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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Photochemical transformation of residential wood combustion emissions: dependence of organic aerosol composition on OH exposure" *by* Anni Hartikainen et al.

Anonymous Referee #2

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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 oxi-

dized 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.

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?

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

Is NO3 chemistry occurring in the reactor and if so, does it vary as a function of the OH exposure or across a given experiment? 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)? 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.

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.

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.

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).

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

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).

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.

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

Line 267 these aren’t units of emissions

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

Line 319: What is meant by “external OH reactivity”?

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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