^=0.1, 1, 10$ and $100 \mu\text{g}/\text{m}^3$. In addition line 10 says authors used a single surrogate species based on Jathar et al. These sentences are confusing and contradictory. Please clarify.*

In the revised manuscript (Sect. 2.4.4), the description of the oxidation scheme based on Jathar et al. (2014) is clarified, and we have made an effort to avoid any statements that might appear to be contradictory. In particular, we explain that following Jathar et al. (2014) we assumed that S-SOA yields from the reactions of any POA(g) species with OH are similar to those from the oxidation of n-pentadecane (C15 n-alkane). Quantitatively, using Table S3 and Eqs.(1,2) in Supporting Information in Jathar et al. (2014), we assumed that the yields of S-SOA into the volatility bins with C^* equal 0.1, 1, 10 and $100 \mu\text{g m}^{-3}$ were 0.044, 0.071, 0.41, and 0.30, respectively; the yields of S-SOA into the other volatility bins were assumed to be zero.

Referee's comment: Also they say that n-pentadecane represents 10 % of NMHC in addition to POA. When I look at their Table 3, none of this is obvious. Suggest re-writing of section 2.4.2 to clarify this.

To clarify the description of the different oxidation schemes considered in our study, the section 2.4.2 has been re-written to a considerable extent and split between four new sub-sections (Sect. 2.4.1 and 2.4.4) of the revised manuscript. In Sect. 2.4.4, it is indicated, in particular, that consistently with the analysis in Jathar et al. (2014),

C5447

we assumed that n-pentadecane chemically represents not only POA species, but also a fraction (10 percent) of the total non-methane VOC emissions from biomass burning. We have also considerably modified the layout and content of Table 2 (Table 3 in the revised manuscript), in which we have additionally indicated that the surrogate species was assumed to chemically represent 10 percent of the total VOC emissions from biomass burning (BB). Please note that Table 3 (Table 1 in the revised version) represents the volatility distribution of only those species that are emitted as POA; this has been additionally clarified in the table caption.

Referee's comment: Also $C^=10,000$ in Table 3 is in the intermediate volatility (IVOC) range. Please use consistent terminologies with previous studies (e.g. Jathar et al. 2014 and references therein).*

There is indeed some difference between terminologies used in our study, in which the species with $C^*=10,000 \mu\text{g m}^{-3}$ are considered as semi-volatile, and in other studies, in which such species are usually called as intermediate volatility organic compounds (IVOC). This point is clarified and explained in the revised manuscript as follows (see Sect. 2.4.2): "Note that unlike most other studies employing the VBS framework, we do not consider so called intermediate volatile compounds (IVOCs) separately from semi-volatile compounds (SVOCs). Usually, a class of IVOCs is intended to represent organic compounds that are more volatile than SVOC but less volatile than VOCs, such that $10^4 < C^* < 10^6 \mu\text{g m}^{-3}$. Under typical environmental conditions, the contribution of IVOCs to the particle phase is assumed to be negligible, although they are still expected to provide a considerable source of SOA after their oxidation, at least in situations with predominant POA emissions from fossil fuel burning (see, e.g., Robinson et al., 2007). However, on the one hand, this study addresses a special situation with OA concentration reaching (in simulations) values of about $3000 \mu\text{g m}^{-3}$: obviously, under such conditions, organic compounds with $C^* \sim 10^4 \mu\text{g m}^{-3}$ should be treated as semi-volatile. On the other hand, there is evidence that BB emits less IVOCs than motor vehicles (Grieshop et al., 2009b), and that they do not contribute significantly to SOA

C5448

formation. Note that consistent with the discussion in Grieshop et al. (2009b), May et al. (2013) did not provide any data regarding emissions of compounds with $C^* > 10^4 \mu\text{g m}^{-3}$; thus, these emissions were not included in our simulations." Unfortunately, we could not find any mention of the terms "IVOC" or "intermediate volatility" in Jathar et al. (2014), except for the title of one reference.

Referee's comment: 3. Section 2.7: Line 20: Authors disregarded secondary inorganic aerosol from fire emissions. This is hard to justify given that authors are comparing PM_{10} . What fraction of measured PM_{10} is organic versus inorganic? Also (comment 7): The authors simulate POA and SOA but they compare PM_{10} . They need to make a case from measurements that organic aerosols dominated PM_{10} concentration.

In our understanding, there is a general consensus based on numerous observations in different regions of the world (see, e.g., Reid et al., 2005; Alves et al., 2010; 2011 and references therein) that inorganic compounds (including water-soluble ions associated with secondary inorganic aerosol) typically constitute only a minor mass fraction (~ 10 percent or less) of both fine and coarse BB aerosol particles, while organic material (OM) (including OC and associated hydrogen, oxygen and nitrogen atoms) provides a predominant contribution (~ 80 percent) to particulate matter originating from fires. We do not see any reason why the composition of aerosol originating from fires in the study region could be significantly different in this respect. Indeed, consistent with this understanding, Popovicheva et al. (2014) found that the ratio of the mass concentration of inorganic ions (sulfate, ammonium and potassium) to that of OC in aerosol observed in Moscow on several "smoky" days in summer 2010 was about 0.12; assuming that the OM/OC ratio was about 2, this observation suggests that the secondary inorganic aerosol contribution to the aerosol mass concentration was much less than 10 percent. In addition, measurements of PM_{10} done in Finland during the transport of the Russian BB plumes show that the aerosol mass was dominated by organics and that the fraction of organics was increased during the BB plumes (Corrigan et al., 2013). A corresponding explanation is added in section 2.8 of the revised manuscript.

C5449

Referee's comment: 4. Authors ran fire emissions without emissions from other sources and zero boundary conditions. Did they do test simulation with just boundary condition turned on to see how much boundary condition contributes to simulated aerosol?

The influx of gas and aerosol species from outside the model domain was in fact taken into account in our "background" simulation (without fire emissions but with other sources turned on); the output of this simulation was added to the simulation performed with fire emissions but with zero boundary conditions. A simple test run (in a standard configuration) with just boundary conditions turned on showed that the contribution of the boundary conditions to the "background" aerosol concentration both in Moscow and in Kuopio, where local (or regional) anthropogenic and biogenic emissions are rather strong, was fairly small ($<5 \mu\text{g m}^{-3}$) compared to concentrations observed there during "smoky" days ($>50 \mu\text{g m}^{-3}$), but it was not neglected anyway (as explained above). Note that we had to run a model with a VBS scheme with zero boundary conditions because the available global model outputs did not provide data for concentrations of organic species involved into our VBS scheme (such as POA and S-SOA). To address this referee's comment, we have extended the discussion of the main assumptions behind the configuration of our numerical experiments in Sect. 2.8 of the revised manuscript. Specifically, we argue that the strong fire emissions taken into account in our simulations were a major driver of the observed variability in the region and period considered in our study.

Referee's comment: 5. Table 2 needs to be more descriptive. Looking at it, the difference between the different VBS scenarios is not obvious. One needs to connect scattered information from various Tables and description in the text to understand these differences. The authors need to make it easier for the readers.

Table 2 (Table 3 in the revised manuscript) has been substantially revised in order to make it more descriptive and informative. Since we do not see a way to present the two types of volatility distributions assumed in our simulations in the same table (that is, in

C5450

Table 3), we have indicated there that the type B volatility distribution assumes a larger fraction of more volatile POA species than the type A distribution; this information may be sufficient for those readers who are not interested in the quantitative details of our simulations. Quantitatively, the volatility distributions are presented in Table 1 of the revised manuscript.

Referee's comment: 6. Table 4 and Figure 7: How were perturbations of PM and CO calculated? Were they the differences between model run with just fire vs. other aerosol? Also was the mean PM_{10} or CO varying spatially and temporally?

We apologize that the description of this point in the reviewed version of our manuscript was incomplete. We improved it in the revised version. Specifically, we explain that to characterize the NEMR values over the whole study period independently both in the observations and simulations, we first estimated the ΔPM_{10} and ΔCO values as the difference between the concentrations with all the sources (either observed or calculated by combining results of the "background" and respective "fire" runs as explained in Sect. 2.8) and the corresponding average concentrations over the "background" days when the contribution of fires to CO concentration was smaller (according to our simulations) than 10 percent. Second, we evaluated the slope of a linear fit to the relationship between ΔPM_{10} and ΔCO values defined in this way for each "smoky" day (that is, when the contribution of fires to CO concentration exceeded 10 percent). Note that, in the revised manuscript, we used a slightly different method to evaluate the relationship between the PM_{10} and CO values: namely, a linear fit "through the origin" was used (taking into account that, ideally, when ΔCO is zero, ΔPM_{10} should be zero, too) instead of an ordinary linear fit as in reviewed manuscript. The mean PM_{10} and CO concentrations reported in our tables and figures were calculated by averaging all daily data at a given location over a study period. Presumably, if they were calculated for a different location and time period, they would be different.

Referee's comment: 7. The authors simulate POA and SOA but they compare PM_{10} . They need to make a case from measurements that organic aerosols dominated PM_{10}

C5451

concentration.

Please see our response to the comment 3 above.

Referee's comment: 8. The authors have used the Grieshop et al. 2009 scheme for aging and volatility decrease. But previous studies showed that this scheme drastically overestimates SOA. See Hodzic et al. 2010. Please comment on the caveats introduced by using this aggressive aging scheme.

We agree with the referee that the Grieshop et al. (2009) scheme may be indeed too "aggressive". The reason is that the presumably infinite chain of functionalization should eventually produce overly heavy molecules (with too high O:C ratio), while in reality fragmentation would split them into several smaller, more volatile molecules. Accordingly, in the revised manuscript, we not only provided a respective caveat, but also we have shifted the focus of our analysis from the scenario VBS-2 based on the Grieshop et al. (2009) scheme to the new VBS-3 scenario in which the Grieshop et al. (2009) scheme fully applies only to the first generation of oxidation, while the second and next generations are affected by fragmentation and condensed-phase transformation processes. We would like to note, however, that taking into account that Hodzic et al. (2010) applied the Grieshop et al. (2009) scheme to simulate both anthropogenic and BB aerosol in a situation where anthropogenic emissions were typically several times stronger than BB emissions (as it is evident in Fig.2 in Hodzic et al. (2010)), it is not quite obvious, in our opinion, that the Grieshop et al. (2009) scheme could be found too aggressive in the Hodzic et al. (2010) study, if it were applied exclusively to biomass burning aerosol (as in our case).

Referee's comment: 9. The authors acknowledged that their method may have compensating errors due to neglecting fragmentation, which is a good point to make. But suggest citing some recent papers which showed the potential importance of fragmentation in 3D models (e.g. Shrivastava et al. 2013, Shrivastava et al. 2015).

The papers by Shrivastava et al. (2013; 2015) are cited in the revised version. More-

C5452

over, we introduced a new modeling scenario in which the fragmentation process was taken into account and represented qualitatively similar to Shrivastava et al. (2013; 2015).

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C5453

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