Responses to the comments of anonymous referee #1

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.

In this paper, Ciarelli et al. combined a volatility basis set box model with smog chamber wood combustion aging experiments to constrain the parameters that control the description of the organic aerosol formation from wood burning emissions in models. This study has the potential to contribute in the organic aerosol modeling field but major revisions needs to be done before publication. In particular, I have two major concerns regarding the validity of the scientific methodology used and several other comments regarding the presentation of the study. Therefore, I would recommend publication only if these comments are addressed.

Major comments:

1. According to the aging scheme presented in section 3 and based on Table 1 and figure 2 the organic material receives 1-1.5 oxygen atoms (for SVOCs) or 2-4 oxygen atoms (for IVOCs) during the first oxidation step. Then, for every additional oxidation step, the organic material receives only around 0.5 oxygen atoms. However, according to Donahue et al. (2013) (Donahue et al., 2013) the oxygen number should be proportional to generation number and they have reported 1-2 oxygen atoms being added per generation of oxidation for SOA from biomass burning. The authors should provide experimental evidences to support their assumption that the number of oxygen atoms added during the first generation step is much higher than the number of oxygen atoms added after each additional oxidation (and explain why is as low as 0.5). Otherwise, they should reconsider their approach for the aging of SVOCs and IVOCs. Furthermore, the above information can be retrieved only from the tables and figures of the manuscript. The authors must extend the paragraph in the text where they describe their aging scheme to include all the necessary details.

The VBS scheme presented in this work is a simplified version of the 2D-VBS scheme proposed by Donahue et al. (2011). This approach, referred to as a hybrid 1.5D-VBS and adapted for regional models, was proposed by Koo et al. (2014). In the 2D-VBS the reaction of every surrogate compound with OH yields multiple other surrogates, spanning a range of volatility and O:C ratios, mathematically represented by a 2D-matrix (abundances vs. log(C*) and O:C ratios). The oxidation products have indeed higher O:C ratios, but higher or lower volatility, depending on whether the products arise from fragmentation or functionalization, respectively. By contrast, in the 1.5D-VBS scheme used here, the oxidation of a surrogate yields only one other surrogate with a specific log(C*) and carbon and oxygen numbers. In this 1.5D space, the compounds O:C ratios are represented as a function of their volatility, with different isopleth functions for different compound families (POA compounds, IVOCs and SVOCs products). While being a further simplification of the system compared to the 2D-VBS, the 1.5D-VBS approach is particularly useful for decreasing the parameter space, especially giving the limited constrains available, namely the IVOC composition, the IVOC concentration, the POA concentration, the aged OA concentration and the O:C ratios. It also decreases the number of oxidation products that are needed to be tracked in the transport model and therefore the overall computational burden.

According to Donahue et al. (2013), while the rate of the increase in oxygen atoms does not decrease with the oxidation generation number, the compounds’ fragmentation significantly increases. The fragmentation branching ratio is often parameterized as a function of the compounds’ O:C ratios (e.g. fragmentation ratio = f(O:C(1/α)), where α is a positive integer often between 3-6 (Jimenez et al., 2009). This results in a general decrease in the 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 imposed a decrease by only one volatility bin and hence a gain of half an oxygen atom per oxidation. That is, tests showed that a greater increase in the oxygen number would yield a significant decrease in the compounds’ volatility (~1.7 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 C6 compounds, especially at lower 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 the SOA precursors to comprise mostly long chain hydrocarbons (e.g. C10-C20 alkanes and alkenes), which may be more subject to fragmentation than aromatics. Therefore, the traditional scheme seems to be not directly applicable to the case of oxygenated aromatic compounds present in biomass smoke (Bruns et al., 2016). The description of the oxidation approach adapted here has been further extended in the new section 3 and section 6, which can be found in the reply to the third and fourth comments, respectively.

2.

The authors are using the emission factors and two different sets of enthalpies of vaporization ($\Delta H$), proposed by May et al. (2013) for wood burning POA emissions, to simulate the Omsv gas/aerosol partitioning in their experiments. However, May et al. (2013) proposed an entire set of parameters (emission factors, accommodation coefficient ($\alpha$), and enthalpies of vaporization) that must be used together to describe the phase partitioning. If one of the parameters is changed (the $\Delta H$ here), then a new set of emission factors has to be used in order to describe the thermodenuder (TD) data within the experimental uncertainty. However, in this work the authors are using the same volatility distribution for both set of $\Delta H$. According to Table S2 in May et al. (2013), for the $\Delta H$ used in SOL2 and $\alpha$=1 there are about 35 volatility distributions that describes the TD within the experimental uncertainty. Therefore, in order to use eq.4, the authors should contact May et al. to make sure that the volatility distribution used in SOL2 is acceptable otherwise they have to use a different one.

Based on the reviewer comment, we have contacted Dr. Andrew May, who shared with us all the combinations of volatility distributions ($\text{OMSV.Vol.dist}$) and $\Delta H$ functions ($\text{OMSV.}\Delta H_{\text{vap}}$). The volatility distribution, referred to as $\text{OMSV.Vol.dist}_{\text{ref}}$, which we have chosen in combination with $\text{OMSV.}\Delta H_{\text{vap}} = \{70'000 - 11'000 \times \log(C^*)\}$ J mol$^{-1}$, was not accepted within the experimental uncertainty, considering one sigma value, but would be within two sigma values. Now, we have tested the combinations of $\text{OMSV.Vol.dist}$ and $\text{OMSV.}\Delta H_{\text{vap}}$ and only functions with lowest OMSV.$\Delta H_{\text{vap}}$ could well explain the change in the measured NTVOC/POA with temperature and $\text{OMSV.}\Delta H_{\text{vap}} = \{70'000 - 11'000 \times \log(C^*)\}$ J mol$^{-1}$ fitted best the observed changes. These low values are consistent with those obtained for SOA – SOA.$\Delta H_{\text{vap}} = [35'000 - 55'000]$ J mol$^{-1}$ vs. the weighted average of $\text{OMSV.}\Delta H_{\text{vap}} \sim 50'000$ J mol$^{-1}$. Meanwhile, the volatility distributions that could explain our observations have an aggregate contribution in the volatility bins $\log(C^*) = 1$ and $2 \leq 0.3$.

In this version of the manuscript and based on the reviewer comment we have assessed the influence of the choice of the primary organics volatility distribution on the resulting NTVOCs/OMSV and the resulting SOA (using the same oxidation scheme and sets of optimal parameters previously obtained). For this analysis, we have only used the combinations of volatility distributions and $\Delta H$ functions that fitted the measured NTVOCs/OMSV ratios at high and low temperatures. We found that the NTVOCs/OMSV ranges between 3.9 and 4.8, which encompasses the value previously reported in the manuscript (4.7). Meanwhile, the use of $\text{OMSV.Vol.dist}_{\text{ref}}$ and $\text{OMSV.}\Delta H_{\text{vap}} = \{70'000 - 11'000 \times \log(C^*)\}$ J mol$^{-1}$ results on average in 7% lower SOA mass than the newly tested combinations at high temperature, while the effect of the chosen combination on SOA formed is less than 2% at low temperatures (Fig. S3). This finding shows the sensitivity of the results to the primary semi-volatile compounds properties, which is expected especially at low temperatures, as the contribution of these compounds to the observed SOA is predicted to be minor compared to that of the NTVOCs. We added this sensitivity analysis in the current version of the manuscript, section 6 (see reply to comment 4). We also modified the result section 5.1, as indicated in the reply to the reviewer’s third comment.
Figure S3: Influence of the chosen volatility distribution (OMSV.Vol.dist) on the resulting SOA formed at low (Exp 1, 2, 3 and 4) and high (Exp 8, 9, 10 and 11) temperatures. Different volatility distributions (OMSV.Vol.dist) from May et al. (2013) were used in combination with OMSV.∆Hvap = {70'000 – 11'000 x log(C*)} J mol⁻¹ and the same oxidation scheme optimized during this study. The resulting SOA formed (grey area) is compared with the one obtained when OMSV.Vol.distref was used (black line). The sensitivity analysis shows that the results are only slightly sensitive to the assumed OMSV.Vol.dist, especially at low temperature.

3. Section 3 needs to be re-organized and split in 3 sections as follow: i) section 3 will present the box model, ii) section 4 will present the set of parameters (∆H, Y, kOH) that gives the best fit and the methodology used to obtain it, and iii) section 5 will present the results based on the optimum set of parameters.

Section 3 was re-organized as follows:

3 Model description

The representation of SOA formation 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, Cᵢ*, and the total concentration of organic aerosol, C_OA:

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

(1)

Here, \( \xi_i \) is the partitioning coefficient of i (condensed-phase mass fraction). Cᵢ* is a semi-empirical property (inverse of the Pankow-type partitioning coefficient, Kᵢ), reflecting not only the saturation vapor pressure of the pure constituents \( \{P_{lii}\} \) 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.
The volatility basis set approach (VBS) proposed by Donahue et al. (2006) provides a framework for the representation of both the chemical aging and the associated volatility of particulate organic matter evolving in the atmosphere. The approach separates the organics into logarithmically spaced bins of effective saturation concentrations \( C^*_i \), at 298 K. This has been later extended (Donahue et al., 2011, 2012) by introducing surrogate compounds with different carbon and oxygen numbers following the group contribution approach based on the SIMPOL method (Pankow and Asher, 2008) (Eq 2).

\[
\log C^*_i = (n_c^0 - n_c^i)b_c - n_o^i b_o - 2 \frac{n_c^i n_o^i}{n_c^i + n_o^i} b_{CO}
\]

where \( b_c \) and \( b_o \) represent the carbon-carbon and oxygen-oxygen interactions, respectively, \( b_{CO} \) describes the non-ideal solution behaviour and \( n_c^0 = 25 \), represents the reference point for pure hydrocarbons (1 \( \mu \)g m\(^{-3}\) of alkene). \( n_c^i \) and \( n_o^i \) are the carbon and oxygen numbers, respectively, for the \( i \)th saturation concentration, at 298 K. In this configuration, the model becomes 2-dimensional (2D-VBS), capable of tracking the volatility and oxidation state (O:C ratios) (Donahue et al., 2011, 2012) of oxidation products arising from functionalization and fragmentation of their precursors.

Here, we have used the VBS scheme proposed by Koo et al. (2014), referred to as a hybrid 1.5D-VBS and adapted for regional models. In this framework, the molecular space is not discretised according to the species saturation concentration and oxidation state, but rather every SOA surrogate is given an average molecular composition \((C_{x}H_{y}O_{z})\) – as a function of its volatility and the precursor it derives from. While a further simplification of the system compared to the 2D-VBS, this approach significantly decreases the degree of freedom of the model, while still providing means to evaluate the bulk aerosol oxidation state based on the knowledge of the surrogate molecular composition. This is especially suitable given the limited constrains available, namely the precursor composition, the precursor concentration, the POA concentration, the aged OA concentration and the O:C ratios.

In practice, five volatility bins ranging from 0.1 to 1000 \( \mu \)g m\(^{-3}\) in saturation concentration were used to model the partitioning of the POA and SOA fractions. The weighted average carbon and oxygen numbers of the NTVOCs mixture retrieved from PTR-MS measurements were used in combination with the group contribution approach (Eq. 2) to estimate the average saturation concentration for SOA precursors yielding \( \sim 10^6 \) \( \mu \)g m\(^{-3}\), which falls within the IVOC saturation concentration range limit (Donahue et al., 2012; Koo et al., 2014; Murphy and Pandis, 2009) (Table 1).

A total number of 3 sets were used to describe the organic material. The first set was used to distribute the primary emissions (set1). Two other sets were used to model the formation and evolution of SOA. Oxidation products of SVOC material arising from primary emissions were allocated to set2, whereas oxidation products from NTVOCs were allocated to set3 (Fig. 1). The specific molecular structures for each of the sets and bins were retrieved using the group contribution approach and the Van Krevelen relation (Table 1) (Donahue et al., 2011; Heald et al., 2010).

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 (\( C_i^* < 0.1 \mu \)g m\(^{-3}\)) and semi-volatile ranges \((\text{OM}_{\text{sv}}) (0.1< C_i^* < 1000 \mu \)g m\(^{-3}\)) in set 1 (Table 1) is based on the work of May et al. (2013). This work revealed that the majority of the emitted primary organic 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 thermos-denuder.

The oxidation of semi-volatile material would tend to increase the compounds’ oxygen number and decrease their volatility and carbon number, due to functionalization and fragmentation. We assume that the oxidation of the primary semi-volatile compounds with \( C_{11}-C_{14} \) decreases their volatility by one order of magnitude and yields \( C_{6}-C_{10} \) surrogates, placed in set2, based on the work of Donahue et al. (2011, 2012). Based on these assumptions and using the group contribution approach, the oxygen numbers for set2 is predicted to vary between 2.26 and 4.56 (Table 1). Thus, the model implicitly accounts for the addition of 1.1 to 1.5 oxygen atoms and the loss of 2.75 to 4.25 carbon atoms, with one oxidation step.

Set3 was constrained based on the PTR-MS data. The measurements suggested an average NTVOC carbon and oxygen number of about 7 and 1, respectively. Based on reported molecular speciation data (e.g. Kleindienst et al., 2007), we expect the products of \( C_7 \) compounds to have a \( C_5-C_6 \) carbon backbone. These products were placed in set3 following a kernel function based on the distribution of naphthalene oxidation
products. At least two oxygen atoms were added to the NTVOC mixture upon their oxidation (Table 1). The overall, O:C ratio in the whole space roughly spans the range from 0.1 to 1.0.

Multi-generation chemistry (aging) is also accounted for by the model. Unlike the 2D-VBS, the 1.5D-VBS does not use different kernel functions, to discretise the distribution of the oxidation products according to their log(C*) and O:C ratios, when functionalization and fragmentation occur. Instead, to reduce the computational 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 may effectively represents the functionalization and fragmentation processes, 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 $4 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ 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), while the rate of increase in oxygen atoms does not decrease with the oxidation generation number, the compounds’ fragmentation significantly increases. The fragmentation branching ratio has often been 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 NTVOCs leads to 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 of decreasing the number of carbon atoms and increasing the number of oxygen atoms adopted here simultaneously describes both processes.

4 Parameterization methodology
The modelling approach involves two steps.

i) First, we modelled the partitioning of POA for the 11 smog chamber experiments (8 experiments at RH=50% and 3 experiments at RH=90%) before aging begins. This step enables constraining the amounts of primary semi-volatile organic matter (OM$_{SV}$) in the different volatility bins (OM$_{SV}$.Vol.dist) and the enthalpy of vaporization of the different surrogates (OM$_{SV}$.$\Delta$H$_{vap}$). Combinations of OM$_{SV}$.Vol.dist and OM$_{SV}$.$\Delta$H$_{vap}$ of primary biomass burning semi-volatile compounds are reported in May et al. (2013), obtained based on thermo-denuder data. Several combinations of OM$_{SV}$.$\Delta$H$_{vap}$ and OM$_{SV}$.Vol.dist were tested. The amount of OM$_{SV}$ was varied until the measured POA mass at $t=0$ (OA$_{t=0}$) was reached and the resulting NTVOCs/OM$_{SV}$ was calculated for the different experiments. The average NTVOCs/OM$_{SV}$ calculated at high and low temperatures were then compared and only combinations of OM$_{SV}$.$\Delta$H$_{vap}$ and OM$_{SV}$.Vol.dist that yielded similar NTVOCs/OM$_{SV}$ ratios at low and high temperatures, within our experimental variability were considered to fit our data.

ii) Second, the obtained volatility distributions were used to model the aging of the emissions and SOA formation within the hybrid 1.5D-VBS framework. The time-dependent OA mass and O:C ratios were used as model constraints and the NTVOC reaction rates ($k$$_{OH}$-NTVOCs) and yields (Y) as well as average enthalpy of evaporation for secondary material in set 2 and 3 (SOA.$\Delta$H$_{vap}$) were retrieved. In section 6 we will discuss how other a priori assumed parameters influence the results.. For the second step, only experiments performed at RH=50% were used, as high RH might favour further uptake of oxygenated secondary organic material into the bulk phase, effectively increasing aerosol yields (Zuend and Seinfeld, 2012). Such effects are beyond the scope of this study.
5 Results

5.1 Inferred OMsv and NTVOCs/OMsv ratios from measurements and partitioning theory

Based on the PTR-MS and AMS measurements of gas and particle phase organic material at t=0, we seek to determine, the ratio NTVOCs/OMsv and the OMsv$_{\Delta H_{vap}}$ that represent best the observations at high and low temperatures. Combinations of enthalpies of vaporization and volatility distributions of primary biomass burning semi-volatile compounds are reported in May et al. (2013), based on thermo-denuder data. We note that in the current version of the 1.5D-VBS the volatility distribution (Table 1), subsequently referred to as OMsv$_{Vol.dist$_{REF}$}$ is used in combination with OMsv$_{\Delta H_{vap}} = \{85'000 – 4'000 \times \log(C*)\} \text{ J mol}^{-1}$, based on recommendations of May et al. (2013). Here, several combinations of OMsv$_{\Delta H_{vap}}$ functions and OMsv$_{Vol.dist}$ were tested.

In table 2, the measured OA$_{t=0}$ for all the 11 experiments, which ranges from 6.0 $\mu$g m$^{-3}$ to 22.6 $\mu$g m$^{-3}$, are reported. The OMsv values that match the measured OA$_{t=0}$ are shown as an example for the cases when OMsv$_{\Delta H_{vap}} = \{85'000 – 4'000 \times \log(C*)\} \text{ J mol}^{-1}$ (recommended by May et al., 2013) and OMsv$_{\Delta H_{vap}} = \{70'000 – 11'000 \times \log(C*)\} \text{ J mol}^{-1}$ were used in combination with OMsv$_{Vol.dist$_{REF}$}$. The average NTVOCs/OMsv ratios obtained using both OMsv$_{\Delta H_{vap}}$ functions are compared at high and low temperatures in Table 3. OMsv$_{\Delta H_{vap}} = \{70'000 – 11'000 \times \log(C*)\} \text{ J mol}^{-1}$ used in combination with OMsv$_{Vol.dist$_{REF}$}$ reduced the observed difference in the average NTVOCs/OMsv ratios at the two temperatures. In general, functions with lowest OMsv$_{\Delta H_{vap}}$ better explained the change in the measured OA$_{t=0}$ with temperature, with OMsv$_{\Delta H_{vap}} = \{70'000 – 11'000 \times \log(C*)\} \text{ J mol}^{-1}$, fitting best our data. The volatility distributions that could explain our observation have an aggregate contribution in the volatility bins Log(C*) = 1 and 2 $\leq$ 0.3.

In the following, OMsv$_{\Delta H_{vap}} = \{70'000 – 11'000 \times \log(C*)\} \text{ J mol}^{-1}$ shall be used in combination with OMsv$_{Vol.dist$_{REF}$}$ as model inputs and in section 6, we assess the sensitivity of the resulting NTVOCs/OMsv ratios and SOA formed on the chosen OMsv$_{Vol.dist}$.

Using these model parameters, the overall NTVOCs/OMsv ratio was determined to be around 4.75. Fig. 2 shows the resolved equilibrium phase partitioning (Eq. 1) between the gas and particle phase at the beginning of each of the 11 smog chamber experiments (OA$_{t=0}$). As expected, most of the material is found in the gas-phase at high temperatures, while at lower temperature only part of the compounds with saturation concentrations (at 20°C) between 100 and 1000 $\mu$g m$^{-3}$ would reside in the gas-phase.

5.2 Wood burning aging at low and high temperatures

In this section, we will focus on the emission aging. Using the NTVOCs/OMsv ratio and the enthalpies of vaporization retrieved in the previous sections, we modelled the eight different smog chamber experiments: No. 1, 2, 3, 4 (low temperature) and No. 8, 9, 10, 11 (high temperature) performed at the same relative humidity (RH = 50%). For each of the eight experiments we injected an average mixture of NTVOCs equal to 4.75 times the OMsv mass before the start of the aging. NTVOCs react solely with OH, whose concentration was retrieved from PTR-MS measurements. The temperature dependence of the reaction rates was also taken into account through the Arrhenius equation. The reaction rates ($k_{\text{OH-NTVOC}}$) and yields (Y) of the NTVOCs as well as enthalpies of vaporization of SOA (SOA$_{\Delta H_{vap}}$) in set2 and set3 were varied within specific physically realistic ranges that were already proposed in literature (Koo et al., 2014; Donahue et al., 2013; Grieshop et al., 2009; Robinson et al., 2007). We varied $k_{\text{OH-NTVOC}}$ between 2 and 4 x 10$^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$ in steps of 0.1 x 10$^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$, and yields between 0.1 and 0.4 ppm ppm$^{-1}$ in steps of 0.01 ppm ppm$^{-1}$. The yields refer to the sum of the aerosol yields of the four volatility bins. A naphthalene kernel mass distribution with increasing contribution as a function of log(C*) is used to distribute the products in the four bins (Murphy and Pandis, 2009). Values for SOA$_{\Delta H_{vap}}$ are still highly uncertain. In this study, we explored a wide range of values from 15’000 J mol$^{-1}$ to 115’000 J mol$^{-1}$ in steps of 20’000 J mol$^{-1}$. The model performance for each combination of SOA$_{\Delta H_{vap}}$ and $k_{\text{OH-NTVOC}}$ was evaluated by calculating the root mean square error (RMSE) on both the O:C ratio and OA mass (giving the same weight on both quantities) for the eight experiments (giving the same weight for all experiments), and the best fitting solution is the one that minimized the RMSE. We performed a total number of 31248 simulations. Figure 3 shows the total errors for the OA mass (left side) and O:C ratio (right side) for different SOA$_{\Delta H_{vap}}$ Y and $k_{\text{OH-NTVOC}}$. The error of the OA mass varies from a minimum of ~25% up to more than 60 %, whereas the error of the O:C ratio are lower, ranging from approximately 15 % up to more than 30 %. For the OA mass, distinct regions with lower errors are visible in the central part of each panel with
different SOA.$\Delta H_{\text{vap}}$ representing the models that fitted best the measured OA. While a similar observation can be made for the O:C ratios, models with high SOA.$\Delta H_{\text{vap}}$ tend to reproduce the data less faithfully. The diamonds in Fig. 3 indicate the absolute best fitting solution ($k_{\text{OH-NTVOCs}} = 4.0 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$; SOA.$\Delta H_{\text{vap}} = 35'000$; $Y = 0.32$ ppm ppm$^{-1}$, in yellow) and the ones retrieved with a likelihood-ratio test allowing for 10% error form the best fit (red diamonds). Regions with lower errors are localized for $k_{\text{OH-NTVOCs}} \geq 2.5 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$ between SOA.$\Delta H_{\text{vap}}$ values of 35'000 and 55'000 J mol$^{-1}$.

Figure 4 shows the modelled and measured OA mass for all the 8 experiments. The primary organic aerosol fraction is reported as well as the SOA fraction from SVOCs and higher volatility NTVOCs. All the low temperature experiments (No. 1, 2, 3, 4 left side of the panel) were reproduced very well along with the concentration gradients at the end of each the experiments even though the model tends in general to slightly over-predict the final OA concentration and to under-predict the production rate. The POA fraction slightly increases at the very beginning of the aging phase, upon the increase in OA mass. POA then decreases as the experiments proceed as a result of its partitioning to the gas phase and subsequent oxidation. Most of the SOA was predicted to be formed from NTVOCs precursors (78-82%) and only a minor amount from SVOCs (18-22%). Meanwhile, at high temperatures, SVOCs contribute more significantly to SOA formation compared to low temperature experiments, although the majority of SOA still arise from NTVOCs. We note that at higher temperature the OA mass was slightly under-predicted for experiments No. 9, 10 and 11, but largely over-predicted for experiment No. 8 (see also Fig. S1). We do not have any experimental evidence to discard experiment No.8 as an outlier, but sensitivity analyses excluding this experiment would yield slightly lower SOA.$\Delta H_{\text{vap}}$ values (~15'000-35'000 J mol$^{-1}$).

Comparisons between measured and modelled O:C ratios are reported in Fig.5. Model and observation results match very well, especially upon aging. However, we note on the one hand that significant differences between measured and modelled O:C ratios at the beginning of the experiments are observed, without any systematic correlation with the chamber conditions (e.g. OA mass or temperature). These differences might be due to the variable nature of primary biomass smoke emissions, which cannot be accounted for in the model. On the other hand, it is noticeable that the model under-predicts in general the measured POA O:C ratios, suggesting that the parameters describing the O:C of primary emissions are suboptimal. These parameters include mainly the carbon and oxygen numbers of species in set 1, and to a lesser extent the OM$_{SV}$.Vol.dist and the OM$_{SV}$.$\Delta H_{\text{vap}}$, which are all adopted from previously published data. While this observation suggests in general the presence of compounds with lower carbon number (higher oxygen number) in the primary aerosols (e.g. C$_6$H$_{10}$O$_5$ anhydrous sugars which contribute ~15% of the POA, Ulevicius et al., 2016), we believe that we do not have suitable data (e.g. analysis at the molecular level) to propose a more accurate representation of POA compounds than currently available in the literature. In addition, the average bias in POA O:C ratios is <30%, well within the experimental uncertainties.

4. Section 4: This section should be renamed to section 6 if you follow my suggestion in the previous comment. The first paragraph here should be moved to the conclusions which are actually missing from the manuscript. Please add after this section the conclusions of your study.

We re-organized the conclusion session as also suggested by referee 2 and in the previous comment. The new section 6 (Discussion and major conclusions) 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 µg 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 the 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 33’000 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 $\Delta H_{vap} = [35'000 - 55'000] \text{kJ mol}^{-1}$ vs. weighted average of $\Delta H_{POA} \sim 50'000 \text{kJ mol}^{-1}$. Results presented here including the average NTVOCs/OMsv 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 µg 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 would yield a significant loss of compounds ‘volatility (~1.7 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\textsubscript{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 (OMsv + NTVOCs) of 6, 60 and 600 µg m\textsuperscript{-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% K\textsuperscript{-1} on average with higher effects predicted at higher loads (0.7% K\textsuperscript{-1} at 600 µg m\textsuperscript{-3} vs. 0.3% at 6 µg m\textsuperscript{-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\textsuperscript{7} molec cm\textsuperscript{-3} 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. \( \frac{\partial Y}{\partial T} = f(T, C_{OA}, OH_{exp}) \). SOA yields increase 0.03, 0.06 and 0.05 % K\textsuperscript{-1} on average for 6, 60 and 600 µg m\textsuperscript{-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 \( \log C_{OA} \) is shown at the different conditions: \( \frac{\partial Y}{\partial \log C_{OA}} = f(T, OH_{exp}) \). An increase in SOA yields with the \( \log C_{OA} \) 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~1.5 \times 10\textsuperscript{7} molec cm\textsuperscript{-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\textsuperscript{6} molec cm\textsuperscript{-3} h, or in 2-10 hours (at OH concentrations of (1-5) \times 10\textsuperscript{6} molec cm\textsuperscript{-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\textsuperscript{6} molec cm\textsuperscript{-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\textsuperscript{6} molec cm\textsuperscript{-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/OMS 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).

1. Abstract: The first sentence does not provide any information for the study presented here, therefore, it can be deleted.

This is done in the corrected version of the manuscript.

2. Page 1 line 17: Please briefly explain why the VBS scheme presented here is called hybrid.

The VBS scheme proposed here does not use different kernel functions for the distribution of the oxidation products when functionalization and fragmentation occur. Instead, to reduce the computational burden of the simulations, the model considers that the oxidation of a given surrogate yields only one other surrogate with lower volatility, higher oxygen number and lower carbon number. These properties should be considered as a weighted average of the properties relative to the complex mixture of compounds arising from the functionalization and fragmentation processes. Accordingly, while a further simplification of the system compared to the 2D-VBS, the 1.5D-VBS approach may effectively represent the functionalization and fragmentation processes, while reducing the parameter space and the computational burden. Based on this and the previous comments, further clarifications were added to the text in the revised section 3 as follows:

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 log(C*) and O:C ratios, when functionalization and fragmentation occur. Instead, to reduce the computational 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 x 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 often been parameterized as a function of the compounds’ O:C ratios (e.g. fragmentation ratio = f(O:C^{1/3}), where \( a \) 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 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 of decreasing the number of carbon atoms and increasing the number of oxygens atoms adopted here, simultaneously describes both processes.

3. Page 2 lines 43-44: with the term “semi-volatile” you refer only to organic compounds or to inorganic as well? Please clarify. Similarly, with the term “fine particulate matter” do you imply only POA or total PM$_{2.5}$?

We refer to organic compounds in this context. We replaced the text as follows:
The fact that some semi-volatile compounds can exist in either gaseous or particulate form results in considerable uncertainties in the emission inventories for primary organic aerosol (POA).

4. Page 3 equations 1,2: Please move the equations to section 3 where they are actually used.

This has been done in the corrected version of the manuscript. Equations are now in section 3.

5. Page 4 line 101: Please add the global models as well that have included the VBS scheme for SVOCs and IVOCs (e.g., Hodzic et al., 2016; Jathar et al., 2011; Shrivastava et al., 2015; Tsimpidi et al., 2014).

We added the suggested references in the introduction and modified the sentence as below.

Regional and global chemical transport models (CTMs) have been increasingly updated with a VBS scheme with varying complexities (Bergström et al., 2012; Ciarelli et al., 2016a; Hodzic et al., 2016; Jathar et al., 2011; Murphy et al., 2011; Shrivastava et al., 2015; Tsimpidi et al., 2014; Zhang et al., 2013).

6. Page 4 line 118: Correct “Founoukis” to “Fountoukis”

We corrected the typos.

7. Page 4 line 124: At this point it will be very useful to add several studies that have reported a possible underestimation of residential wood combustion emissions (e.g., move Bergström et al., 2012 here and also add Kostenidou et al., 2013) and difficulties in models to reproduce OA due to lack of information for BBOA emissions and aging (e.g., Fountoukis et al., 2016; Tsimpidi et al., 2016). Please add even more studies if possible. This will help you highlight the importance of the presented study.

We added the missing studies suggested by the referee and reformulate the sentence. The new text reads as follows:

Fountoukis et al. (2014) were among the first to implement the VBS approach into a large-scale aerosol model, following the multiple distribution framework approach proposed by Tsimpidi et al. (2010). They found that the approach considerably improved the model result for OA when compared to a range of observations from the EUCAARI field campaign (Kulmala et al., 2009, 2011) and from EMEP monitoring network (Tørseth et al., 2012). Bergström et al. (2012) used the EMEP model for the period of 2002-2007 to compare different partitioning and aging schemes. Their results indicate the importance as well as a potential underestimation of wood-burning emissions in Europe in line with other studies (Kostenidou et al., 2013; Fountoukis et al., 2016; Tsimpidi et al., 2016).

8. Page 5 lines 129-132: This discussion is not needed here. A lot of VBS modeling studies in the past have reported the importance of the chemical aging. However, at this point, you should emphasize in the need to constrain the parameters that control the simulation of the OA formation specifically from the wood burning sources.
We do agree with the reviewer that additional information to justify the importance of constraining parameters that control OA formation especially from wood burning sources are needed. Accordingly, the text has been modified in the introduction as below:

*Radiocarbon dating (Mohr et al., 2012; Zotter et al., 2014) and measurements of specific molecular markers including methyl-nitrocatechols (Iinuma et al., 2010; El Haddad et al., 2013), during winter reveal the importance of residential wood burning for SOA formation. However, parameters needed for the simulation of the aging of biomass smoke remain not well constrained.*

9.
Page 5 lines 143-144: Remove the parenthesis from Heringa et al. and Bruns et al.

Done as suggested.

10.
Page 7 line 193: Which are these several sets tested? Later in the manuscript you only report two (Eq. 3 and 4).

The sentence was removed in the revised manuscript.

11.
Page 7 line 198: Why the VBS approach presented here is called hybrid? Please explain.

This has been explained above in comment 2.

12.
Page 7, line 200: “Unlike previous 2D-VBS schemes”: in which schemes do you refer to? Please add references.

We included the missing reference (Donahue et al., 2011).

13.
Page 8, line 234: Please add reference for the group contribution approach and the Van Krevelen relation.

We included the missing reference (Donahue et al., 2011; Heald et al., 2010).

14.
Page 10 line 285: change “and” with “to”.

Done as suggested.

15.
Page 10 lines305-307: Why the ranges used here are “physically realistic”? Please add references to support your assumption.

We limited our analysis to values that were already proposed in literature (Koo et al., 2014; Donahue et al., 2013; Grieshop et al., 2009; Robinson et al., 2007). We modified the sentence as below in the manuscript.

*The reaction rates \(k_{\text{OH-NTVOC}}\) and yields \(Y\) of the NTVOCs as well as enthalpies of vaporization of SOA \(\Delta H_{\text{vap}}\) in set2 and set3 were varied within specific physically realistic ranges that were already proposed in the literature (Koo et al., 2014; Donahue et al., 2013; Grieshop et al., 2009; Robinson et al., 2007).*

16.
Page 10 line 308: Are the yields used here, the total aerosol yields (sum of the aerosol yields of the four volatility bins used)? If so, how you distribute them in the four volatility bins? Do you use a constant ratio? Please add this information here and a reference to support it.
The yields used here are the sum of the aerosol yields of the four volatility bins. A naphthalene kernel mass distribution with increasing contribution as a function of log(C*) is used to distribute the products in the four bins (Murphy and Pandis, 2009). The sentence was modified in the manuscript as below:

The yields refer to the sum of the aerosol yields of the four volatility bins. A naphthalene kernel mass distribution with increasing contribution as a function of log(C*) is used to distribute the products in the four bins (Murphy and Pandis, 2009).

17. Page 10 line 311: i,j, and k are not set. Use $\Delta H_{vapSOA}, Y, k_{OH-NTVOCs}$ instead

Done as suggested as well as for the other occurrence in the manuscript.

18. Page 11, line 324-325: Please provide the values of the set of parameters ($\Delta H_{vapSOA}, Y, k_{OH-NTVOCs}$) that gives the absolute best fitting (the yellow diamond). This is the major contribution of this study since it can be used in large scale models and it should be reported clearly.

We added the information about the best fitting solution in session 5.2 as below:

The diamonds in Fig. 3 indicate the absolute best fitting solution ($k_{OH-NTVOCs} = 4.0 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$; SOA-$\Delta H_{vap} = 35'000$; $Y = 0.32$ ppm ppm$^{-1}$, in yellow), and the ones retrieved with a likelihood-ratio test allowing for 10% error form the best fit (red diamonds).

19. Page 11 line 336-337: Please be more specific by reporting the fraction of SOA that is formed from NTVOCs and SVOCs. Furthermore, I would change the “NTVOCs” to IVOCs in the entire manuscript in order to be more consistent to the terminology used widely in the field, but this is a personal preference.

We added the fraction of SOA that is formed from the two classes of precursors, as follows:

Most of the SOA was predicted to be formed from NTVOCs precursors (78-82%) and only a minor amount from SVOCs (18-22%).

In the first VBS publications (e.g. Robinson et al., 2007), the term IVOCs has been proposed to designate SOA precursors thought to be of intermediate volatility. However, the term has been changed since (e.g. Jathar et al., 2014 PNAS), and a more general term (non-traditional) was used to describe the aggregate of SOA precursors whose chemical and physical properties (including volatility) are unknown and therefore they are not traditionally considered in models. We chose to use this term as it describes accurately the compound class of both volatile and intermediate volatility compounds that can act as SOA precursors in our case, but is not yet considered in models.

20. Page 13 line 398: Please remove “our”. It is not the same group of authors.

Done as suggested.

21. Page 15 Table 1: Table 1 provides the same information with figures 1 and 2. You can add a line for NTVOCs and two columns for emission factors and $\Delta H_{in}$ Table 1 and erase Figures 1 and 2. Otherwise just erase Table 1 and keep Figures 1 and 2.

We agree with the referee. We modified Table 1 as below and erased Figure 1 and Figure 2.

Table 1. Properties of the VBS space. Oxygen numbers for each volatility bin were calculated using the group-contribution of Donahue et al. (2011). Hydrogen numbers were calculated from the van Krevelen
relation (Heald et al., 2010).

<table>
<thead>
<tr>
<th></th>
<th>Log (C*)</th>
<th>Oxygen number</th>
<th>Carbon number</th>
<th>Hydrogen number</th>
<th>O:C ratio</th>
<th>Molecular weight</th>
<th>Emission factors</th>
<th>( \Delta H ) (\text{J mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>POA set1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-1</td>
<td>4.11</td>
<td>11.00</td>
<td>17.89</td>
<td>0.37</td>
<td>216</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>3.43</td>
<td>11.75</td>
<td>20.07</td>
<td>0.29</td>
<td>216</td>
<td>0.1</td>
<td>85'000-70'000</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2.73</td>
<td>12.50</td>
<td>22.27</td>
<td>0.22</td>
<td>216</td>
<td>0.1</td>
<td>81'000-59'000</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.01</td>
<td>13.25</td>
<td>24.49</td>
<td>0.15</td>
<td>216</td>
<td>0.2</td>
<td>77'000-48'000</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.27</td>
<td>14.00</td>
<td>26.73</td>
<td>0.09</td>
<td>215</td>
<td>0.4</td>
<td>73'000-37'000</td>
</tr>
<tr>
<td><strong>SOA set2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-1</td>
<td>4.53</td>
<td>9.00</td>
<td>13.47</td>
<td>0.50</td>
<td>194</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>4.00</td>
<td>9.25</td>
<td>14.50</td>
<td>0.43</td>
<td>189</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3.40</td>
<td>9.50</td>
<td>15.60</td>
<td>0.36</td>
<td>184</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.83</td>
<td>9.75</td>
<td>16.67</td>
<td>0.29</td>
<td>179</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td><strong>SOA set3</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-1</td>
<td>5.25</td>
<td>5.00</td>
<td>4.75</td>
<td>1.05</td>
<td>149</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>4.70</td>
<td>5.25</td>
<td>5.80</td>
<td>0.90</td>
<td>144</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.20</td>
<td>5.50</td>
<td>6.80</td>
<td>0.76</td>
<td>140</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.65</td>
<td>5.75</td>
<td>7.85</td>
<td>0.63</td>
<td>135</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.15</td>
<td>6.00</td>
<td>8.85</td>
<td>0.52</td>
<td>131</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td><strong>NTVOCs</strong></td>
<td>6</td>
<td>1.22</td>
<td>7.22</td>
<td>7.14</td>
<td>0.16</td>
<td>113</td>
<td>4.75(OMsv)</td>
<td>-</td>
</tr>
</tbody>
</table>

As described above, we think that the term NTVOCs better describes the compounds detected by the PTR, which are not traditionally considered in models and may contain both volatile and intermediate volatility species. The term IVOCs would imply that all of these compounds have a log(C*) between 4 and 6, which is not necessarily the case. The new table 2 in the corrected version of the manuscript is represented below:

Page 16 Table 2: Personally I prefer the use of “IVOCs” instead of “NTVOCs” in the entire manuscript. If you keep using the term “NTVOCs” please change the “measured IVOC” in the first column of the table with “measured NTVOCs.”
Table 2. Modelled and experimental data for 11 wood burning experiments. The OM$_{sv}$ mass at the beginning of each chamber experiment is reported together with the measured OA$_{t=0}$ and the initial NTVOCs concentration. NTVOCs/OM$_{sv}$ is the ratio between the measured NTVOCs and the calculated OM$_{sv}$ mass at the beginning of each experiment for the two different OM$_{SV}$.ΔH$_{vap}$ functions: SOL1: OM$_{SV}$.ΔH$_{vap}$ = {85'000 – 4'000 x log(C*)} J mol$^{-1}$ and SOL2: OM$_{SV}$.ΔH$_{vap}$ = {70'000 – 11'000 x log(C*)} J mol$^{-1}$, used in combination with OM$_{SV}$.Vol.dist$_{ref}$ presented in Table 1.

<table>
<thead>
<tr>
<th>Exp</th>
<th>T=263 K</th>
<th>T=263 K</th>
<th>T=263 K</th>
<th>T=263 K</th>
<th>T=288 K</th>
<th>T=288 K</th>
<th>T=288 K</th>
<th>T=288 K</th>
<th>T=288 K</th>
<th>T=288 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RH=50%</td>
<td>RH=50%</td>
<td>RH=50%</td>
<td>RH=90%</td>
<td>RH=50%</td>
<td>RH=50%</td>
<td>RH=50%</td>
<td>RH=50%</td>
<td>RH=50%</td>
<td>RH=50%</td>
</tr>
<tr>
<td>Measured NTVOCs [μg/m$^3$]</td>
<td>185.1</td>
<td>-</td>
<td>-</td>
<td>79.3</td>
<td>143.5</td>
<td>91.7</td>
<td>68.7</td>
<td>121.5</td>
<td>190.4</td>
<td>174.6</td>
</tr>
<tr>
<td>Measured OA$_{t=0}$ [μg/m$^3$]</td>
<td>12.3</td>
<td>8.1</td>
<td>16.7</td>
<td>9.3</td>
<td>12.0</td>
<td>17.7</td>
<td>6.0</td>
<td>22.6</td>
<td>17.5</td>
<td>18.7</td>
</tr>
<tr>
<td>SOL1 Modelled OM$_{sv}$ [μg/m$^3$]</td>
<td>17.3</td>
<td>12.1</td>
<td>22.4</td>
<td>13.6</td>
<td>16.9</td>
<td>23.5</td>
<td>9.5</td>
<td>46.6</td>
<td>37.7</td>
<td>39.8</td>
</tr>
<tr>
<td>SOL2 Modelled OM$_{sv}$ [μg/m$^3$]</td>
<td>22.7</td>
<td>15.8</td>
<td>29.5</td>
<td>17.8</td>
<td>22.2</td>
<td>31.0</td>
<td>12.3</td>
<td>49.7</td>
<td>40.1</td>
<td>42.4</td>
</tr>
<tr>
<td>SOL1 (NTVOCs)/(OM$_{sv}$)</td>
<td>10.7</td>
<td>-</td>
<td>-</td>
<td>5.1</td>
<td>8.5</td>
<td>3.9</td>
<td>7.2</td>
<td>2.6</td>
<td>5.0</td>
<td>4.4</td>
</tr>
<tr>
<td>SOL2 (NTVOCs)/(OM$_{sv}$)</td>
<td>8.1</td>
<td>-</td>
<td>-</td>
<td>4.4</td>
<td>6.4</td>
<td>3.0</td>
<td>5.6</td>
<td>2.4</td>
<td>4.7</td>
<td>4.1</td>
</tr>
</tbody>
</table>
23. Page 18 Figure 1: I would keep the Table 1 instead of the figures 1 and 2. If you decide to keep the figures do not show the emission factors to all of them. Use a different subfigure for the emission factors and use columns for all the other variables in the rest of the subfigures. Also change the “volatility distribution” to “emission factors” in the y-axis label of the figure. Finally, give a $\Delta H$ value for the specie with $C^*=10^{-1}$.

We agreed with the referee. We kept Table 1 and removed Figure 1 and 2.

24. Page 20 Figure 3: Where is the specie of the set2 with $C^*=10^3$ is coming from? This specie should not exist. Please delete it from table 1 as well.

Done as suggested.

25. Page 24 Figure 6: Does the underestimation of OA mass in the high temperature experiments indicate that you have overestimate the volatility of OM$_w$? According to my second major comment you have chosen a volatility distribution which is not proposed by May et al. (2013) for use with the $\Delta H$ used in this simulations.

We have to disagree with the reviewer comment. We do not underestimate the SOA at higher temperatures. Indeed, much higher experimental variability occurred at higher temperature, but the average model bias is close to 0, with a significant overestimation of the SOA mass for 1 experiment (No. 8) and much lower underestimation for the other 3 experiments (see figure S1). We have chosen not to discard any of the experiments, without any experimental evidence suggesting any of them to be an outlier. We have to also add that the $\Delta H$ function for primary emissions does not have a significant influence on the amounts of SOA formed at different temperatures (see the new Figure S3 and the related discussion in section 6). We have chosen this function, instead of that recommended by May et al. (2013), as it fitted much better the observed POA and NTVOCs at both low and high temperatures, under our conditions. Meanwhile, the change in the amounts of SOA formed with temperature is mostly controlled by the $\Delta H$ of SOA species, which is here included as a fitting parameter. These explanations have been added to the new version of the manuscript, in section 5.2, as follows:

Figure 4 shows the modelled and measured OA masses for all the 8 experiments. The primary organic aerosol fraction is reported as well as the SOA fraction from SVOCs and higher volatility NTVOCs. All the low temperature experiments (No. 1, 2, 3, 4 left side of the panel) were reproduced very well along with the concentration gradients at the end of each the experiments even though the model in general tends to slightly over-predict the final OA concentration and to under-predict the production rate. The POA fraction slightly increases at the very beginning of the aging phase, upon the increase in OA mass. As the experiments proceed, POA decreases as a result of its partitioning to the gas phase and subsequent oxidation. Most of the SOA was predicted to be formed from NTVOCs precursors (78-82%) and only a minor amount from SVOCs (18-22%). Meanwhile, at high temperatures, SVOCs contribute more significantly to SOA formation compared to low temperature experiments, although the majority of SOA still arise from NTVOCs. We note that at higher temperature the OA mass was slightly under-predicted for experiments No. 9, 10 and 11, but largely over-predicted for experiment No. 8 (see also Fig. S1). We do not have any experimental evidence to discard experiment No.8 as an outlier, but a sensitivity analysis with excluding this experiment yielded slightly lower SOA $\Delta H_{vap}$ values ($\sim 15'000-35'000$ J mol$^{-1}$).

26. Page 25 Figure 7: Why the measured O:C decreases at the beginning of the experiment No. 4?

Primary aerosols with high O:C ratios (up to 0.9) has been previously reported under certain burning conditions from AMS measurements. Based on Heringa et al. (2010), such oxygenated aerosols can be emitted from efficient burners, e.g. pellet stoves. This might be the case for experiment 4 where the O:C ratio of primary emissions is around 0.7 and decreases with the addition of less oxygenated SOA. Indeed, the model which represents all primary emissions with a single volatility distribution set, does not account for
the variation in the primary emission composition, but does satisfactorily (bias below 30%) capture the O:C ratio of average primary emissions. Additional explanations have been added to the manuscript in section 5.2:

Comparisons between measured and modelled O:C ratios are reported in Fig.5. Model and observation results match very well, especially upon aging. However, we note on the one hand that significant differences between measured and modelled O:C ratios at the beginning of the experiments can be observed, without any systematic correlation with the chamber conditions (e.g. OA mass or temperature). These differences might be due to the variable nature of primary biomass smoke emissions, which cannot be accounted for in the model. On the other hand, it is noticeable that the model generally under-predicts the measured POA O:C ratios, suggesting that the parameters describing the O:C of primary emissions are suboptimal. These parameters include mainly the carbon and oxygen numbers of species in set 1, and to a lesser extent the OM_Vol.dist and the OM_Vol.ΔH_vap, which are all adopted from previously published data. While this observation suggests the general presence of compounds with lower carbon number (higher oxygen number) in the primary aerosols (e.g. C₆H₁₀O₅ anhydrous sugars which contribute ~15% of the POA, Ulevicius et al., 2016), we believe that we do not have suitable data (e.g. analysis at the molecular level) to propose a more accurate representation of POA compounds. In addition, the average bias in the POA O:C ratios is <30%, well within the experimental uncertainties.

References


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 µg m⁻³ saturation concentration range (OMsv). 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 \( \Delta H_{vap} \) 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 cm³ s⁻¹, the \( Y \) of semi-volatile SOA surrogates ranged between 0.3 and 0.35 ppm ppm⁻¹, and the \( \Delta H_{vap} \) 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 \( \Delta H_{vap} = [35’000 - 55’000] \) kJ mol⁻¹ vs. weighted average of \( \Delta H_{POA} \approx 50’000 \) kJ mol⁻¹. Results presented here including the average NTVOCs/OmSV ratios and parameters required for representing SOA formation are all based on the use of one OMsv, Vol.dist. In Fig. S3, we have performed a sensitivity analysis where several OMsv, Vol.dist were tested in combination with the same SOA,ΔHvap function and the same reaction scheme. This analysis shows that the NTVOCs/OMsv 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 µg 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 (~1.7 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 µg 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% K^{-1} on average with higher effects predicted at higher loads (0.7% K^{-1} at 600 µg m^{-3} vs. 0.3% at 6 µg 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
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. \( \frac{\partial Y}{\partial T} = f(T, C_{OA}, OH_{exp}) \). SOA yields increase 0.03, 0.06 and 0.05 % K\(^{-1}\) on average for 6, 60 and 600 µg 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 \( \log C_{OA} \) is shown at the different conditions: \( \frac{\partial Y}{\partial \log C_{OA}} = f(T, OH_{exp}) \). An increase in SOA yields with \( \log C_{OA} \) 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 ~1.5 \( \times 10^7 \) molec 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 cm\(^{-3}\) h, or in 2-10 hours (at OH concentrations of (1-5) \( \times 10^6 \) 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 \( \times 10^6 \) molec 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 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/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).

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, $C_{OA}$:

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

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 ($p_i^*$) 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±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 $C^* = (0.01, 0.1) \mu g m^{-3}$ range, whereas semi-volatile compounds into the $C^* = (1, 10, 100) \mu g m^{-3}$ 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 $10^2 \mu g m^{-3}$ in saturation concentration range ($C^*$) as semi-volatile organic compounds (SVOCs). In this approach, the lowest volatility bin ($C^* = 0.1 \mu g m^{-3}$) represents all the organic compounds with $C^* \leq 0.1 \mu g m^{-3}$, 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 ($C_i^+ = 0.1 \mu g m^{-3}$), and semi-volatile ranges ($OM_{sv}$) ($0.1 < C_i^+ < 1000 \mu g m^{-3}$) 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. $10^6 \mu g m^{-3}$). 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 ~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 (~1.7 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 Log(C*) and O:C ratios, when functionalization and fragmentation occur. Instead, to reduce the
computational 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 $4 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ 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 = $f(O:C^{1/\alpha})$, 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 at 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$_{30}$ 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$_{SV}$ 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$_{SV}$ ratio of 4.75 was retrieved from recent state-of-the-art wood burning chamber experiments conducted at different temperatures (Bruns 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 ~1.5 x 10$^7$ molec 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 x 10$^6$ molec cm$^{-3}$ h, or in 2-10 hours (at OH concentrations of (1-5) x 10$^6$ molec 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 x 10$^6$ molec 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) x 10$^6$ 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).*

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/OMSV 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/OMSV 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.

References


Constraining a hybrid volatility basis set model for aging of wood burning emissions using smog chamber experiments: A box-model study based on the VBS scheme of the CAMx model (v5.40)

Giancarlo Ciarelli¹, Imad El Haddad¹, Emily Bruns¹, Sebnem Aksoyoglu¹, Ottmar Möhler², Urs Baltensperger¹ and André S.H. Prévôt¹.

[¹]{Paul Scherrer Institute, Laboratory of Atmospheric Chemistry, 5232 Villigen PSI, Switzerland}  
[²]{Karlsruhe Institute of Technology, Institute of Meteorology and Climate Research, Germany}

Correspondence to: I. El Haddad and S. Aksoyoglu (imad.el-haddad@psi.ch and sebnem.aksoyoglu@psi.ch)

Abstract

Semi-volatile and intermediate volatility organic compounds (SVOCs, IVOCs) are not included in the current non-methane volatile organic compounds (NMVOCs) emission inventories but may be important for the formation of secondary organic aerosol (SOA). In this study, novel wood combustion aging experiments performed at different temperatures (263 K and 288 K) in a ~7 m³ smog chamber were modelled using a hybrid volatility basis set (VBS) box model, representing the emission partitioning and their oxidation against OH. We combine aerosol-chemistry box model simulations with unprecedented measurements of non-traditional volatile organic compounds (NTVOCs) from a high-resolution proton transfer reaction mass spectrometer (PTR-MS) and with organic aerosol measurements from an aerosol mass spectrometer (AMS). In so-doing, we are able to observationally-constrain the amounts of different NTVOCs aerosol precursors (in the model) relative to low-volatility and semi-volatile primary organic material (OMsv) which is partitioned based on current published volatility distribution data. By comparing the NTVOCs/OMsv ratios at different temperatures, we determine the enthalpies of vaporization of primary biomass burning organic aerosols. Further, the developed model allows for evaluating the evolution of oxidation products of the semi-volatile and volatile precursors with aging. More than 30,000 box model simulations were performed to retrieve the combination of parameters that fit best the observed organic
aerosol mass and O:C ratios. The parameters investigated include the NTVOC reaction rates and yields as well as enthalpies of vaporization and the O:C of secondary organic aerosol surrogates. Our results suggest an average ratio of NTVOCs to the sum of non-volatile and semi-volatile organic compounds of ~4.75. The mass yields of these compounds determined for a wide range of atmospherically relevant temperatures and organic aerosol (OA) concentrations were predicted to vary between 8 and 30 % after 5 hours of continuous aging. Based on the reaction scheme used, reaction rates of the NTVOC mixture range from 3.0 x 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} to 4.0 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}. The average enthalpy of vaporization of SOA surrogates was determined to be between 55,000 J mol^{-1} and 35,000 J mol^{-1} which implies a yield increase of 0.03 - 0.06 % K^{-1} with decreasing temperature. The improved VBS scheme is suitable for implementation into chemical transport models to predict the burden and oxidation state of primary and secondary biomass burning aerosols.

1 Introduction

The fact that some semi-volatile compounds can exist in either gaseous or particulate form results in considerable uncertainties in the emission inventories for primary organic aerosol (POA) and fine particulate matter (PM_{2.5}) and non-methane volatile organic compounds (NMVOCs). Emissions of PM_{2.5} are generally based on emission factors (EF) of primary organic aerosol (POA) which may be over- or under-predicted depending on the measurement method used (Lipsky and Robinson, 2006; Nussbaumer et al., 2008a, 2008b.). In Europe, residential wood-burning emissions constitute one of the main anthropogenic sources of POA and potentially secondary organic aerosol (SOA), especially during winter periods with contribution from 15% to 50% of the total organic mass (Crippa et al., 2013; Waked et al., 2014). Thus, great effort was devoted in the past to better constrain the uncertainties related to wood burning emissions and their evolution in the atmosphere (Denier van der Gon et al., 2015; May et al., 2013). Recent year-long source apportionment studies based on ACSM (aerosol chemical speciation monitor) measurements in central Europe suggest that winter secondary organic aerosol fingerprints resembles those measured during chamber studies of biomass burning emission aging (Canonaco et al., 2015).

One of the main complications when dealing with organic aerosol (OA) is imposed by the semi-volatile and highly reactive nature of organic material (Robinson et al., 2007). Depending on ambient conditions freshly emitted primary organic particles can undergo evaporation. The fraction of an organic compound \(i\) in the condensed phase can be inferred...
based on the absorptive partitioning theory of Pankow (1994) (Eq. 1). The critical parameters driving the gas-particle partitioning of this compound are its effective saturation concentration, \( C_i^* \), and the total concentration of organic aerosol, \( C_{OA} \):

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

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, \( K_i \)), reflecting not only the saturation vapor pressure of the pure constituents \( (p_i^0) \) but also the way they interact with the organic mixture (effectively including liquid-phase activities). This formulation essentially determines 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.

The volatility basis set approach (VBS) was proposed by Donahue et al., (2006) to provide a framework to enable models to represent both the chemical ageing and the associated evolving volatility of particulate organic matter in the atmosphere. The approach is to separate organics into logarithmically spaced bins of effective saturation concentrations \( C_i^* \) at 298 K and it was later extended (Donahue et al., 2011, 2012) by introducing surrogate compounds with different carbon and oxygen numbers following the group contribution approach based on the SIMPOL method (Pankow and Asher, 2008) (Equation 2). The model becomes 2-dimensional, capable of tracking compound volatility and oxidation state (O:C ratios) (Donahue et al., 2011, 2012):

\[
\log_{10} C_i = (n_i^0 - n_i^1) b_c + n_i^2 h_o - 2 \frac{n_i^0 n_i^1}{n_i^2 + n_i^0} b_{e+o} \quad (2)
\]

where \( b_c \) and \( h_o \) represent the carbon-carbon and oxygen-oxygen interactions, respectively, \( b_{e+o} \) describes the non-ideal solution behaviour and \( n_i^0 \), equal to 25, represents the reference point for pure hydrocarbons (1 \( \mu \)g m\(^{-3}\) of alkene). \( n_i^0 \) and \( n_i^1 \) are the carbon and oxygen numbers, respectively, for the \( t \)th saturation concentration \( (C_i^*) \). For biomass burning in particular, May et al., (2013) 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 thermodenuder. Based on their results, they proposed a volatility distribution function and enthalpies of vaporization for wood burning smoke (May et al., 2013).
Once emitted in the atmosphere, organic compounds are highly reactive towards various oxidants such as the hydroxyl radical (OH), ozone (O3) and the nitrate radical (NO3). These oxidants can strongly alter the chemical structure of the reacted precursors by generating secondary products with lower or higher volatilities. Linking partitioning and oxidation processes of thousands of emitted organic compounds is one of the main challenges in atmospheric chemistry. The VBS scheme can delineate the transformation of the surrogates upon their functionalization or fragmentation, by changing the compounds’ volatility and O:C ratios, consistently with the dominant representative species in that part of the parameter space. Regional and global chemical transport models (CTMs) have been increasingly updated with a VBS scheme with varying complexities (Bergström et al., 2012; Ciarelli et al., 2016a; Hodzic et al., 2016; Jathar et al., 2011; Murphy et al., 2011; Shrivastava et al., 2015; Tsimpidi et al., 2014; Zhang et al., 2013). A recent landmark paper within the international AeroCom initiative (Tsiganidis et al., 2014), brought together several benchmark observational datasets and intercompared and evaluated the OA simulated by a large number of global aerosol models against them. Results indicate that simulated OA greatly varies between models in terms of POA emissions, SOA formation and complexity of OA parameterizations and the amount of OA remains under-predicted. In the latest EURODELTA III (EDD-III) European model intercomparison, seven different regional models were applied in the European domain during different periods with a focus on the February-March 2009 EUCAARI winter episode (Bessagnet et al., 2014). All models under-predicted the total measured organic fraction during the February-March 2009 winter episode mainly due the uncertainties in SOA representation (Bessagnet et al., 2014). Knote et al. (2011) used the COSMO-ART model to investigate its performance as online-coupled chemistry-climate model. In their study domestic wood burning emissions were not included and POA was assumed to be non-volatile, which resulted in a severe under-prediction of OA over the studied domain (Knote et al., 2011). Bergström et al. (2012) used the EMEP model for the period of 2002-2007 comparing different partitioning and aging schemes, and their results indicate a potential underestimation of wood burning emissions in Europe. Fountoukis et al. (2014) were among the first to implement the VBS approach into a large-scale aerosol model, following the multiple distribution framework approach proposed by Tsimpidi et al.
(2010). They found that the approach considerably improved the model result for OA when compared to a range of observations from the EUCAARI field campaign. They found that the approach considerably improved the model result for OA when compared to a range of observations from the EUCAARI field campaign (Kulmala et al., 2009, 2011) and from EMEP monitoring network (Tørseth et al., 2012). Bergström et al. (2012) used the EMEP model for the period of 2002-2007 comparing to compare different partitioning and aging schemes, and their results indicate the importance as well as a potential underestimation of wood-burning emissions in Europe in line with other studies (Kostenidou et al., 2013; Fountoukis et al., 2016; Tsimpidi et al., 2016). Recently, an important new initiative to provide improved information on residential wood combustion (RWC) emission inventory for Europe was carried out by Denier van der Gon et al. (2015) and used as an input in two CTMs (PMCAMx and EMEP MSC-W) for the EUCAARI winter periods (February-March 2009). The new RWC emissions, which are higher by a factor of 2-3 compared to previous emission inventories, improved the model performance for total OA (Denier van der Gon et al., 2015).

Radiocarbon dating (Mohr et al., 2012; Zotter et al., 2014) and measurements of specific molecular markers including methyl-nitrocatechols (Inuma et al., 2010; El Haddad et al., 2013) during winter reveal the importance of residential wood burning for SOA formation. However, parameters needed for the simulation of the aging of biomass smoke remain not well constrained. Jo et al. (2013) deployed the GEOS-Chem global model to investigate the effect of using different aging constants on modelled SOA. They concluded that model simulations are improved when chemical aging is taken into account, especially for rural regions (Jo et al., 2013). These novel investigations highlight the critical need for a representation of semi-volatile organic species and their evolution in chemical transport models.

In this study we perform extensive box-model simulations of wood burning combustion aging experiments performed in a ~7 m$^3$ smog chamber at different temperatures. Most uncertain parameters namely enthalpies of vaporization of SOA, NTVCs (non-traditional volatile organic compounds) reaction rates and their yields were investigated by means of brute force simulation approach, and a best fitting solution, within acceptable physical limits and errors ranges, was retrieved.
2 Experimental Method

Beech (*Fagus sylvatica*) logs were combusted in a residential wood burner (model type: Avant, Attika from 2009), following the procedure described in (Heringa et al., 2012) and (Bruns et al., 2015). The resulting emissions were sampled from the chimney through a heated line (473 K), diluted by a factor of ~8-10 using an ejector diluter (473 K, DI-1000, Dekati Ltd.) and injected into the smog chamber (~7 m$^3$) through a heated line (423 K). Emissions were only sampled during the stable flaming phase of the burn, for 11-21 min and total dilution factors ranged from ~100 to 200. Four replicate experiments were conducted at 288 K and another four experiments at 263 K. The smog chamber had an average relative humidity of 50% over all eight experiments. Another three experiments were conducted at 90% relative humidity and 263 K. After the characterization of the primary emissions, a single dose of d9-butanol (butanol-D9, 98%, Cambridge Isotope Laboratories) was injected into the chamber, to trace the OH concentration (Barmet et al., 2012). A continuous flow of nitrous acid (2.3-2.6 l min$^{-1}$, ≥99.999%, Air Liquide) into the chamber served as an OH precursor. The chamber was then irradiated with UV light (40 lights, 90-100 W, Cleo Performance, Philips) for 4.5-6 h (Platt et al., 2013). The evolution of the gas-phase and particulate phase composition and concentration were monitored in real-time throughout aging. Non-refractory primary and secondary particulate emissions were characterized using a high resolution time-of-flight aerosol mass spectrometer (AMS). Equivalent black carbon (eBC) was quantified using a 7-wavelength aethalometer (AE33 Magee Scientific Company, flow rate 2 l min$^{-1}$) (Drinovec et al., 2015). Particle wall loss rates in the chamber were determined using the decay of eBC assuming all particles were lost equally to the walls and that condensable material partitions only to suspended particles. Non-methane organic gases with a proton affinity greater than that of water were measured using a high-resolution proton transfer reaction mass spectrometer (PTR-ToF-MS 8000, Ionicon Analytik G.m.b.H.). The PTR-ToF-MS was operated with hydronium ([H$_2$O+H]$^+$) as reagent, a drift tube pressure of 2.2 mbar, a drift tube voltage of 543 V and a drift tube temperature of 90°C leading to a ratio of the electric field ($E$) and the density of the buffer gas ($N$) in the drift tube ($E/N$) of 137 Townsend (Td). The analysis of PTR-ToF-MS data and the identification of the precursors’ chemical nature are described in Bruns et al. (2016). The elemental composition of the detected gases was analyzed using the Tofware post-processing software (version 2.4.5), running in the Igor Pro 6.3 environment (version 6.3, Wavemetrics Inc.). More than 95% of the detected peaks could be assigned to a molecular formula. Approximately 70% of
the compounds’ chemical structures could be assigned to the observed ions guided by previously reported compounds emitted during the residential wood combustion. Here, the lumped sum of the precursors’ molar concentrations will be used to constrain the total amount of NTVOCs (Table S1) in the model. Their weighted average O:C ratio, volatility, reaction rate and carbon number will also be presented.

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±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.

## 3 Model description

The representation of SOA formation 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, $C_{OA}$:

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

(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 ($p_i^*$) but also the way they interact with the organic mixture (effectively including liquid phase activities). This formulation...
essentially implies that at high \( C_{\text{OA}} \) almost all semi-volatile organic aerosols are in the condensed phase with only species with the highest vapour pressures remaining in the gas phase.

The volatility basis set approach (VBS) proposed by Donahue et al., (2006) provides a framework for the representation of both the chemical aging and the associated volatility of particulate organic matter evolving in the atmosphere. The approach separates the organics into logarithmically spaced bins of effective saturation concentrations \( C_i^* \), at 298 K. This has been later extended (Donahue et al., 2011, 2012) by introducing surrogate compounds with different carbon and oxygen numbers following the group contribution approach based on the SIMPOL method (Pankow and Asher, 2008) (Eq 2).

\[
\log C_i^* = (n_c^0 - n_c^1)b_c - n_o^0b_o - 2\frac{n_c^1n_o^1}{n_c + n_o}b_{\text{CO}}
\]

where \( b_c \) and \( b_o \) represent the carbon-carbon and oxygen-oxygen interactions, respectively, \( b_{\text{CO}} \) describes the non-ideal solution behaviour and \( n_c^0 \), equal to 25, represents the reference point for pure hydrocarbons (1 \( \mu g \) m\(^{-3}\) of alkene). \( n_c^1 \) and \( n_o^1 \) are the carbon and oxygen numbers, respectively, for the \( i \)th saturation concentration, at 298 K. In this configuration, the model becomes 2-dimensional (2D-VBS), capable of tracking the volatility and oxidation state (O:C ratios) (Donahue et al., 2011, 2012) of oxidation products arising from functionalization and fragmentation of their precursors.

Here, we have used the VBS scheme proposed by Koo et al., (2014), referred to as a hybrid 1.5D-VBS and adapted for regional models. In this framework, the molecular space is not discretised according to the species saturation concentration and oxidation state, but rather every SOA surrogate is given an average molecular composition \( (C_{x}H_{y}O_{z}) \) – as a function of its volatility and the precursor it derives from. While a further simplification of the system compared to the 2D-VBS, this approach significantly decreases the degree of freedom of the model, while still providing means to evaluate the bulk aerosol oxidation state based on the knowledge of the surrogate molecular composition. This is especially suitable given the limited constrains available, namely the precursor composition, the precursor concentration, the POA concentration, the aged OA concentration and the O:C ratios.

In practice, five volatility bins ranging from 0.1 to 1000 \( \mu g \) m\(^{-3}\) in saturation concentration were used to model the partitioning of the POA and SOA fractions. The weighted average
carbon and oxygen numbers of the NTVOCs mixture retrieved from PTR-MS measurements were used in combination with the group contribution approach (Eq. 2) to estimate the average saturation concentration for SOA precursors yielding $\sim 10^6 \mu g \, m^{-3}$, which falls within the IVOC saturation concentration range limit (Donahue et al., 2012; Koo et al., 2014; Murphy and Pandis, 2009) (Table 1).

A total number of 3 sets were used to describe the organic material. The first set was used to distribute the primary emissions (set1). Two other sets were used to model the formation and evolution of SOA. Oxidation products of SVOC material arising from primary emissions were allocated to set2, whereas oxidation products from NTVOCs were allocated to set3 (Fig. 1). The specific molecular structures for each of the sets and bins were retrieved using the group contribution approach and the Van Krevelen relation (Table 1) (Donahue et al., 2011; Heald et al., 2010).

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 ($C^*_1 = 0.1 \mu g \, m^{-3}$), and semi-volatile ranges (OMsv) (0.1 $< C^*_1 < 1000 \mu g \, m^{-3}$) in set 1 (Table 1) is based on the work of May et al. (2013). This work revealed that the majority of the emitted primary organic 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 thermodenuder.

The oxidation of semi-volatile material would tend to increase the compounds’ oxygen number and decrease their volatility and carbon number, due to functionalization and fragmentation. We assume that the oxidation of the primary semi-volatile compounds with $C_{11}-C_{14}$ decreases their volatility by one order of magnitude and yields $C_9-C_{10}$ surrogates, placed in set2, based on the work of Donahue et al. (2011, 2012). Based on these assumptions and using the group contribution approach, the oxygen numbers for set-2 is predicted to vary between 2.26 and 4.56 (Table 1). Thus, the model implicitly accounts for the addition of 1.1 to 1.5 oxygen atoms and the loss of 2.75 to 4.25 carbon atoms, with one oxidation step.

Set3 was constrained based on the PTR-MS data. The measurements suggested an average NTVOC carbon and oxygen number of about 7 and 1, respectively. Based on reported molecular speciation data (e.g. Kleindienst et al., 2007), we expect the products of C7 compounds to have a C5-C6 carbon backbone. These products were placed in set3 following a
kernel function based on the distribution of naphthalene oxidation products. At least two oxygen atoms were added to the NTVOC mixture upon their oxidation (Table 1). The overall, O:C ratio in the whole space roughly spans the range from 0.1 to 1.0.

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 log(C*) and O:C ratios, when functionalization and fragmentation occur. Instead, to reduce the computational 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 may effectively represents the functionalization and fragmentation processes, 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 $4 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ 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), while the rate of increase in oxygen atoms does not decrease with the oxidation generation number, the compounds’ fragmentation significantly increases. The fragmentation branching ratio has often been parameterized as a function of the compounds’ O:C ratios (e.g., fragmentation ratio $= f(O:\text{C}^{(1/\alpha)})$, 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 significant functionalization (addition of at 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 of decreasing the number of carbon atoms and increasing the number of oxygen atoms adopted here simultaneously describes both processes.

4 Parameterization methodology

The modelling approach involves two steps.

i) First, we modelled the partitioning of POA for the 11 smog chamber experiments (8 experiments at RH=50% and 3 experiments at RH=90%) before aging begins. This step enables constraining the amounts of primary semi-volatile organic matter (OM<sub>SV</sub>) in the different volatility bins (OM<sub>SV</sub>.Vol.dist) and the enthalpy of vaporization of the different surrogates (OM<sub>SV</sub>.ΔH<sub>vap</sub>). Combinations of OM<sub>SV</sub>.Vol.dist and OM<sub>SV</sub>.ΔH<sub>vap</sub> of primary biomass burning semi-volatile compounds are reported in May et al. (2013), obtained based on thermodenuder data. Several combinations of OM<sub>SV</sub>.ΔH<sub>vap</sub> and OM<sub>SV</sub>.Vol.dist were tested. The amount of OM<sub>SV</sub> was varied until the measured POA mass at t=0 (OA<sub>t=0</sub>) was reached and the resulting NTVOCS/OM<sub>SV</sub> was calculated for the different experiments. The average NTVOCS/OM<sub>SV</sub> calculated at high and low temperatures were then compared and only combinations of OM<sub>SV</sub>.ΔH<sub>vap</sub> and OM<sub>SV</sub>.Vol.dist that yielded similar NTVOCS/OM<sub>SV</sub> ratios at low and high temperatures, within our experimental variability were considered to fit our data.

ii) Second, the obtained volatility distributions were used to model the aging of the emissions and SOA formation within the hybrid 1.5D-VBS framework. The time-dependent OA mass and O:C ratios were used as model constraints and the NTVOC reaction rates (k<sub>OH-NTVOCs</sub>) and yields (Y) as well as average enthalpy of evaporation for secondary material in set 2 and 3 (SOA.ΔH<sub>vap</sub>) were retrieved. In section 6 we will discuss how other a priori assumed parameters influence the results. For the second step, only experiments performed at RH=50% were used, as high RH might favour further uptake of oxygenated secondary organic material into the bulk phase, effectively increasing aerosol yields (Zuend and Seinfeld, 2012). Such effects are beyond the scope of this study.

In the present study, the bulk micro-physical properties of the condensed phased 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 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 of chamber and ambient aerosols are not significantly different.

Five volatility bins ranging from 0.1 to 1000 \( \mu g \) m\(^{-3}\) in saturation concentration were used to model the partitioning of the POA and SOA fractions. The weighted average carbon and oxygen numbers of the NTVOCs mixture retrieved from PTR-MS measurements were used in combination with the group contribution approach (Eq. 2) to estimate the average saturation concentration for SOA precursors yielding about \( 10^6 \mu g \) m\(^{-3}\), which falls within the IVOC saturation concentration range limit (Donahue et al., 2012; Koo et al., 2014; Murphy and Pandis, 2009) (Figure 2).

A total number of 3 sets were chosen to describe the evolution of organic material. The first set was used to distribute the primary emissions (set1). Two other sets were used to model the formation and evolution of SOA. Oxidation products of SVOC material arising from primary emissions were allocated to set2, whereas oxidation products from NTVOCs were allocated to set3 (Figure 3).

The specific molecular structures for each of the sets and bins were retrieved using the group contribution approach and the Van Krevelen relation (Table 1). 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 (Eq. 2). The oxidation of semi-volatile material would tend to increase the compounds’ oxygen number and decrease their volatility and carbon number, due to functionalization and fragmentation. We assume that the oxidation of the primary semi-volatile compounds with C_{11}-C_{14} decreases their volatility by one order of magnitude and yields C_{9}-C_{10} surrogates, placed in set2, based on the work of Donahue et al. (2011, 2012). Based on these assumptions and using the group contribution approach, the oxygen numbers for set2 is predicted to vary between 2.26 and 4.56 (Figure 2). Thus, the model implicitly accounts for the addition of 1.1 to 1.5 oxygen atoms and the loss of 2.75 to 4.25 carbon atoms, with one oxidation step.

Set3, was directly constrained based on the PTR-MS data. The measurements suggested an average NTVOC carbon and oxygen number of about 7 and 1, respectively. Based on reported molecular speciation data (Kleindienst et al., 2007), we expect that the products of C_7 compounds have a C_5-C_6 carbon backbone. These products were placed in set3 following a kernel function based on the distribution of naphthalene oxidation products. At least two
oxygens atoms were added to the NTVOC mixture upon their oxidation (Figure 2 and Figure 3). The overall, O:C ratio in the whole space roughly spans the range from 0.1 to 1.0.

Multigeneration chemistry (aging) is also accounted for by the model. 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.

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.

In addition to the constrains mentioned above, three parameters were determined based on experimentally constrained time-dependent OA mass and O:C ratios, i.e., NTVOCs reaction rates and yields as well as average enthalpies of vaporization values for the set 2 and 3. Detailed explanations are presented in the next two sections.

5 Results

5.1 Inferred OMsv and NTVOCs/OMsv ratios from measurements and partitioning theory

We seek to determine, based on the PTR-MS and AMS measurements of gas and particle phase organic material at \(t=0\), the ratio NTVOCs/OMsv and the enthalpies of vaporization of compounds of the semi-volatile compounds that represent best the observations at high and low temperatures. We modelled the OA partitioning using two different proposed \(\Delta H_{\text{vapPOA}}\) for wood burning:

\[
\Delta \text{_____} = -4 \log_{10}(\frac{\text{_____}}{288}) + 85 \tag{3}
\]
Table 2 reports the measured OA$_{t=0}$ for all the 11 experiments, which ranges from 6.0 μg m$^{-3}$ to 22.6 μg m$^{-3}$. The amount of OM$_w$ that matches the measured OA$_{t=0}$ is reported for both SOL1 and SOL2. The average NTVOCs/OM$_w$ ratios for high and low temperature experiments are reported together with the standard deviation in Table 3. For SOL1 we calculated an average ratio of 4.2±1.1 for high temperatures and 7.2±2.6 for low temperatures. SOL2 reduces the differences in the average NTVOCs/OM$_w$ ratios at the two temperatures, and therefore will be used to describe the dependency of the primary organic compounds.

For SOL2 the overall NTVOCs/OM$_w$ ratio between high and low temperature experiments is around 4.75. Figure 2 shows the resolved equilibrium phase partitioning (Eq. 1) between the gas and particle phase at the beginning of each of the 11 smog chamber experiments (OA$_{t=0}$) using SOL2. As expected, most of the material is found in the gas-phase at high temperatures, while at lower temperature only part of the compounds with saturation concentrations (at 20°C) between 100 and 1000 μg m$^{-3}$ would reside in the gas-phase.

Based on the PTR-MS and AMS measurements of gas and particle phase organic material at $t=0$, we seek to determine the ratio NTVOCs/OM$_{sv}$ and the OM$_{SV}$ΔH$_{vap}$ that represent the observations at high and low temperatures. Combinations of enthalpies of vaporization and volatility distributions of primary biomass burning semi-volatile compounds are reported in May et al. (2013), based on thermodenuder data. We note that in the current version of the 1.5D-VBS the volatility distribution (Table 1), subsequently referred to as OM$_{SV}$.Vol.distREF, is used in combination with OM$_{SV}$.ΔH$_{vap}$ = {85’000 – 4’000 x log(C*)} J mol$^{-1}$, based on recommendations of May et al. (2013). Here, several combinations of OM$_{SV}$.ΔH$_{vap}$ functions and OM$_{SV}$.Vol.dist were tested.

In Table 2, the measured OA$_{t=0}$ for all the 11 experiments, which ranges from 6.0 μg m$^{-3}$ to 22.6 μg m$^{-3}$, are reported. The OM$_{sv}$ values that match the measured OA$_{t=0}$ are shown as an example for the cases when OM$_{SV}$.ΔH$_{vap}$ = {85’000 – 4’000 x log(C*)} J mol$^{-1}$ (recommended by May et al., 2013) and OM$_{SV}$.ΔH$_{vap}$ = {70’000 – 11’000 x log(C*)} J mol$^{-1}$ were used in combination with OM$_{SV}$.Vol.distREF. The average NTVOCs/OM$_{sv}$ ratios obtained using both OM$_{SV}$.ΔH$_{vap}$ functions are compared at high and low temperatures in
Table 3. OMSV.ΔHvap = \{70'000 – 11'000 \times \log(C*)\} J mol\(^{-1}\) used in combination with
OMSV.Vol.distREF reduced the observed difference in the average NTVOCs/OM\(_v\) ratios at the
two temperatures. In general, functions with lowest OMSV.ΔHvap better explained the change
in the measured OA\(_{t=0}\) with temperature with OMSV.ΔHvap = \{70'000 – 11'000 \times \log(C*)\} J
mol\(^{-1}\), fitting best our data. The volatility distributions that could explain our observation have
an aggregate contribution in the volatility bins \log(C*) = 1 and 2 ≤ 0.3. In the following,
OMSV.ΔHvap = \{70'000 – 11'000 \times \log(C*)\} J mol\(^{-1}\) shall be used in combination with
OMSV.Vol.distREF as model inputs and in section 6, we assess the sensitivity of the resulting
NTVOCs/OMSV ratios and SOA formed on the chosen OMSV.Vol.dist.

Using these model parameters, the overall NTVOCs/OM\(_v\) ratio was determined to be around
4.75. Figure 2 shows the resolved equilibrium phase partitioning (Eq. 1) between the gas and
particle phase at the beginning of each of the 11 smog chamber experiments (OA\(_{t=0}\)). As
expected, most of the material is found in the gas-phase at high temperatures, while at lower
temperature only part of the compounds with saturation concentrations (at 20°C) between 100
and 1000 μg m\(^{-3}\) would reside in the gas-phase.

In this section we will focus on the emission aging. Using the NTVOCs/OM\(_v\) ratio and
the enthalpies of vaporization retrieved in section 3.1.1, we modelled the eight different
smog chamber experiments: No. 1, 2, 3, 4 (low temperature) and No. 8, 9, 10, 11 (high
temperature) performed at the same relative humidity (RH = 50%). For each of the eight
experiments we injected an average mixture of NTVOCs equal to 4.75 times the OM\(_v\)
mass before the start of the aging. NTVOCs react solely with OH, whose concentration
was retrieved from PTR-MS measurements. The temperature dependence of the
reaction rates was also taken into account through the Arrhenius equation. The reaction
rates (k\(_{\text{OH-NTVOC}}\)) and yields (Y) of the NTVOCs as well as enthalpies of vaporization
of SOA (ΔH\(_{vapSOA}\)) for set2 and set3 were varied within specific physically realistic
ranges. We varied k\(_{\text{OH-NTVOC}}\) between 2 and 4 x 10\(^{-11}\ \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}\) in steps of 0.1 x
10\(^{-11}\ \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}\), and yields between 0.1 and 0.4 ppm ppm\(^{-1}\) in steps of 0.01 ppm
ppm\(^{-1}\). Values for ΔH\(_{vapSOA}\) are still highly uncertain. In this study we explored a wide
range of values from 15,000 J mol\(^{-1}\) to 115,000 J mol\(^{-1}\) in steps of 20,000 J mol\(^{-1}\). The
model performance for each combination of Y and k was evaluated in terms of the root
mean square error (RMSE) for the eight experiments and a best fitting solution retrieved
as the one that minimized the sum of the errors on both the O:C ratio and OA mass.
(giving the same weight on both quantities). We performed a total number of \(J \times k \times n_{\text{exp}}\) = \((21 \times 31 \times 6 \times 9) - 31248\) simulations, where \(n_{\text{exp}}\) are the numbers of aging experiments. Figure 5 shows the total errors for the OA mass (left side) and O:C ratio (right side) for different \(\Delta H_{\text{vapSOA}}\) and \(k_{\text{OH-NTVOC}}\). These global errors are root mean squared deviations (i.e., for the eight experiments) adjusted to the number of points per experiment. The error on the OA mass varies from a minimum of ~25% up to more than 60% whereas the errors on the O:C ratio (Figure 5 right side) are lower and they range from approximately 15% up to more than 30%. For the OA mass, distinct regions with lower errors are visible in the central part of each panel with different \(\Delta H_{\text{vapSOA}}\), representing the models that fitted best to the measured OA. While a similar observation can be made for the O:C, models with high \(\Delta H_{\text{vapSOA}}\) tend to reproduce the data less faithfully. The diamonds in Figure 5 indicate the absolute best fitting solution (in yellow) and the ones retrieved with a likelihood ratio test allowing for 10% error form the best fit (red diamonds). Regions with lower error are localized for \(k_{\text{OH-NTVOC}}\) \(\geq 2.5 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}\) between \(\Delta H_{\text{vapSOA}}\) values of 35,000 and 55,000 J mol\(^{-1}\).

Figure 6 shows the modelled and measured OA mass for all the 8 aging experiments. The primary organic aerosol fraction is reported as well as the SOA fraction from SVOCs and higher volatility NTVOCs. All the low temperature experiments (No. 1, 2, 3, 4 left side of the panel) were reproduced very well along with the concentration gradients at the end of each experiment, even though the model tends in general to slightly over-predict the final OA concentration. The primary fraction slightly increases at the very beginning of the aging phase and it decreases as the experiments proceed as a result of its partitioning to the gas phase and subsequent oxidation. Most of the SOA was predicted to be formed from NTVOCs precursors and only a minor amount from SVOCs. On the other hand, for experiments conducted at higher temperature (No. 8, 9, 10, 11) the OA mass was under-predicted except for experiment No. 8 (see also Figure S1). In this case, SVOCs contribute more significantly to SOA formation compared to low temperature experiments, although the majority of SOA still arises from NTVOCs.

Comparisons between measured and modelled O:C ratios are reported in Fig. 7. Model and observation results match very well, especially upon aging. Significant differences between measured and modelled O:C ratios at the beginning of the experiments...
highlight on the one hand the variable nature of primary biomass smoke emissions. This variability cannot be accounted for in the model. On the other hand, for some experiments the model under-predicts the measured O:C ratios suggesting that the model parameters describing the O:C of primary emissions are suboptimal. These parameters include directly the carbon and oxygen number of species in set 1, and indirectly the volatility distributions and enthalpy of vaporization, which are all adopted from previous published data. The average bias in POA O:C ratios is ~30%, well within the experimental uncertainties.

5.2 Wood burning aging at low and high temperatures

In this section, we will focus on the emission aging. Using the NTVOCs/OM$_{sv}$ ratio and the enthalpies of vaporization retrieved in the previous sections, we modelled the eight different smog chamber experiments: No. 1, 2, 3, 4 (low temperature) and No. 8, 9, 10, 11 (high temperature) performed at the same relative humidity (RH = 50%). For each of the eight experiments we injected an average mixture of NTVOCs equal to 4.75 times the OM$_{sv}$ mass before the start of the aging. NTVOCs react solely with OH, whose concentration was retrieved from PTR-MS measurements. The temperature dependence of the reaction rates was also taken into account through the Arrhenius equation. The reaction rates ($k_{OH-NTVOC}$) and yields (Y) of the NTVOCs as well as enthalpies of vaporization of SOA (SOA.$\Delta$H$_{vap}$) in set2 and set3 were varied within specific physically realistic ranges that were already proposed in the literature (Koo et al., 2014; Donahue et al., 2013; Grieshop et al., 2009; Robinson et al., 2007). We varied $k_{OH-NTVOC}$ between $2 \times 0.1 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$ in steps of $0.1 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$, and yields between 0.1 and 0.4 ppm ppm$^{-1}$ in steps of 0.01 ppm ppm$^{-1}$. The yields refer to the sum of the aerosol yields of the four volatility bins. A naphthalene kernel mass distribution with increasing contribution as a function of log(C*) is used to distribute the products in the four bins (Murphy and Pandis, 2009). Values for SOA.$\Delta$H$_{vap}$ are still highly uncertain. In this study, we explored a wide range of values from 15'000 J mol$^{-1}$ to 115'000 J mol$^{-1}$ in steps of 20'000 J mol$^{-1}$. The model performance for each combination of SOA.$\Delta$H$_{vap}$, Y and $k_{OH-NTVOC}$ was evaluated by calculating the root mean square error (RMSE) on both the O:C ratio and OA mass (giving the same weight on both quantities) for the eight experiments (giving the same weight for all experiments), and the best fitting solution is the one that minimized the RMSE. We performed a total number of 31248 simulations.
Figure 3 shows the total errors for the OA mass (left side) and O:C ratio (right side) for different SOA, $\Delta H_{\text{vap}}$, Y and $k_{\text{OH-NTVOCs}}$. The error on the OA mass varies from a minimum of ~25% up to more than 60%, whereas the errors on the O:C ratio are lower, ranging from approximately 15% up to more than 30%. For the OA mass, distinct regions with lower errors are visible in the central part of each panel with different SOA, $\Delta H_{\text{vap}}$, representing the models that fitted best the measured OA. While a similar observation can be made for the O:C ratios, models with high SOA, $\Delta H_{\text{vap}}$ tend to reproduce the data less faithfully. The diamonds in Fig. 3 indicate the absolute best fitting solution ($k_{\text{OH-NTVOCs}} = 4.0 \times 10^{-11} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$; SOA, $\Delta H_{\text{vap}} = 35'000$; Y = 0.32 ppm ppm$^{-1}$, in yellow), and the ones retrieved with a likelihood-ratio test allowing for 10% error form the best fit (red diamonds). Regions with lower errors are localized for $k_{\text{OH-NTVOCs}} \geq 2.5 \times 10^{-11} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$ between SOA, $\Delta H_{\text{vap}}$ values of 35’000 and 55’000 J mol$^{-1}$.

Figure 4 shows the modelled and measured OA mass for all the 8 experiments. The primary organic aerosol fraction is reported as well as the SOA fraction from SVOCs and higher volatility NTVOCs. All the low temperature experiments (No. 1, 2, 3, 4 left side of the panel) were reproduced very well along with the concentration gradients at the end of each the experiments even though the model generally tends to slightly over-predict the final OA concentration and to under-predict the production rate. The POA fraction slightly increases at the very beginning of the aging phase, upon the increase in OA mass. As the experiments proceed, POA decreases as a result of its partitioning to the gas phase and subsequent oxidation. Most of the SOA was predicted to be formed from NTVOCs precursors (78-82%) and only a minor amount from SVOCs (18-22%). Meanwhile, at high temperatures, SVOCs contribute more significantly to SOA formation compared to low temperature experiments, although the majority of SOA still arise from NTVOCs. We note that at higher temperatures, the OA mass was slightly under-predicted for experiments No. 9, 10 and 11, but largely over-predicted for experiment No. 8 (see also Fig. S1). We do not have any experimental evidence to discard experiment No.8 as an outlier, but sensitivity analysis with excluding this experiment yielded slightly lower SOA, $\Delta H_{\text{vap}}$ values (~15’000-35’000 J mol$^{-1}$).

Comparisons between measured and modelled O:C ratios are reported in Fig. 5. Model and observation results match very well, especially upon aging. However, we note on the one hand that significant differences between measured and modelled O:C ratios at the beginning of the experiments can be observed, without any systematic correlation with the chamber conditions (e.g. OA mass or temperature). These differences may be due to the variable nature...
of primary biomass smoke emissions, which cannot be accounted for in the model. On the other hand, it is noticeable that the model generally under-predicts in general the measured POA O:C ratios, suggesting that the parameters describing the O:C of primary emissions are suboptimal. These parameters include mainly the carbon and oxygen numbers of species in set 1, and to a lesser extent the \( \text{OM}_{\text{SV, Vol.dist}} \) and the \( \text{OM}_{\text{SV, } \Delta \text{H}_{\text{vap}}} \) which are all adopted from previously published data. While this observation suggests the presence of compounds with lower carbon number (higher oxygen number) in the primary aerosols (e.g. \( \text{C}_6\text{H}_{10}\text{O}_5 \) anhydrous sugars which contribute ~15% of the POA, Ulevicius et al., 2016), we believe that we do not have suitable data (e.g. analysis at the molecular level) to propose a more accurate representation of POA compounds. In addition, the average bias in the POA O:C ratios is <30%, well within the experimental uncertainties.

### 36 Implications for large-scale models Discussions and major conclusions

**Discussions and major conclusions**

We performed extensive box model simulations of wood burning experiments conducted at two different temperatures (263 and 288 K) in a ~7 m" smog chamber facility. By combining new NTVOCs measurements and already available partitioning data for primary wood burning emission, 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 (\( \text{OM}_{\text{sv}} \)). This ratio can be directly used in CTM models in the absence of explicit NTVOCs emissions for wood burning in combination with the proposed aging scheme. Specific parameters such as NTVOCs reaction rates \( (k_{\text{OH-NTVOCs}}) \), yields \( (Y) \) and enthalpies of vaporization of secondary organic aerosol \( (\Delta \text{H}_{\text{vap,SOA}}) \) were varied using brute force simulations, and their values were retrieved for best fitting solutions falling within a physically realistic range. The model predicted that the majority of the SOA formed during the aging-phase arose from NTVOCs precursors and only a smaller amount from SVOCs.

Based on our best fitting solutions, we can now predict the OA mass and composition as well as SOA yields at any given temperature, emission load and OH exposure. This is illustrated in Figure 8 for 3 different OM emission loads (\( \text{OM}_{\text{sv}} + \text{NTVOCs} \)) 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% K\(^{-1}\) on average with higher...
effects predicted at higher loads (0.7% K⁻¹ at 600 μg m⁻³, 0.3% at 6 μg m⁻³). The partitioning coefficient of the primary material increases by about a factor of 1.5 for a 10-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) x 10⁷ molec cm⁻³ h, the trend is inversed and POA mass decreases due to the oxidation of semi-volatile primary compounds. This effect is more visible at high loads.

From Figure 8, 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. \( \frac{\partial Y}{\partial T} = f(T, C_{OA}, OH_{exp}) \). SOA yields increase by 0.03, 0.06 and 0.05 % K⁻¹ on average for 6, 60 and 600 μg m⁻³ respectively, with higher effects predicted in general at lower temperatures. The temperature effect on the yields is also greater 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 Figure S2, an average change in the yield with \( \log C_{OA} \) is shown at the different conditions: \( \frac{\partial Y}{\partial \log C_{OA}} = f(T, OH_{exp}) \). Note that an increase in SOA yields with the \( \log C_{OA} \) was observed as expected. This increase is not solely due to additional partitioning, but is partially 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 different temperatures. We determined a yield increase of 4-9% for a 10-fold increase in emissions, with a higher effect at higher OH exposures and lower temperatures.

From Figure 8, one may evaluate the minimum OH exposure values required for SOA to exceed POA. SOA is predicted to exceed POA after \( 1.5 \times 10^7 \) molec 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 cm⁻³ h, or in 2-10 hours (at OH concentrations of \( 1.5 \times 10^6 \) molec 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 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 cm⁻³. These results confirm previous observations that
SOA formation is very rapid and the SOA fraction might exceed primary emissions within time scales of hours, even during haze events.

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 µg m⁻³ saturation concentration range (OMsv). 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 the 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_OHNTVOCs), SOA yields (Y) and enthalpies of vaporization of secondary organic aerosol (SOA.ΔHvap) 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_OHNTVOCs ranged between 3.5 and 4.0 x 10⁻¹¹ molecules⁻¹ cm³ s⁻¹, the Y of semi-volatile SOA surrogates ranged between 0.3 and 0.35 ppm ppm⁻¹, and the SOA.ΔHvap 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.ΔHvap = [35’000 - 55’000] J mol⁻¹ vs. weighted average of ΔH_POA ~ 50’000 J mol⁻¹. Results presented here including the average NTVOCs/OMsv ratios and parameters required for representing SOA formation are all based on the use of one OMsv.Vol.dist. In Fig. S3, we have performed a sensitivity analysis where several OMsv.Vol.dist were tested in combination with the same SOA.ΔHvap function and the same reaction scheme. This analysis
shows that the NTVOCs/OMSV 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$_{SV,\text{Vol.dist}}$ used, especially at low temperature. This is because the OM$_{SV,\text{Vol.dist}}$ 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 (set 1 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 would be necessary for better constraining these parameters.

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 factor representing the total yield $Y$ of these products in the semi-volatility range. Initial tests indicated that the measurements used as constrains 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 would be required for better constraining the volatility distribution of the biomass burning NTVOCs oxidation products, with a special focus on lower concentrations (between 1-20 µg 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 would yield a significant loss of compounds’ volatility ($-1.7 \log(C^*)$ 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 µg 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 ambient concentrations. The primary organic aerosol mass (POA) decreases with temperature by 0.5% K$^{-1}$ on average with higher effects predicted at higher loads (0.7% K$^{-1}$ at 600 µg m$^{-3}$ vs. 0.3% at 6 µg 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 \( (1.0-1.5) \times 10^7 \) molec cm\(^{-3}\) 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. \( \frac{\partial Y}{\partial T} = f(T, C_{O_A, OH_{exp}}) \). SOA yields increase 0.03, 0.06 and 0.05 % K\(^{-1}\) on average for 6, 60 and 600 µg 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 \( \log C_{O_A} \) is shown at the different conditions: \( \frac{\partial Y}{\partial \log C_{O_A}} = f(T, OH_{exp}) \). An increase in SOA yields with the \( \log C_{O_A} \) 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 Figure 6, one may also evaluate the minimum OH exposure values required for SOA to exceed POA. SOA is predicted to exceed POA after ~1.5 \( \times 10^7 \) molec 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 cm\(^{-3}\) h, or in 2-10 hours (at OH concentrations of \( (1-5) \times 10^6 \) 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 \( \times 10^6 \) molec 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 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/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).

Acknowledgements
This study was financially supported by the Swiss Federal Office of Environment (FOEN). I. El Haddad was financially supported by the Swiss National Science Foundation. We appreciate the availability of VBS framework in CAMx and support of RAMBOLL ENVIRON.

**Code and/or data availability**

The VBS box model was written in Fortran and was compiled using the Portland group compilers. Simulations were performed under Scientific Linux SL distribution using C shell scripts in order to brute force the chemical and physical parameters. Model output was written in tab-separated text format. Routines to perform the oxidation reactions of SOA precursors and partitioning between particle and gas-phase phase organic material were taken from the CAMx model (available at http://www.camx.com/) and based on the work of Koo et al. (2014). Please contact the corresponding authors of this publication if you are interested in the model code or applications and/or scientific collaboration.
Tables and Figures

Table 1. Properties of the VBS space. Oxygen numbers for each volatility bin were calculated using the group-contribution of Donahue et al. (2011). Hydrogen numbers were calculated from the van Krevelen relation (Heald et al., 2010).

<table>
<thead>
<tr>
<th>Log (C*)</th>
<th>Oxygen number</th>
<th>Carbon number</th>
<th>Hydrogen number</th>
<th>O:C ratio</th>
<th>Molecular weight</th>
<th>Emission factors</th>
<th>AH (J mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>4.11</td>
<td>11.00</td>
<td>17.89</td>
<td>0.37</td>
<td>216</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>3.43</td>
<td>11.75</td>
<td>20.07</td>
<td>0.29</td>
<td>216</td>
<td>0.1</td>
<td>85'000-70'000</td>
</tr>
<tr>
<td>1</td>
<td>2.73</td>
<td>12.50</td>
<td>22.27</td>
<td>0.22</td>
<td>216</td>
<td>0.1</td>
<td>81'000-59'000</td>
</tr>
<tr>
<td>2</td>
<td>2.01</td>
<td>13.25</td>
<td>24.49</td>
<td>0.15</td>
<td>216</td>
<td>0.2</td>
<td>77'000-48'000</td>
</tr>
<tr>
<td>3</td>
<td>1.27</td>
<td>14.00</td>
<td>26.73</td>
<td>0.09</td>
<td>215</td>
<td>0.4</td>
<td>73'000-37'000</td>
</tr>
<tr>
<td>-1</td>
<td>4.53</td>
<td>9.00</td>
<td>13.47</td>
<td>0.50</td>
<td>194</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>4.00</td>
<td>9.25</td>
<td>14.50</td>
<td>0.43</td>
<td>189</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td>1</td>
<td>3.40</td>
<td>9.50</td>
<td>15.60</td>
<td>0.36</td>
<td>184</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td>3</td>
<td>2.83</td>
<td>9.75</td>
<td>16.67</td>
<td>0.29</td>
<td>179</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td>-1</td>
<td>5.25</td>
<td>5.00</td>
<td>4.75</td>
<td>1.05</td>
<td>149</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>4.70</td>
<td>5.25</td>
<td>5.80</td>
<td>0.90</td>
<td>144</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td>1</td>
<td>4.20</td>
<td>5.50</td>
<td>6.80</td>
<td>0.76</td>
<td>140</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td>2</td>
<td>3.65</td>
<td>5.75</td>
<td>7.85</td>
<td>0.63</td>
<td>135</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td>3</td>
<td>3.15</td>
<td>6.00</td>
<td>8.85</td>
<td>0.52</td>
<td>131</td>
<td>-</td>
<td>35'000</td>
</tr>
<tr>
<td>NTVOCs</td>
<td>6</td>
<td>1.22</td>
<td>7.22</td>
<td>7.14</td>
<td>0.16</td>
<td>113</td>
<td>4.75 (OMsv)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Log (C*)</th>
<th>Oxygen number</th>
<th>Carbon number</th>
<th>Hydrogen number</th>
<th>O:C ratio</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>4.11</td>
<td>11.00</td>
<td>17.89</td>
<td>0.37</td>
<td>216</td>
</tr>
<tr>
<td>0</td>
<td>3.43</td>
<td>11.75</td>
<td>20.07</td>
<td>0.29</td>
<td>216</td>
</tr>
<tr>
<td>1</td>
<td>2.73</td>
<td>12.50</td>
<td>22.27</td>
<td>0.22</td>
<td>216</td>
</tr>
<tr>
<td>2</td>
<td>2.01</td>
<td>13.25</td>
<td>24.49</td>
<td>0.15</td>
<td>216</td>
</tr>
<tr>
<td></td>
<td>1.27</td>
<td>14.00</td>
<td>26.73</td>
<td>0.09</td>
<td>215</td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
<td>-------</td>
<td>-------</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>1</td>
<td>4.53</td>
<td>0.00</td>
<td>13.42</td>
<td>0.50</td>
<td>194</td>
</tr>
<tr>
<td>0</td>
<td>4.00</td>
<td>9.25</td>
<td>14.50</td>
<td>0.43</td>
<td>189</td>
</tr>
<tr>
<td>SOA set2</td>
<td>1</td>
<td>3.00</td>
<td>0.50</td>
<td>15.68</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.83</td>
<td>9.75</td>
<td>16.67</td>
<td>0.29</td>
</tr>
<tr>
<td>3</td>
<td>2.26</td>
<td>10.00</td>
<td>17.74</td>
<td>0.23</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>4.25</td>
<td>5.00</td>
<td>4.75</td>
<td>1.05</td>
<td>149</td>
</tr>
<tr>
<td></td>
<td>4.70</td>
<td>5.25</td>
<td>5.80</td>
<td>0.99</td>
<td>144</td>
</tr>
<tr>
<td>SOA set3</td>
<td>1</td>
<td>4.20</td>
<td>5.50</td>
<td>6.80</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.65</td>
<td>5.75</td>
<td>7.85</td>
<td>0.63</td>
</tr>
<tr>
<td>3</td>
<td>3.15</td>
<td>6.00</td>
<td>8.85</td>
<td>0.53</td>
<td>134</td>
</tr>
</tbody>
</table>
Table 2. Modelled and experimental data for 11 wood burning experiments. The OMsv mass at the beginning of each chamber experiment is reported together with the measured OA$_{t=0}$ and the initial NTVOCs concentration. NTVOCs/OMsv is the ratio between the measured NTVOCs and the calculated OMsv mass at the beginning of each experiment for the two different OMsv-$\Delta H_{vap}$ functions: SOL1: OMsv-$\Delta H_{vap}$ = \{85'000 – 4'000 x Log(C*)\} J mol$^{-1}$ and SOL2: OMsv-$\Delta H_{vap}$ = \{70'000 – 11'000 x Log(C*)\} J mol$^{-1}$, used in combination with OMsv.Vol.dist presented in Table 1.

<table>
<thead>
<tr>
<th>Exp</th>
<th>T=263 K</th>
<th>T=263 K</th>
<th>T=263 K</th>
<th>T=263 K</th>
<th>T=263 K</th>
<th>T=263 K</th>
<th>T=288 K</th>
<th>T=288 K</th>
<th>T=288 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH=50%</td>
<td>RH=50%</td>
<td>RH=50%</td>
<td>RH=50%</td>
<td>RH=90%</td>
<td>RH=90%</td>
<td>RH=50%</td>
<td>RH=50%</td>
<td>RH=50%</td>
<td>RH=50%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measured NTVOCs [μg/m$^3$]</td>
<td>185.1</td>
<td>-</td>
<td>-</td>
<td>79.3</td>
<td>143.5</td>
<td>91.7</td>
<td>68.7</td>
<td>121.5</td>
<td>190.4</td>
</tr>
<tr>
<td>Measured OA$_{t=0}$ [μg/m$^3$]</td>
<td>12.3</td>
<td>8.1</td>
<td>16.7</td>
<td>9.3</td>
<td>12.0</td>
<td>17.7</td>
<td>6.0</td>
<td>22.6</td>
<td>17.5</td>
</tr>
<tr>
<td>SOL1 Modelled OMsv [μg/m$^3$]</td>
<td>17.3</td>
<td>12.1</td>
<td>22.4</td>
<td>13.6</td>
<td>16.9</td>
<td>23.5</td>
<td>9.5</td>
<td>46.6</td>
<td>37.7</td>
</tr>
<tr>
<td></td>
<td>SOL2 Modeled OM(_v) [µg/m(^3)]</td>
<td>SOL1 (NTVOCs)/(OM(_v))</td>
<td>SOL2 (NTVOCs)/(OM(_v))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>-------------------------------------</td>
<td>---------------------------</td>
<td>---------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>22.7  15.8  29.5  17.8  22.2  31.0  12.3  49.7  40.1  42.4  42.2</td>
<td>10.7  -  -  5.1  8.5  3.9  7.2  2.6  5.0  4.4  4.9</td>
<td>8.1  -  -  4.4  6.4  3.0  5.6  2.4  4.7  4.1  4.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Solutions used for primary organic aerosol enthalpies of vaporization with averages and standard deviations of the (NTVOCs)/(OMsv) ratio.

<table>
<thead>
<tr>
<th>SOL1</th>
<th>(\Delta H_{\text{vap POA}}) (\text{J mol}^{-1})</th>
<th>(NTVOCs)/(OMsv) Average High-T (288) K</th>
<th>(NTVOCs)/(OMsv) Average Low-T (263) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>({85'000 – 4'000 \times \log(C^*)}) J mol(^{-1})</td>
<td>4.2±1.1</td>
<td>7.2±2.6</td>
<td></td>
</tr>
<tr>
<td>({70'000 – 11'000 \times \log(C^*)}) J mol(^{-1})</td>
<td>4.0±1.1</td>
<td>5.5±2.0</td>
<td></td>
</tr>
</tbody>
</table>

\(\text{log (C})_{298}^\ast\) = 70
Figure 1. Properties of the wood burning POA set. a) O:C ratio, b) ΔH_vap, c) C number, d) O number. Volatility distribution and enthalpies of vaporization were taken from May et al. (2013). Carbon and oxygen numbers were calculated using the group contribution approach of Donahue et al. (2011). Wood burning POA carbon numbers were placed from 14 to 11 and linearly interpolated between the volatility bins.
Figure 2. Properties of the wood burning POA and SOA sets. a) C number b) O number.

Wood burning SOA carbon numbers were placed from 10 to 5 and linearly interpolated between the volatility bins. Oxygen numbers were calculated using the group approach of Donahue et al. (2011). NTVOCs carbon and oxygen numbers were retrieved from PTR-MS data. The red bars indicate the OM emission factors.
Figure 13. Proposed oxidation scheme: an average mixture of NTVOCs compounds are allowed to react with the hydroxyl radical following a naphthalene kernel mass distribution. Secondary products in the SOA set (set3) are allowed to further react with a reaction rate of $k_{OH} = 4.0 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$. Oxidation products from semi-volatile vapours from the POA set (set1) are allowed for further aging in set2. The numbers on the red arrows indicate the NTVOCs yields for each bin for the best fitting solution (ppm ppm$^{-1}$).
Figure 24. Partitioning of wood burning POA before the start of the aging for 11 smog chamber experiments (SOL2). Gas-phase in red and particle phase in blue.
Figure 35. Total error on the OA mass (left side) and on the O:C ratio (right side). White regions have an error larger than 60% for the OA mass and 26% for the O:C ratio. The number of simulations per experiment is 3906. The red diamonds indicate the likelihood ratio test results for solutions within 10% error from the best one (yellow diamond).
Figure 46. Modelled and observed OA mass for low temperature experiments (left side) and high temperature experiments (right side). The model results for the best fitting solution...
(yellow diamond in Figure 5). SOA from NTVOCs and SVOCs as well as POA are reported in green, red and blue, respectively.
Figure 57. Modelled (black lines) and observed (red lines) O:C ratio for low temperature experiments (left side) and high temperature experiments (right side).

Figure 68. Predicted OA mass (upper panels, note different scales), POA mass, SOA/POA ratio (middle panels) and yields (lower panels) at different OMsv + NTVOCs initial load and atmospheric conditions (T).
Table S1. List of NTVOCs compounds considered for the average mixture

<table>
<thead>
<tr>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol</td>
</tr>
<tr>
<td>m-, o-, p-cresol</td>
</tr>
<tr>
<td>m-, o-, p-benzenediol /2-methylfuraldehyde</td>
</tr>
<tr>
<td>dimethylphenols</td>
</tr>
<tr>
<td>guaiacol /methylbenzenediols</td>
</tr>
<tr>
<td>naphthalene</td>
</tr>
<tr>
<td>2-methylnaphthalene /1-methylnaphthalene</td>
</tr>
<tr>
<td>acenaphthylene</td>
</tr>
<tr>
<td>syringol</td>
</tr>
<tr>
<td>biphenyl /acenaphthene</td>
</tr>
<tr>
<td>dimethylnaphthalene</td>
</tr>
</tbody>
</table>

Figure S1. Best fitting solution error frequency distributions (counts per bin) for low (blue) and high temperature (red) experiments. Right side is the OA mass. Left side for the O:C ratio. Gaussian normal curve fit (for both temperatures) is reported in dark blue.
Figure S2. Variation of SOA yields with log(C_OA) (at 6, 60, 600 μg/m³) as a function of T and OH exposure (from Figure 8, bottom panel).
Figure S3: Influence of the chosen volatility distribution ($OM_{SV, Vol.dist}$) on the resulting SOA formed at low (Exp 1, 2, 3 and 4) and high (Exp 8, 9, 10 and 11) temperatures. Different volatility distributions ($OM_{SV, Vol.dist}$) from May et al. (2013) were used in combination with $\Delta H = \{70'000 – 11'000 \times \log(C^*)\}$ J mol$^{-1}$ (referred as SOL2 in the manuscript) and the same oxidation scheme optimized during this study. The resulting SOA formed (grey area) is compared with the one obtained when $OM_{SV, Vol.dist_{ref}}$ was used (black line). The sensitivity analysis shows that the results are only slightly sensitive to the assumed $OM_{SV, Vol.dist}$, especially at low temperature.
References


Evaluation of European air quality modelled by CAMx including the volatility basis set scheme, Atmos. Chem. Phys., 16, 10313-10332, doi:10.5194/acp-16-10313-2016, 2016.


Steenrod, S. D., Takemura, T., Tiitta, P., Tilmes, S., Tost, H., van Noije, T., van Zyl, P. G.,
and Zhang, X.: The AeroCom evaluation and intercomparison of organic aerosol in global

Tsimpidi, A. P., Karydis, V. A., Zavala, M., Lei, W., Molina, L., Ulbrich, I. M., Jimenez, J. L.
and Pandis, S. N.: Evaluation of the volatility basis-set approach for the simulation of organic
aerosol formation in the Mexico City metropolitan area, Atmos. Chem. Phys., 10, 525–546,
2010.

(v1.0): module to simulate the organic aerosol composition and evolution in the atmosphere,

of organic aerosols: model comparison with 84 AMS factor-analysis data sets, Atmos. Chem.

Ulevicius, V., Byčenkiene, S., Bozzetti, C., Vlachou, A., Plauškaitė, K., Mordas, G., Dudoitis,
V., Abbaszade, G., Remeikis, V., Garbaras, A., Masalaite, A., Blees, J., Fröhlich, R.,
Dällenbach, K. R., Canonaco, F., Slowik, J. G., Dommen, J., Zimmerman, R., Schnellle-
non-fossil source contributions to atmospheric carbonaceous aerosols during extreme spring
grassland fires in Eastern Europe, Atmos. Chem. Phys., 16, 5513-5529, doi:10.5194/acp-16-
5513-2016, 2016.

Waked, A., Favez, O., Alleman, L. Y., Piot, C., Petit, J.-E., Delaunay, T., Verlinden, E.,
Golly, B., Besombes, J.-L., Jaffrezo, J.-L. and Leoz-Garziandia, E.: Source apportionment of
PM10 in a north-western Europe regional urban background site (Lens, France) using positive
matrix factorization and including primary biogenic emissions, Atmos. Chem. Phys., 14(7),

Yokelson, R. J., Burling, I. R., Gilman, J. B., Warneke, C., Stockwell, C. E., de Gouw, J.,
Akagi, S. K., Urbanski, S. P., Veres, P., Roberts, J. M., Kuster, W. C., Reardon, J., Griffith,
R.: Coupling field and laboratory measurements to estimate the emission factors of identified
and unidentified trace gases for prescribed fires, Atmos. Chem. Phys., 13, 89-116,

Zhang, Q. J., Beekmann, M., Drewnick, F., Freutel, F., Schneider, J., Crippa, M., Prevot, A.
S. H., Baltensperger, U., Poulain, L., Wiedensohler, A., Sciare, J., Gros, V., Borbon, A.,
Colomb, A., Michoud, V., Doussin, J.-F., Denier van der Gon, H. A. C., Haefelin, M.,
Dupont, J.-C., Siour, G., Petetin, H., Bessagnet, B., Pandis, S. N., Hodzic, A., Sanchez, O.,
Honoré, C. and Perrussel, O.: Formation of organic aerosol in the Paris region during the


