Response to Anonymous Referee #2   **Manuscript acp-2019-1078**

The authors thank the reviewer for the comments, which improved especially the description of the atmospheric relevance of the results through the revision of the description of the aging conditions during the experiments. In the following comments we provide point-by-point responses to the questions and comments made by the referee. The replies to the comments are indicated as red text. The revised manuscript showing the changes made to the text is available in an additional comment in the manuscript discussion thread.

Overview

The manuscript by Hartikainen et al investigates how gas- and particle-phase emissions from residential wood combustion vary with respect to combustion conditions (including stove type) and fuel. Additionally, the emissions are aged in a photochemical reactor to investigate how composition evolves with atmospheric age. Numerous analytical techniques are used allowing the authors to broadly characterize both gases and aerosols. Overall, the authors find that emissions depend on combustion conditions and that photochemical aging alters composition, generally by creating more oxidized species. Emissions from residential wood combustion is an important and poorly understood contributor to air quality issues and the understanding of the influence of aging is poor. Thus, although this is a largely descriptive paper with few quantitative or testable conclusions, the experiments are of interest to the community. However, I have several major concerns that should be addressed prior to acceptance. My main critique is that the manuscript claims to investigate the aging that occurs over multiple days but there is no discussion about how the experimental conditions differ from the atmosphere nor is there discussion/consideration about how important reactions such as peroxy radical fate differ between the OFR and the real atmosphere.

Major Comments

1) The description and analysis of the OFR experiments is insufficient and requires substantial expansion. Interpreting the chemistry of OFRs is difficult and there needs to be careful consideration of the dilution effects, gas-phase peroxy radical fate, NO and NO2 mixing ratios, and potential for unwanted chemistry if the results are to be applied to the atmosphere. This is particularly true when making claims about multiple day aging timescales as is done here.

In terms of the description, details such as the mixing ratio of ozone and butanol should be included as should the residence time. In terms of analysis, the authors need to more carefully consider the operation of the OFR, how this impacts the results, and the subsequent implications for atmospheric relevance. I list some specific questions below, but there needs to be a more general consideration of this chemistry.

Description of the aging conditions and reactor use is naturally crucial for an OFR study, and consideration of the questions pointed out by the reviewer clearly improves the credibility of this assessment in this manuscript. In the following sections we provide point-to-point answers to the specific questions presented by dividing the comments by topic.

Mixing ratios of O_3 (2-11 ppm) are included in Table 1 and are now indicated more pronouncedly in the text of Material and methods Section 2.2 together with the initial mixing ratio of butanol-d9, which was 80-200 ppb. Residence time (139 s) is now also stated clearly in the Section 2.2.

For instance, in the atmosphere the emissions will experience dilution over the course of several days aging – how might dilution alter the implications of this work?

Dilution has important impacts to the gas-particle partitioning of organic aerosol. Under higher dilutions, semivolatile compounds measured in this work would have had higher concentrations in the gas phase and, in turn, lower concentrations in the particulate phase from where they were assessed with the IDTD-GCMS. During the lifetime of the emissions from the emission source until long-range transported smoke, a high range of different dilution ratios exist. For practical reasons (e.g. limited measurement time), we could perform the experiment only by using a certain range of dilution ratios. The usage of very high dilution ratios, which would be most representative to atmosphere, would be possible to in the OFR, but it would hamper the possibilities for comprehensive chemical and physical analyses of aerosols, due to sensitivity limits of the instruments. Thus, we used lower dilution in the PEAR than what normally occurs in atmosphere but have the advantage of better quality in the chemical analysis results. This is now mentioned also in the text (Section 3.3).

How representative is the peroxy radical chemistry (Peng et al., 2019) and how might this alter in particular the gas-phase measurements?

Due to the high OH and HO_2 concentrations in the PEAR OFR, the shortened lifetime of RO_2 decreases its isomerization compared to atmospheric conditions (Peng et al., 2019). Further, the HO2-to-OH ratio (roughly approximating in the range of ~10-50:1) is lower than in atmosphere (~100:1). Consequently, the importance of RO_2+OH reactions is enhanced. The RO_2 fate in the PEAR OFR was roughly estimated using the RO_2 fate estimator by Peng et al. (2019). The estimation of the RO_2 fates during the first minute, during which majority of the OGC have reacted, is given below for two different experiments: first with high OH exposure (Masonry heater Exp. 2), second with high OHR$_{ext}$ (Chimney stove Exp. 5).
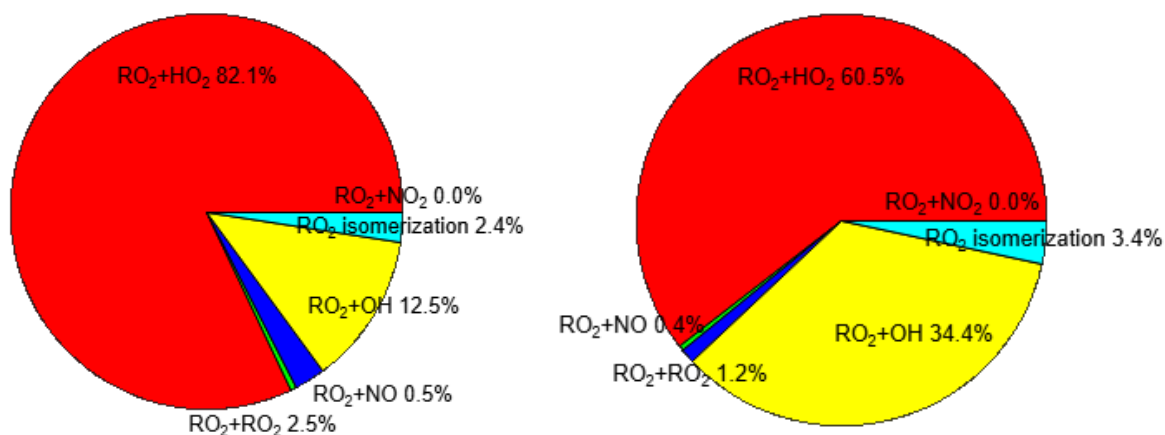
Discussion of the peroxy radical chemistry is now included in Section 3.3 discussing OFR chemistry and noted also in the discussion of VOC transformation, as fragmentation in the PEAR OFR may be enhanced due to the different RO_2 chemistry than in atmosphere or in chamber experiments.

Is NO_3 chemistry occurring in the reactor and if so, does it vary as a function of the OH exposure or across a given experiment?

We assume NO_3 to be negligible due to its slow formation rate and fast photolysis in the PEAR. This is supported by the low AMS NO-to-NO_2 ratio, based on which all particulate nitrate was inorganic.

The formation of compounds such as nitroaromatics will depend on NO2. Is it possible that nitrophenols decreased with increased aging because the NO/NO2 chemistry was altered in the reactor and thus the formation of nitrophenols was altered (rather than nitrophenols being oxidized by the increased OH as is implied in the manuscript)?

Although the ratio of NO-to-NO_2 prior to aging was in the range of ~10-40:1, NO is rapidly oxidized to NO_2 in the PEAR OFR and the amount of NO measured downstream the PEAR OFR is negligible (<0.02 ppb) in all experiments. Similar NO-to-NO_2 conversation takes place also in environmental chamber, where formation of nitrophenols has been observed previously (Hartikainen et al., 2018). Furthermore, exposure level was not observed to affect the observed NO_2 levels.

Although we cannot explicitly state the reason for nitrophenol decay in the scope of this manuscript, we find it likely that the after the rapid conversion of the precursor compounds (i.e., phenols) has taken place at the first stages of aging, the change in nitrophenol concentrations in the PEAR OFR is governed by nitrophenol-OH reactions and photolysis (Hems and Abbatt, 2018), which are both enhanced in the high-aging experiments due to the high photon fluxes and OH concentrations.

Overall, the OFR chemistry needs to be considered more thoroughly in order for meaningful conclusions to be drawn about how the emissions will be transformed in the atmosphere.

We hope that the above-mentioned improvements on the explanations of the chemistry in the PEAR OFR and the overall revision of the manuscript text now provide satisfactory information for validation of the used method and comparison against atmospheric conditions.

2) I find the manuscript difficult to read given the number of different variables explored and the number of analytical techniques used. While it is an advantage that multiple instruments measured the same thing, it is often not clear in the figures or the text which measurement or condition is being discussed. This makes it difficult for the reader to identify the main conclusions and findings. Clarification of the combustion/oxidation conditions and analytical instrumentation being discussed needs to be made more explicit throughout the text. For instance, in Fig. 6 are the values averaged over all the batches? I assume that Fig. S2 is FTIR measurements, but it would be useful to explicitly state.

In Figure 6 (now Fig. 4) the values are indeed averaged over all the batches per experiments and Fig. S2 is based on the FTIR measurements. Clarification of the conditions and analytical instrumentation employed for each finding was added when necessary, for example in Sections 3.5.4 and 3.5.5 and in the supplementary figures (Figs. S2, S5-S8, S16-S17 and S19).

Minor Comments

Sect 3.5.2 Did the authors consider performing PMF with the rBC peaks included? It would be interesting to see if the rBC peaks supported the PMF factor interpretation.

We thank referee for the valuable idea of performing PMF analyses with the rBC peaks included. However, it falls outside of the main focus of this paper, which is the dependence of organic aerosol composition on OH exposure.

We performed a test run with PMF applying SP-AMS data using refractory carbon clusters. Two-factor solution showed that timeseries of the rBC-dominated factor correlated best with the timeseries of flaming-BBOA factor (see figure below). This observation supports the PMF interpretation since it is well-known that the refractory black carbon is formed mainly during the flaming phase (Kortelainen et al., 2018; Nielsen et al., 2017).
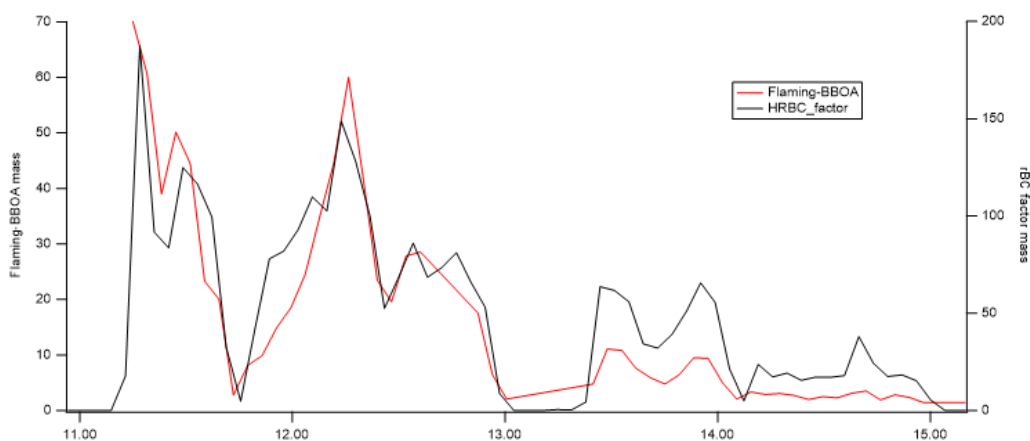
In future work we would also like to connect refractory black carbon with the high-resolution NR-OA to analyze rBC-associated coating of OA.

Line 494: The statement about diminished health effects is not well supported, particularly since it is followed with a statement that the heteroatom containing PACs may have negative health impacts. Without any measurements of for instance ROS generation, I think the more accurate statement is that the health effects would likely change (but no indication of better or worse).

True. This sentence in Section 3.5.3 was revised, and now reads:

"The change in the PACs also alters the potential health effects of the exhaust: although the total PAC concentration decayed, the simultaneous formation of oxy- and nitro-PAC derivatives known to be detrimental to health was observed."

Technical comments

Why only consider m/z 40-180 for the PTR?

According to our experience, the compounds reliably measurable from RWC exhaust with PTR fall within this range, which was stated mainly to specify the observable range to the reader. The sentences in Section 3.2.1 and 3.4. describing the use of PTR-MS are now rephrased ("-- for OGC in the primary emissions were identified in the m/z range of 40–180 --" and "aging may also lead to the growth of compounds outside the observable mass range", respectively).

I think "oxygenated" rather than "oxidized" would be a better choice for describing the compounds measured in the unoxidized exhaust in order to avoid confusion (for instance in Fig. S3).

This is true. We also used "oxygenated" instead of "oxidized" in the text and for example in the previous Fig. 3 and Table S1. The description is now unified and "oxygenated" used also in e.g. Fig. S2 and the previous Fig. S3 (now revised and replacing Fig. 3 in the main text).

S3 and S4 are difficult to interpret since the x-axis and groupings are changed. It would be easier to compare if they were kept in the same format.

Figure S3 was revised to share the format of Fig. S4 (now S3) and moved to the main text where it now replaces the previous Fig. 3.

Line 65 and elsewhere, please clarify what is meant by "semi-VOCs"

Rephrased to more general term, organic gaseous compound (OGC).

Line 267 these aren't units of emissions

We revised the terminology to "concentrations" in this section (3.2.2) considering the primary emissions. The concentrations in the secondary exhaust are normalized to 13 % flue gas excess oxygen, which is a common procedure to present emissions from logwood fired stoves. The fact that the emission concentration is normalized to a certain oxygen level means that the values corrected for the changing air-to-fuel ratios and are therefore directly proportional to emission factors as #/fuel energy content or #/consumed fuel mass. The emission factor calculation procedures are presented more thoroughly by e.g. Reda et al., (2015, supplement). We have now also stated clearly in e.g. figures which concentrations are normalized to 13% flue gas excess oxygen.

Line 287: Figure S14 referenced out of order. Other references may be out of order as well.

Due to the length of the supplementary information, it is structured by subject matter. In other words, all material related to each subject are all grouped under the respective title, rather than included in the order of first appearance. We also decided to keep figures with the same structure/topic together, which is the case with Fig. S14 (now Fig. S15), where thermal-optical EC and OC are compared to AMS rBC and OA, respectively.

In some cases, this also leads to references in the main text to be out of order. With this, we aim to help the reader in finding the information related to each subject.

Line 319: What is meant by "external OH reactivity"?

External OH reactivity refers to the OH reactivity of the gases in the sample that is input PEAR OFR (Li et al., 2015). It is defined in the Material and methods section 2.2.

Reference Peng, Z., Lee-Taylor, J., Orlando, J. J., Tyndall, G. S. and Jimenez, J. L.: Organic peroxy radical chemistry in oxidation flow reactors and environmental chambers and their atmospheric relevance, Atmospheric Chem. Phys., 19(2), 813–834, doi:https://doi.org/10.5194/acp-19-813-2019, 2019.

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