

Response to reviewer's comments:

Title: Secondary organic aerosol formation from smoldering and flaming combustion of biomass: a box model parametrization based on volatility basis set

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Dear Editor,

We thank the reviewers for their comments. Our detailed point-by-point responses to the reviewers' comments (in black regular typeset) are provided in blue regular typeset and the revised text (highlighted in the main text) is in grey italic typeset.

Reviewer 2:

Summary:

This paper is an interesting study on secondary organic aerosol formation from biomass burning. The authors conducted 14 experiments under two burning conditions (flaming, smoldering and flaming) and with different types of stove. Emissions from the burned stoves were sampled and were aged via OH-oxidation reactions to investigate the secondary organic aerosol yields and the chemical properties of the oxidation products from smoldering and flaming. A box model and a genetic algorithm approach were used to quantify the contribution of the VOC oxidation products to SOA yield and to better explain the SOA formation process. However, many portions of the paper were made difficult to follow due to missing details. I recommend that this study be published but with minor revisions. I request that the authors consider the following points as they revise this manuscript:

General comments:

1/ As the title indicates, this paper should focus mainly on SOA formation from smoldering and flaming combustion of biomass. However, few information is given in that issue. The authors should better describe the burning conditions of smoldering and flaming by adding more details especially on how the authors reproduce experimentally the flaming and smoldering combustion.

The first reviewer also asked for more details about the combustion conditions. In the new version of the manuscript, we now describe how we achieved the two different burning conditions. The new Section 2.1 reads as follows:

“Two smog chamber campaigns were conducted to investigate SOA production from multiple domestic wood combustion appliances as a function of combustion phase, initial fuel load, and OH exposure. These experiments were previously described in detail (Bruns et al., 2016; Ciarelli et al., 2017; Bertrand et al., 2017, 2018a) and are summarized here. Experiments from Bertrand et al. (2017, 2018a) will be referred to as Set1 and experiments from Bruns et al. (2016) and Ciarelli et al. (2017) as Set2. The emissions were generated by three different logwood stoves for residential wood combustion: stove 1 manufactured before 2002 (Cheminées Gaudin Ecochauff 625), stove 2 fabricated in 2010 (Invicta Remilly) and stove 3 (Avant, 2009, Attika). For each stove three to four replicate experiments were

performed with a loading of 2-3 kg of beech wood having a total moisture content ranging between 2 and 19%. The fire was ignited with 3 starters made of wood wax, wood shavings, paraffin and 5 natural resin. The starting phase was not studied. In total, 14 experiments were performed, consisting of two experiments at -10°C, seven experiments at 2°C and five experiments at 15°C. These experiments cover the typical range of European winter temperatures and are summarized in Table 1.

Ward and Hardy (1991) define the flaming and smoldering conditions according to the modified combustion efficiency, $MCE = CO_2/(CO+CO_2)$. Specifically, $MCE > 0.9$ is identified as flaming condition, while $MCE < 0.85$ is identified as smoldering condition. MCE values for the different experiments are reported in Table 1. According to this parameter, Set1 and Set2 experiments were dominated by smoldering and flaming, respectively. Practically, we achieved the different burning conditions by varying the amount of air in the stoves, therefore changing the combustion temperature. For Set1, closing the air window decreased the flame temperature, resulting in a transition from a flaming to a smoldering fire. This could be visibly identified, together with the development of a thick white smoke from the chimney. We note that this conduct is very common in residential stoves, to keep the fire running for longer. Meanwhile, for Set2, after lighting the fire, we kept a high air input to maintain a flaming fire. At the same time, we monitored the MCE in real time and only injected the emissions into the chamber when the MCE increased above 0.9.”

2/ According to Majdi et al. (2019), Koo et al. (2014), Konovalov et al. (2015) and Ciarelli et al. (2017), Intermediate and Semi Volatile Organic Compounds (I-SVOCs) are considered as one of the most important SOA precursors emitted by biomass burning. Why did the authors focus only on SOA from VOCs ?

There is a general inconsistency in the nomenclature in the literature. The studies cited above are mainly modelling studies, where the precursors are not measured, but are constrained in the model to improve its agreement with the measurements (Majdi et al. 2019, Koo et al. 2014, Konovalov et al. 2015). These authors refer to these precursors as I/SVOCs as it has been traditionally the case. While unidentified non-traditional precursors are indeed important for SOA formation from biomass burning, claims about the volatility of these precursors cannot be supported without measurements. We prefer to term these missing compounds as non-traditional precursors, without referring to their volatility, which in any case is not required in the model. Recently, Bruns et al. (2016) identified the main SOA precursors in flaming biomass, using a proton transfer reaction mass spectrometer (PTR-MS). These consist of mainly IVOC and VOCs, which have not been traditionally considered in the models. Ciarelli et al. (2017) used the same data to constrain the amounts of non-traditional precursors (the authors termed them non-traditional VOCs, NT-VOC) in a VBS model. They show that while the oxidation of primary SVOCs takes place, increasing the bulk O:C ratio, the net amount of mass gained from these precursors is not substantial (i.e. POA before aging compares well to the remaining POA + oxidized SVOCs after aging). Meanwhile, the oxidation of NT-VOCs are responsible for the majority of the observed enhancement in the OA mass, consistent with the results of Bruns et al. (2016). Based on the reviewer comment and to avoid any confusion, we will replace the term VOCs with OGs (organic gases) in the corrected version of the manuscript.

Specific comments:

1/ Page 4, lines 31-32: Why did the authors choose these experiments? How could the authors study the effect of smoldering/flaming combustion of biomass when the other experimental parameters (OH exposure, temperature of the smog chamber, stove....) change at the same time ?

Extracting class specific yields essentially resides on the variability in the contributions of different classes to condensable species, between experiments (due to variability in the emissions) or within an experiment (due to differences in the precursors reaction rates). By nature, emissions are very complex and therefore hard to control and typically several parameters co-vary. It is important in fitting for the class specific yields in such a multivariate problem that the contributions of the different precursors to the condensable gases do not co-vary with other parameters (e.g. temperature, OH exposure), otherwise their respective effects cannot be distinguished and biases in the yields may arise. The main variability in the contribution of different classes to condensable species is due to variability in the emissions between Set1 and Set2. Most of the other parameters in Set1 and Set2 are consistent or have a significant overlap, allowing the retrieval of class specific yields and a direct comparison between the experiments. In the following, we compare Set1 and Set2 with respect to the different combustion and aging parameters:

- Combustion conditions: The combustion conditions between the two sets are comparable, in terms of the starting procedure and the type and the amount of wood burned. The main difference is related to the air input, which favored smoldering and flaming conditions for Set1 and Set2, respectively. This is directly reflected in the composition of the SOA precursors and such variability is key to deconvolve the class specific yields. Despite this, the emission composition for Set2 is variable, with some experiments showing a similar composition as Set1, ensuring an overlap between Set1 and Set2 chemical composition when other parameters varied.
- OH exposure: The OH exposure is ~7 times higher for Set2 compared to Set1. This is because the OH production rate was similar between the two experiments, but its sink was significantly higher for Set1 due to the injection of higher emissions. However, we note that the OH exposure is not directly considered in the model. Instead, the integrated production of condensable species, inferred from the precursor decay, is used as inputs, which takes into account the differences in the OH exposures. Besides, we note that most of the SOA production occurs at OH exposures $< 8 \cdot 10^6$ molecules cm^{-3} h, which is reached in both experiments.
- Emission loading: On average, higher concentrations were injected during Set1 compared to Set2. This was not intentional, but occurred as smoldering emissions rates were much more important and therefore it was more challenging to control the amounts injected. That said it is important that the concentrations span a wide range (here 1.5 orders of magnitude) to be able to constrain the amounts of oxidation products in the different volatility bins. As mentioned in the manuscript, the volatility distributions are well constrained in the saturation concentrations between 10-1000 $\mu\text{g m}^{-3}$, corresponding to the range of OA concentrations studied here. We finally note that the concentration ranges in Set1 and Set2 have a significant overlap (for Set1, SOA = 50-800 $\mu\text{g m}^{-3}$ vs. 20-140 $\mu\text{g m}^{-3}$), ensuring that the fitting is not biased due to difference in the loadings between the two sets.
- Aging temperature: conducting the experiments at different temperatures is essential for constraining the condensable species enthalpy of evaporation. Set1 experiments were conducted at 2°C, right in the middle of the two temperatures examined in Set2: -10°C and 15°C. Therefore, the temperature does not co-vary with the changes in the emission composition between Set1 and Set2 and the retrieval of the yields is not affected by the temperature.

To compare the SOA produced from smoldering and flaming emissions, we used the specific yields retrieved from box modeling and varied the initial emission composition keeping every other parameter constant. This is presented in Figures 10 and 11.

2/ Page 5, line 27: Flaming combustion occurs at high temperature. Can the authors give an order of magnitude of this high temperature ?

For flaming combustion, the temperature inside the stove was around 600°C.

3/ Page 5, line 31: Why did the authors choose to combine flaming and smoldering emissions in set 1?

We now describe clearly how the stoves were operated and how the different burning conditions were achieved. Practically, we achieved the different burning conditions by varying the amount of air in the stoves, therefore changing the combustion temperature. For Set1, closing the air window decreased the flame temperature, resulting in a transition from a flaming to a smoldering fire. This was identified visibly, together with the observation of a thick white smoke from the chimney. Here, we cannot exclude that flaming and smoldering occurred at the same time in the stove (we still observed some flames, but much less vivid). Therefore, we referred to Set1 as smoldering dominated. This is supported by the values of MCE~0.85. Meanwhile, for Set2, after lighting the fire, we kept a high air input to maintain a flaming fire. At the same time, we monitored the MCE in real time and only injected the emissions in the chamber when the MCE increased above 0.9.

4/ Page 7, line 7: What did the authors mean by “other processes”?

Other oxidative processes (e.g. NO₃ chemistry) or any other process that could deplete VOC concentrations upon aging.

5/ Page 9, line 6: Can the authors give more information about this common set of 263 ions used to identify the most important SOA precursors?

The 263 ions refer to all the HR fitted m/z values from the PTR analysis while the selected 86 compounds were selected as SOA precursors according to their clear decay upon oxidation in the smog chamber. The major SOA precursors amongst these 86 compounds were described in Bruns et al. (2016).

6/ Page 11, line 22-23: Why did the authors choose to set the number of volatility bins to 6 ? How was the volatility C* determined ? Did the authors measure the volatility of each species ?

The volatility basis set (VBS) scheme was used to distribute the oxidation products from the different precursor classes into logarithmically spaced volatility bins. These bins are preset; 6 bins were considered with a saturation concentration $C^* = \{10^{-1}; 10^0; 10^1; 10^2; 10^3; 10^4\} \mu\text{g m}^{-3}$ for the oxidation products of all precursor classes. These bins are chosen to cover the range of OA concentrations measured in our study (higher volatility compounds are not expected to contribute at our conditions). The box model using a genetic algorithm as a solver determines the fraction of the oxidation products in each of the bins, or what can be referred to as the volatility distribution of the oxidation products, to best fit the measured OA concentration. This is thoroughly described in Section 3.3.

7/ Page 11: More clarification is needed in section 3.3.2. Did the given chemical properties of surrogates represent the average of the compounds that are classified in a determined volatility bin ?

We did not measure the condensing compounds in the different volatility bins arising from the oxidation of the different precursor classes. As mentioned in the comment before, the amounts of these compounds are fitted to best represent the measured OA during the different experiments. The molecular composition of these compounds, needed to calculate their molecular weight, is inferred from that of their precursors (C# and H#).

8/ Page 12, line 11: How did the authors assume this single ΔH value for all surrogates? Did the authors consider any assumptions to determine this value?

The ΔH is one of the eight free parameters in the model along with the parameters describing the volatility distribution kernels. Therefore, ΔH is not assumed but fitted to best explain the temperature dependence of the yields. This is described in the modified Section 3.3.4 as follows:

“The model is optimized to determine the volatility distributions of the oxidation products from different precursor classes described by μ_j , σ and their temperature-dependence described by ΔH_{vap} , to best fit the observed OA concentrations.”

9/ Page 13, section 3.3.4 is very short. Can the authors clarify how did this algorithm work to identify the optimized parameters and what did the authors mean by the process of “natural selection”?

We rephrased Section 3.3.4 (in Page 14 Lines 1-15), adding more details about the genetic algorithm.

“The model is optimized to determine the volatility distributions of the oxidation products from different precursor classes described by μ_j , σ and their temperature-dependence described by ΔH_{vap} , to best fit the observed OA concentrations. For the model optimization, we used a genetic algorithm (GA), a metaheuristic procedure inspired by the theory of natural selection in biology, including selection, crossover and mutation processes, to efficiently generate high-quality solutions to optimize problems (Goldberg et al., 2007; Mitchell, 1996). The GA is initiated with a population of randomly selected individual solutions. The performance of each of these solutions is evaluated by a fitness function, and the fitness values are used to select more optimized solutions, referred to as parents. The new generation of solutions (denoted children) are produced either by randomly changing a single parent (as mutation) or by combining the vector entries of a pair of parents (as crossover). The evolution process will be repeated until the termination criterion is reached, here maximum iteration time. In this study, a population of 50 different sets of model parameters (μ_j , σ and ΔH_{vap}) was considered for each GA generation. The sum of mean bias and RMSE between measured and modelled C_{OA} of the 14 experiments were used as fitness function to evaluate the solutions. We assume the termination criterion is reached if no improvement in the fitness occurs after 50 generations, with a maximum of 500 total iterations allowed. The GA calculations were performed using the package “GA” for R (Scrucca et al., 2017). A bootstrap method was then adopted to quantify the uncertainty in the constrained parameters.”

10/ Page 13, Figure 2: The 'others' VOC emissions show the highest relative contribution mainly in set 1. What are these 'others' VOCs emissions?

'Others' include the class of species below m/z 66, which comprises compounds that do not show a clear decay upon oxidation and are therefore not considered as SOA precursors in the further analysis. The major contributor is acetic acid, previously reported to be dominant in residential wood burning emissions (Bhattu et al., 2019). We have this information in the modified version of the manuscript (Page 13, line 17):

"The chemical class referred to as 'Others' comprise compounds that do not show a clear decay upon oxidation and are therefore not considered as SOA precursors in the following analysis. 'Others' is dominated by acetic acid, previously reported as a major species in residential wood burning emissions (Bhattu et al., 2019)."

11/ Page 14, line 11: "Relevant compounds in the latter class are benzene, toluene and xylene." According to Bruns et al. (2016) experimental SOA yields, benzene is the third principal contributor to SOA after phenol and naphthalene. Did the authors characterize these SAH compounds?

The SAH are included in the study and contains benzene, toluene and xylene (table S1). These species exhibit higher contribution to the primary emissions for the flaming phase set of experiments compared to the smoldering phase.

12/ Page 14, line 20: "The SOA/POA ranges between 2 and 6, similar to ratios observed in previous studies." Please add references.

Following the reviewers comment, we added in the main text the following references: (Heringa et al., 2011a, Bruns et al., 2015, Grieshop et al., 2009a, Tiitta et al., 2016).

13/ Page 14, lines 22-23: "Such inconstancy in behavior is either due to differences in the chemical composition within the same class." How did the authors defined these chemical compositions? And how can these compositions change within the same class? Can this be explained by differences in the burned stoves? How can the authors compare SOA contribution from the different classes if the chemical composition can change? Please explain this further.

The chemical compounds considered in each class are consistent among datasets and single experiments. However, the relative abundance of these species within the same class may vary, although this variability is not significant. We calculated an average k_{OH} per class for each experiment (Table 2), to show that the reaction rate within the same class of compounds is consistent among experiments and datasets.

14/ Page 18, lines 17-18: "In general for both phases studied, higher contributions to SOA formation was found for cresol and phenol species and chemically similar compounds." This conclusion is not well supported and not discussed in the paper. Please clarify or add a reference.

Cresol, phenol and chemically similar species belong to the family called OxyAH (see table S1). Figure 11 shows the fractional contribution to SOA for each family for the different Sets as a function of OH exposure, temperature and initial OM load. Overall the higher contribution for both phases investigated belongs to the OxyAH family. We modified this sentence to better relate it to the Figure 11:

"For both phases, SOA formation is found to be dominated by OxyAH (e.g. phenols and cresols), emitted from lignin pyrolysis."

Technical comments:

1) Figure 7 caption: Please replace “the model tend to underestimate ... ”by “the model tends to underestimate...”.

We replaced ‘tend’ by ‘tends’.

2) Eq (1) page 7: Is there any missing bracket in the equation ? Please verify.

Yes, we apologize for this. The bracket was added in the equation.

3) Figure 2 caption: Did Set1 represent only smoldering phase or smoldering and flaming as defined in page 5 line 31? Please correct.

Set1 represents smoldering dominated combustion and Set2 represents flaming dominated combustion. We cannot rule out the possibility of partial inclusion of the other type of combustion because of the challenging operation of the stoves investigated.

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