

## Responses to the comments of anonymous referee #2

Thank you for your comments that helped to improve our manuscript. Please find below your comments in blue, our responses in black and modifications in the revised manuscript in *italic*.

The manuscript by Ciarelli et al. presents combined chamber experiments with a large ensemble of model simulations, in order to study the volatility distribution and its evolution of organic aerosols originating from wood burning. The work presented is original and of interest to the GMD readers, and the brute-force approach adopted which resulted to tens of thousands of simulations is very informative and helps understand the sensitivity of the system, within the limitations of the work. The degeneration of the large 2d VBS parameter space into a narrower area is also important in future model development in terms of model performance. Although not all possible parameters are studied, and the dependence of results to experimental design and the limitations of past work used in the manuscript is not thoroughly presented, I believe that the work has a lot of value and deserves publication, following my minor comments below. I would like to stress out that the parameter space of such a work is practically infinite, so no study is able to perform all possible sensitivity simulations in a finite amount of time.

We thank the referee for his general comment. In the corrected version of the manuscript, we will also discuss the parameters to which the sensitivity of the model results has not been assessed. This has been done in the new conclusion section 6, that has been re-organized and further expanded as also suggested by referee 1. The new conclusion section reads as follows:

### **6 Discussion and major conclusions**

*We performed extensive box model simulations of wood burning smog chamber experiments conducted at two different temperatures (263 and 288 K). By combining new NTVOCs and organic aerosol measurements we constrained the amounts of NTVOCs that act as SOA precursors. Our estimates indicate that NTVOCs are approximately 4.75 times the amount of total organic material in the 0.1 and 1000  $\mu\text{g m}^{-3}$  saturation concentration range ( $OM_{SV}$ ). This ratio can be directly used in CTM models in combination with the proposed aging scheme, in the absence of explicit NTVOCs emissions from wood burning. Our results suggest that only lowest enthalpies of evaporation of primary SVOCs reported by May et al. (2013) could reproduce the NTVOCs and organic aerosol measurements at both temperatures. These calculations were performed using a single volatility distribution function.*

*Parameters required for representing SOA formation such as NTVOCs reaction rates ( $k_{OH-NTVOCs}$ ), SOA yields ( $Y$ ) and enthalpies of vaporization of secondary organic aerosol ( $SOA.\Delta H_{vap}$ ) were varied within physically realistic ranges and parameters fitting best the observed OA mass and O:C ratios were retained. The use of time resolved data and performing the experiments at two different temperatures significantly aided constraining these parameters. Based on the reaction scheme used, best fitting  $k_{OH-NTVOCs}$  ranged between 3.5 and 4.0  $\times 10^{-11}$  molecules $^{-1}$  cm $^3$  s $^{-1}$ , the  $Y$  of semi-volatile SOA surrogates ranged between 0.3 and 0.35 ppm ppm $^{-1}$ , and the  $SOA.\Delta H_{vap}$  was determined to be between 35'000 J mol $^{-1}$  and 55'000 J mol $^{-1}$ . The model predicted that the majority of the SOA formed during the aging-phase arose from NTVOCs and only a small amount from SVOCs.*

*Many parameters were not varied within the fitting procedure, but a priori assumed. In the following, we discuss the approach used for the selection of these parameters and their influence on the model results. Our results suggest that only lowest enthalpies of evaporation of primary SVOCs reported by May et al. (2013) could reproduce the NTVOCs and organic aerosol measurements at both temperatures. These low values are consistent, with those obtained for  $SOA.\Delta H_{vap} = [35'000 - 55'000]$  kJ mol $^{-1}$  vs. weighted average of  $\Delta H_{POA} \sim 50'000$  kJ mol $^{-1}$ . Results presented here including the average NTVOCs/ $OM_{SV}$  ratios and parameters required for representing SOA formation are all based on the use of one  $OM_{SV}.$ Vol.dist. In Fig. S3, we have performed a sensitivity analysis where several  $OM_{SV}.$ Vol.dist were tested in combination with the same  $SOA.\Delta H_{vap}$  function and the same reaction scheme. This analysis shows that the NTVOCs/ $OM_{SV}$  ranges between 3.9 and 4.8, which encompasses the value reported here (4.75) and that the resulting SOA is only*

slightly sensitive to the assumed  $OM_{SV}$ . Vol. dist used, especially at low temperature. This is because the  $OM_{SV}$  is predicted to contribute to a lesser extent to the measured SOA compared to NTVOCs.

The parameters describing the molecular characteristics (e.g. oxygen and carbon numbers) of the primary SVOCs and their oxidation products (set1 and 2) were identical to those proposed by Donahue et al. (2012) and Koo et al. (2014). As SVOCs contributed less than NTVOCs to SOA, the modelled OA mass and O:C ratios were not very sensitive to the assumed parameters. Therefore, these assumptions could not be tested and additional measurements at the molecular level are necessary to constrain these parameters better.

Meanwhile, we have assumed that the volatility distribution of the NTVOCs oxidation products follows the same function as that of naphthalene oxidation products, scaled by a scaler representing the total yield  $Y$  of these products in the semi-volatility range. Initial tests indicated that the measurements used as constraints did not allow the determination of the exact shape of this function, due to the limited concentration span during our experiments, within only one order of magnitude. Therefore, the function was fixed during the fitting procedure and only the  $Y$  was varied. Further experiments spanning a larger range of concentrations are required for better constraining the volatility distribution of the biomass burning NTVOCs oxidation products, with a special focus on lower concentrations (between 1-20  $\mu\text{g m}^{-3}$ ), representative of moderately polluted atmospheres, e.g. in Europe.

The carbon number of the NTVOCs oxidation products was based on the characterization of the chemical nature of these precursors by the PTR-ToF-MS (Bruns et al., 2016), mostly comprising benzene and naphthalene and their methylated derivatives, oxygenated aromatic products and furans with an average carbon number of around 7. Based on Donahue et al. (2013), we have assumed that the oxidation of moderately oxygenated NTVOCs leads to significant functionalization (addition of three oxygens on average), while the further aging of the resulting oxidation products leads to both functionalization and fragmentation. Representing both processes by only one compound in the 1.5D-VBS approach imposed a decrease by only one volatility bin and hence a gain of only half oxygen atom per oxidation. This oxidation scheme is different than that proposed by Donahue et al. (2013), where significant fragmentation occurs with aging combined with the gain of more oxygen atoms. Initial tests showed that a higher increase in the oxygen number with aging yield a significant loss of compounds' volatility ( $\sim 1.7 \text{ Log}(C^*)$  bins per one oxygen atom) and hence an overestimation of the increase in SOA yields with aging. An increase of one oxygen atom per oxidation step while decreasing the compounds' volatility by only one bin would imply significant fragmentation with the loss of up to two carbon atoms, impossible in the case of  $C_6$  compounds, especially for low volatility bins. We have attempted a further increase in the fragmentation compared to the current scheme and the result was an overestimation in the increase of the bulk O:C ratio with aging. We note that the traditional functionalization and fragmentation scheme in the initial volatility basis set was developed by considering SOA precursors to comprise mostly long chain hydrocarbons (e.g.  $C_{10}$ - $C_{20}$  alkanes and alkenes), which are expected to be much more subject to fragmentation than aromatics. Therefore, we consider the scheme proposed here to be more suitable for  $C_7$  aromatic and furan oxidation products.

In the present study, the bulk micro-physical properties of the condensed phase were not measured. Therefore, for all calculations, we assumed instantaneous reversible absorptive equilibrium of semi-volatile organic species into a well-mixed liquid phase; i.e. the model does not invoke diffusion limitations within the condensed phase. These assumptions may influence our results, especially at lower temperatures; e.g. if diffusion limitations were to be considered, higher reaction rates would be required to explain the observations. However, the same assumptions are considered in CTMs and therefore we expect that resulting biases will partially cancel out, providing that the bulk phase properties and condensational sinks of chamber and ambient aerosols are not significantly different.

Based on our best fitting solutions, the OA mass and composition can be predicted at any given temperature, emission load and OH exposure. This is illustrated in Fig. 6 for three different OM emission loads ( $OM_{SV}$  + NTVOCs) of 6, 60 and 600  $\mu\text{g m}^{-3}$  and for a wide range of atmospherically relevant temperatures (from 253.15 K to 313.15 K). Partitioning of POA depends on the temperature and the injection amounts. The primary organic aerosol mass (POA) decreases with temperature by 0.5%  $\text{K}^{-1}$  on average with higher effects predicted at higher loads (0.7%  $\text{K}^{-1}$  at 600  $\mu\text{g m}^{-3}$  vs. 0.3% at 6  $\mu\text{g m}^{-3}$ ). The partitioning coefficient of the primary material increases by about a factor of 1.5 for a ten-fold increase in the emissions. As aging proceeds, POA mass slightly increases as a result of additional partitioning, but after an OH exposure of (1.0-

$1.5) \times 10^7 \text{ molec cm}^{-3} \text{ h}$ , the trend is inversed and POA mass decreases due to the oxidation of semi-volatile primary compounds. This effect is more pronounced at high loads.

From Fig. 6, we can also assess the impact of temperature, OH exposure and emission concentrations on SOA yields. The temperature effect on SOA yields is a function of OH exposure, aerosol load, and temperature: i.e.  $\partial Y/\partial T = f(T, C_{\text{OA}}, \text{OH}_{\text{exp}})$ . SOA yields increase 0.03, 0.06 and 0.05 %  $\text{K}^{-1}$  on average for 6, 60 and  $600 \mu\text{g m}^{-3}$  respectively, with higher effects predicted in general at lower temperatures. The temperature effect on the yields is also larger at higher OH exposures (except for very high loads). An analysis typically performed to estimate the volatility distribution of SOA products is based on SOA yields from chamber data performed at different precursor concentrations. We investigated the impact of the OA concentration on the yield at different temperatures and OH exposure. In Fig. S2, an average change in the yield with  $\log C_{\text{OA}}$  is shown at the different conditions:  $(\partial Y/\partial \log C_{\text{OA}}) = f(T, \text{OH}_{\text{exp}})$ . An increase in SOA yields with the  $\log C_{\text{OA}}$  was observed as expected, which is not solely due to additional partitioning, but is also related to changes in the actual chemical composition and hence volatility distribution of the SOA surrogates, as they age to different extents at different concentrations and temperatures. We determined a yield increase of 4-9 percentage points for a 10-fold increase in emissions, with a higher effect at higher OH exposures and lower temperatures.

From Fig. 6, one can also evaluate the minimum OH exposure values required for SOA to exceed POA. SOA is predicted to exceed POA after  $\sim 1.5 \times 10^7 \text{ molec cm}^{-3} \text{ h}$ , for typical ambient concentrations and temperatures. At low temperatures (263 K) and high loads, SOA might exceed POA at an OH exposure of  $9 \times 10^6 \text{ molec cm}^{-3} \text{ h}$ , or in 2-10 hours (at OH concentrations of  $(1-5) \times 10^6 \text{ molec cm}^{-3}$ ), in line with previously estimated values for biomass burning emissions for the typical conditions of haze events (Huang et al., 2014). Comparatively, at 288.15K an OH exposure of  $7 \times 10^6 \text{ molec cm}^{-3} \text{ h}$  would be required for SOA to exceed POA, which might be reached within 2 hours or less at typical summer OH concentrations, i.e.  $(5-10) \times 10^6 \text{ molec cm}^{-3}$ . These results confirm previous observations during haze events in China that SOA formation is very rapid and SOA mass might exceed primary emissions within time-scales of hours, even during haze events (Huang et al., 2014).

Mounting evidence underlines the importance of accurately assessing the emission and evolution of wood burning emission in the CTMs in order to properly predict the SOA levels retrieved from ambient measurements (Ciarelli et al., 2016a; Denier van der Gon et al., 2015; Shrivastava et al., 2015). The simplified VBS scheme proposed here allows for including a mixture of NTVOCs retrieved from latest state-of-the-art wood burning smog chamber experiments (Bruns et al., 2016). The amount of the new NTVOCs material included in the model was found to be in the range of estimates proposed by previous biomass burning studies (Shrivastava et al., 2015; Yokelson et al., 2013; Dzepina et al., 2009) and to reproduce most of the chamber experiments successfully. Including the fragmentation and multigeneration chemistry of SOA precursors, allows for a reasonable description of the chemical properties of the SOA species including their volatility distribution and their O:C ratios.

The applicability of the parameters to other burning conditions and other emission types should be evaluated in future studies. It has to be noticed that the scheme relies exclusively on chamber experiments conducted with only one type of wood (Beech, *Fagus Sylvatica*). Even though the effects of temperature, OH exposure and different emission loads on the predicted OA concentrations were presented in this study, differences in the nature of the emitted organic species (e.g. NTVOCs/ $\text{OM}_{\text{SV}}$  and NTVOC composition) might be expected depending on the different burning conditions and biomass used. Therefore, special care is required when extrapolating the results to a global scale, including more detailed emission information related to the wood burning habits of the different countries. Currently, an application of the proposed scheme, limited to the European scale, is under evaluation (Ciarelli et al., 2016b).

### Specific comments

Lines 61-62: This is valid only if equilibrium is assumed. Later in the manuscript this is made clear and indeed this assumption is followed, so please add a relevant statement here as well.

We have revised this part of the text, as below:

The representation of SOA formation in models may be based on the absorptive partitioning theory of Pankow (1994), assuming instantaneous reversible absorptive equilibrium. In this representation, the critical parameters driving the partitioning of a compound  $i$  between the gas and the condensed phases are its effective saturation concentration,  $C_i^*$ , and the total concentration of organic aerosol,  $C_{OA}$ :

$$\xi_i = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}; C_{OA} = \sum_i \xi_i C_i, \quad (1)$$

Here,  $\xi_i$  is the partitioning coefficient of  $i$  (condensed-phase mass fraction).  $C_i^*$  is a semi-empirical property (inverse of the Pankow-type partitioning coefficient,  $K_p$ ), reflecting not only the saturation vapor pressure of the pure constituents ( $P_{Li}^o$ ) but also the way they interact with the organic mixture (effectively including liquid phase activities). This formulation essentially implies that at high  $C_{OA}$  almost all semi-volatile organic aerosols are in the condensed phase with only species with the highest vapour pressures remaining in the gas phase.

Line 138: “simulations” -> “approach”.

Done.

Line 139: “physical and error” -> “physical limits and error”

Done.

Lines 161-163: How good is this assumption, given the present literature? How sensitive are the results based on this assumption, if it is not valid? How big a chamber needs to be for this assumption to be correct? Please make a statement here.

We added more details regarding wall loss corrections in section 2, as follows:

*Particle wall loss rates in the chamber were determined using the decay of eBC assuming all particles were lost equally to the walls and condensable material partitions only to suspended particles. The average particle half-life in the chamber was  $3.4 \pm 0.7$  h. NTVOCs were stable in the chamber prior to aging, indicating that the chamber walls are not an effective sink for NTVOCs (Bruns et al., 2016). This is because NTVOCs acting as SOA precursors are largely composed of volatile compounds. By contrast, the NTVOCs oxidation products are expected to be semi-volatile and partition to both the walls and the particles. Zhang et al. (2014) show that the bias created by the wall loss is inversely proportional to seed aerosol concentration and OH concentration, both of which were relatively high in the current experiments (Bruns et al., 2016). Therefore, under our experimental conditions, wall losses of NTVOCs oxidation products are not expected to be large and thus this effect was not corrected for and yields presented should be considered as lowest estimates.*

Line 188: Is the range 0.1-1000 both for the low-volatile and semi-volatile compounds?  
Regardless, can you please present individual ranges for each of the two groups of volatilities?

Following the classification proposed by Donahue et al. (2012), low-volatile organic compounds are classified into the  $C^* = (0.01, 0.1) \mu\text{g m}^{-3}$  range, whereas semi-volatile compounds into the  $C^* = (1, 10, 100) \mu\text{g m}^{-3}$  range. Our approach is based on the work of Koo et al. (2014), which refers to the 5 volatility bins in the  $10^{-1}$  to  $10^3 \mu\text{g m}^{-3}$  in saturation concentration range ( $C^*$ ) as semi-volatile organic compounds (SVOCs). In this approach, the lowest volatility bin ( $C^* = 0.1 \mu\text{g m}^{-3}$ ) represents all the organic compounds with  $C^* \leq 0.1 \mu\text{g m}^{-3}$ , and they are treated as non-volatile in the model (Koo et al., 2014). We modified the text in the corrected version of the manuscript to be consistent with, the classification of the individual ranges as described in Koo et al. (2014).

*Primary wood burning emissions were placed to range from 14 to 11 carbons (set1) in line with previous studies (Donahue et al., 2012; Koo et al., 2014) and appropriate numbers of oxygen atoms were retrieved*

using Eq. 2. The distribution of the primary organic material in the low-volatility ( $C_i^* = 0.1 \mu\text{g m}^{-3}$ ), and semi-volatile ranges ( $OM_{sv}$ ) ( $0.1 < C_i^* < 1000 \mu\text{g m}^{-3}$ ) in set 1 (Table 1) is based on the work of May et al. (2013), who revealed that the majority of the emitted primary OA mass is semi-volatile, with 50 to 80 % of the POA mass evaporating when diluted from plume to ambient concentrations or when heated up to 100°C in a thermo-denuder.

Lines 218-219: Why resulting biases cancel out? And, even more, what do the GCMs have to do with this?

In chemical transport models (CTMs), instantaneous reversible absorptive equilibrium of semi-volatile organic species into a well-mixed liquid phase is assumed; i.e. no bulk diffusion limitations. Here, for our yield calculations we have made the same assumption which might lead to lower results (Chuang and Donahue, 2016). However, if the bulk micro-physical properties of the ambient aerosols and aerosols in the chamber are similar, biases would cancel out.

Lines 242-245: I got really confused with the calculations here. Where do these numbers come from? How many oxygens are added per oxidation step? Also, probably relevant with this discussion, how many oxygens are contained in the most volatile group at emission time?

The numbers of oxygen and carbon in the VBS space were distributed according to the work of Donahue et al. (2011) and using a combination of PTR-MS data with previously proposed carbon and oxygen numbers of wood burning POA (Koo et al., 2014).

The most volatile group (bin) in the VBS space used here was retrieved from the PTR-MS data. We first calculated an average number of carbon and oxygen for the NTVOCs mixture, i.e. 7 carbons and 1 oxygen (using PTR-MS data). Using the group contribution approach (Equation 2 in the manuscript) we could retrieve the saturation concentration corresponding to those numbers of carbon and oxygen (i.e.  $\approx 10^6 \mu\text{g m}^{-3}$ ). For the NTVOCs mixture, first generation oxidation accounts for an addition of at least two oxygens using a naphthalene oxidation product distribution. The set that allocates the oxidation products of the NTVOCs (set3) was constrained based on the measured number of carbon from PTR-MS data. Giving a measured average carbon number of  $\sim 7$ , set3 is placed to have a carbon number that varies from 6 to 5, and values in between the bins were linearly interpolated. We would like to note that such combination of oxygen and carbon number satisfies Eq 2 in the manuscript yielding the saturation concentrations in the semi-volatile and low-volatility range.

According to Donahue et al. (2013), while the rate of the increase in oxygen atoms do not decrease with the oxidation generation number, the compounds' fragmentation significantly increase; the fragmentation branching ratio is often parameterized as a function of the compounds' O:C ratios (e.g. fragmentation ratio =  $f(O:C^{(1/\alpha)})$ , where  $\alpha$  is a positive integer often between 3-6 (Jimenez et al., 2009). This results in a general decrease in the OA compounds' carbon number and hence the number of oxygen added per molecule, but not in the O:C ratio or the carbon oxidation state. Therefore, the oxidation of moderately oxygenated IVOCs leads to significant functionalization compared to fragmentation, while the further aging of the resulting oxidation products leads to both functionalization and fragmentation. Representing both processes by only one compound imposes a decrease by only one volatility bin and hence a gain of half oxygen atom per oxidation. That is, tests showed that a higher increase in the oxygen number would yield a significant loss of compounds volatility ( $\sim 1.7 \text{ Log}(C^*)$  bins per one oxygen atom) and hence an overestimation of increase in SOA yields with aging. An increase of one oxygen atom per oxidation step while decreasing the compounds' volatility by only one bin would imply a significant fragmentation with the loss of up to two carbon atoms, impossible in the case of C6 compounds. We have attempted a further increase in the fragmentation compared to current scheme and the result was an overestimation in the increase of the bulk O:C ratio with aging. We note that the traditional functionalization and fragmentation scheme in the initial volatility basis set was developed by considering SOA precursors IVOCs to comprise mostly long chain hydrocarbons (e.g. C10-C20 alkanes and alkenes). This scheme seems to be not directly applicable to the case of oxygenated aromatic compounds present in biomass smoke (Bruns et al., 2016). We added the information regarding the numbers for the oxygen number added during the multigeneration chemistry in section 3 as suggested:

*Multigeneration chemistry (aging) is also accounted for by the model. Unlike the 2D-VBS, the 1.5D-VBS does not use different kernel functions, to discretize the distribution of the oxidation products according to their  $\text{Log}(C^*)$  and O:C ratios, when functionalization and fragmentation occur. Instead, to reduce the com-*



putational burden of the simulations, the model assumes that the oxidation of a given surrogate yields one other surrogate with lower volatility, higher oxygen number and lower carbon number. These properties should be considered as a weighted average of those relative to the complex mixture of compounds arising from functionalization and fragmentation processes. Accordingly, the 1.5D-VBS approach represents the functionalization and fragmentation processes effectively, while reducing the parameter space and the computational burden. Gas-phase products in the semi-volatile range in set2 and set3, once formed, can further react with a rate constant of  $4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  as proposed by previous studies (Donahue et al., 2013; Grieshop et al., 2009; Robinson et al., 2007), further lowering the volatility of the products by one order of magnitude. This implies that for every additional oxidation step, the organic material receives around 0.5 oxygen atoms (Table 1). According to Donahue et al. (2013), the compounds' fragmentation significantly increases, while the rate of increase in oxygen atoms does not decrease with the oxidation generation number. The fragmentation branching ratio has been often parameterized as a function of the compounds' O:C ratios (e.g. fragmentation ratio =  $f(\text{O:C}^{1/\alpha})$ ), where  $\alpha$  is a positive integer often between 3-6 (Jimenez et al., 2009). This results in a general decrease in the OA compounds' carbon number and hence the number of oxygen added per molecule, but not in the O:C ratio or the carbon oxidation state. Therefore, the oxidation of moderately oxygenated NTVOCs leads to a significant functionalization (addition of a least two oxygen atoms) compared to fragmentation, while the further aging of the resulting oxidation products leads to both functionalization and fragmentation. Representing both processes by only one compound imposes a decrease by only one volatility bin and hence a gain of only half an oxygen atom per oxidation. As the modelled species' average carbon number systematically decreases with aging, this approach effectively takes into consideration the compounds' fragmentation. In parallel, the addition of oxygen reflects the compounds' functionalization with aging and the increase in the measured O:C ratio. Therefore, unlike previous 2D-VBS schemes where functionalization and fragmentation are disentangled, the approach adopted here, by decreasing the number of carbon atoms and increasing the number of oxygens atoms, simultaneously describes both processes.

Lines 326-328: This is a great result, which demonstrates the value of the modeling approach. Understanding that this is outside the scope of this work, if a statement can be made on potential applicability beyond wood burning, it would greatly enhance this statement.

The work presented here, aims to assess the determination of the kinetic and thermodynamic parameters relevant for SOA formation from complex mixtures and the applicability of these parameters to other emissions should be tested in future work. This has been highlighted in the conclusion section (section 6) of the corrected version of the manuscript:

*Mounting evidence underlines the importance of accurately assessing the emission and evolution of wood burning emission in the CTMs in order to properly predict the SOA levels retrieved from ambient measurements (Ciarelli et al., 2016a; Denier van der Gon et al., 2015; Shrivastava et al., 2015). The simplified VBS scheme proposed here allows for including a mixture of NTVOCs retrieved from latest state-of-the-art wood burning smog chamber experiments (Bruns et al., 2016). The amount of the new NTVOCs material included in the model was found to be in the range of estimates proposed by previous biomass burning studies (Shrivastava et al., 2015; Yokelson et al., 2013; Dzepina et al., 2009) and to reproduce most of the chamber experiments successfully. Including the fragmentation and multigeneration chemistry of SOA precursors, allows for a reasonable description of the chemical properties of the SOA species including their volatility distribution and their O:C ratios.*

*The applicability of the parameters to other burning conditions and other emission types should be evaluated in future studies. It has to be noticed that the scheme relies exclusively on chamber experiments conducted with only one type of wood (Beech, Fagus Sylvatica). Even though the effects of temperature, OH exposure and different emission loads on the predicted OA concentrations were presented in this study, differences in the nature of the emitted organic species (e.g. NTVOCs/OM<sub>SV</sub> and NTVOC composition) might be expected depending on the different burning conditions and biomass used. Therefore, special care is required when extrapolating the results to a global scale, including more detailed emission information related to the wood burning habits of the different countries. Currently, an application of the proposed scheme, limited to the European scale, is under evaluation (Ciarelli et al., 2016b).*

Line 357: The 4.75 factor is a very useful number that comes out from this work. How does this compare

with other estimates (e.g. Shrivastava et al., 2008; 2015), and why it is different? How much does it change when different types of wood are burned (e.g. tropical vs. boreal forests, domestic heating, cooking)?

The base emission scenario used in the work of Shrivastava et al. (2008) relies on volatility distributions proposed by Robinson et al. (2007). It was derived by fitting gas particle partitioning data for diesel exhaust and assuming that the missing mass of IVOC emissions is equivalent to 1.5 times the U.S. Environmental Protection Agency National Emissions Inventory (NEI) POA emissions.

Shrivastava et al. (2015) used a top-down approach to retrieve an average IVOC/OM<sub>SV</sub> ratio. They performed several global simulations using the Community Atmosphere Model version 5 (CAM5) with different SOA schemes to predict the global SOA burden. In their study, organic carbon emissions were taken from version 3 of the Global Fire Emissions Database (GFED3.0) (van der Werf et al., 2010) and the (Lamarque et al., 2010) Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report (AR5) emission data set (IPCC-AR5). In their study, the intermediate volatile POA species from fossil fuel and biomass burning were calculated as 6.5 times the POA emissions, which is much higher than the author's first bottom-up estimates. The authors argued that such ratio is within the range of large potential variations (and uncertainty) of gas-phase IVOC emissions (Yokelson et al., 2013; Dzepina et al., 2009). The authors also stressed the point that semi and intermediate-volatile VOC emissions may also vary with type and combustion conditions so that application of one constant value at global scale represent a large source of uncertainty.

Here, we have used instead a much more constrained bottom-up approach: The IVOC/OM<sub>SV</sub> ratio of 4.75 was retrieved from recent state-of-the-art wood burning chamber experiments conduct at different temperatures (Brunns et al., 2016), where both gas and particle phases were measured. This ratio compares well with that determined based on the top-down approach of Shrivastava et al. (2015).

It has to be noted that the smog chamber experiments used in study were performed using only one type of wood as fuel (Beech, *Fagus Sylvatica*) rendering challenging the prediction of how the of organic material emitted will change in terms of emission loads and type of compounds if different types of wood were used. However, we do want to highlight that while our results are subject to burn-to-burn variability, the presented model does estimate SOA concentration within only 25% error. Indeed, additional work would be needed to assess the applicability of the parameters determined here to other burning conditions.

Line 370: Maybe a better term for “injection amounts” is “ambient concentrations”? The partitioning depends on amount present, not a flux.

We replaced the term in the text as suggested by the referee.

Line 402: “confirm previous observations”: which? Please don't just add a list of references, be explicit.

We have modified the sentence as follows:

*From Fig. 6, one can also evaluate the minimum OH exposure values required for SOA to exceed POA. SOA is predicted to exceed POA after  $\sim 1.5 \times 10^7$  molec  $\text{cm}^{-3}$  h, for typical ambient concentrations and temperatures. At low temperatures (263 K) and high loads, SOA might exceed POA at an OH exposure of  $9 \times 10^6$  molec  $\text{cm}^{-3}$  h, or in 2-10 hours (at OH concentrations of  $(1-5) \times 10^6$  molec  $\text{cm}^{-3}$ ), in line with our previously estimated values for biomass burning emissions for the typical conditions of haze events (Huang et al., 2014). Comparatively, at 288.15K an OH exposure of  $7 \times 10^6$  molec  $\text{cm}^{-3}$  h would be required for SOA to exceed POA, which might be reached within 2 hours or less at typical summer OH concentrations, i.e.  $(5-10) \times 10^6$  molec  $\text{cm}^{-3}$ . These results confirm previous observations during haze events in China that SOA formation is very rapid and SOA mass might exceed primary emissions within time-scales of hours, even during haze events (Huang et al., 2014).*

The manuscript ends very abruptly. Where is the conclusions section? Maybe some implications of how things are modeled right now compared to this new approach? Any future plans for similar studies on organic aerosol sources other than wood burning?

We are currently investigating other OA sources that could be important for ambient OA concentrations (e.g. gasoline and diesel cars) using latest available chamber data. We adjusted the conclusion section as also suggested by the other referee. Moreover, we included additional information regarding potential implications, advantages and disadvantages of the approach as mentioned above.

*Mounting evidence underlines the importance of accurately assessing the emission and evolution of wood burning emission in the CTMs in order to properly predict the SOA levels retrieved from ambient measurements (Ciarelli et al., 2016a; Denier van der Gon et al., 2015; Shrivastava et al., 2015). The simplified VBS scheme proposed here allows for including a mixture of NTVOCs retrieved from latest state-of-the-art wood burning smog chamber experiments (Bruns et al., 2016). The amount of the new NTVOCs material included in the model was found to be in the range of estimates proposed by previous biomass burning studies (Shrivastava et al., 2015; Yokelson et al., 2013; Dzepina et al., 2009) and to reproduce most of the chamber experiments successfully. Including the fragmentation and multigeneration chemistry of SOA precursors, allows for a reasonable description of the chemical properties of the SOA species including their volatility distribution and their O:C ratios.*

*The applicability of the parameters to other burning conditions and other emission types should be evaluated in future studies. It has to be noticed that the scheme relies exclusively on chamber experiments conducted with only one type of wood (Beech, *Fagus Sylvatica*). Even though the effects of temperature, OH exposure and different emission loads on the predicted OA concentrations were presented in this study, differences in the nature of the emitted organic species (e.g. NTVOCs/ $OM_{SV}$  and NTVOC composition) might be expected depending on the different burning conditions and biomass used. Therefore, special care is required when extrapolating the results to a global scale, including more detailed emission information related to the wood burning habits of the different countries. Currently, an application of the proposed scheme, limited to the European scale, is under evaluation (Ciarelli et al., 2016b).*

A statement that is not really present in the manuscript is how results might change if different experimental conditions were to be used for the chamber experiments. Can the proposed mechanism here be used in a global model, under the wide range of ambient conditions and different types of wood burning around the globe? How valid (or not) is an extrapolation from the studied conditions to the global scale?

The proposed mechanism is suitable to predict the OA composition for a wide range of ambient conditions (e.g. temperature and OH exposure) as presented in Fig. 6 of the revised version of the manuscript. However, it has to be noted that the scheme relies exclusively on chamber experiments conducted with only one type of wood (Beech, *Fagus Sylvatica*). We included the following statement in the conclusion section as presented in the previous comment, in order to add further details regarding the extrapolation of the method at global scale.

*The applicability of the parameters to other burning conditions and other emission types should be evaluated in future studies. It has to be noticed that the scheme relies exclusively on chamber experiments conducted with only one type of wood (Beech, *Fagus Sylvatica*). Even though the effects of temperature, OH exposure and different emission loads on the predicted OA concentrations were presented in this study, differences in the nature of the emitted organic species (e.g. NTVOCs/ $OM_{SV}$  and NTVOC composition) might be expected depending on the different burning conditions and biomass used. Therefore, special care is required when extrapolating the results to a global scale, including more detailed emission information related to the wood burning habits of the different countries. Currently, an application of the proposed scheme, limited to the European scale, is under evaluation (Ciarelli et al., 2016b).*

Code and data availability: The way I read the statement is that the code is NOT publicly available. Please correct me if I am wrong, but if this is indeed the case, I am not certain if this is ok with GMD guidelines.

The code is available upon request to the corresponding authors.  
We modified the text as below to make the statement more clear.

*Please contact the corresponding authors of this publication if you are interested in the model code or applications and/or scientific collaboration.*



Figure 1: In my printout the red color is too dark, and the black text inside it is hard to read. Consider using a lighter color in the bars.

This figure has been removed based on the suggestion of the first referee.

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