

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 #1

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GENERAL COMMENTS:

This article addresses photochemical aging of residential wood combustion (RWC) emission from two stoves at the home-built PEAR oxidation flow reactor, reaching OH exposures representative of aging of up to one week in the atmosphere. This is one of few studies addressing the topic of RWC aging in OFRs with a suite of state-of-the-art mass spectrometric online and offline techniques and adds value for the scientific community.

C1

In my view, the manuscript is of high scientific quality and presents relevant results from a comprehensive study. The language and structure, however, lack clarity and some information is redundant which makes the manuscript unnecessarily long and the core findings quite dilute. I suggest that this be improved to make the article more concise and easier to follow and understand for the readers. I believe this is feasible with major revisions of text and paragraph structure in order to allow more clarity on the main findings, conclusions and limitations of the study. Aside of specific comments below, re-formatting of units, table layouts, etc., into one consistent format and re-structuring paragraphs may help to achieve this. As a general comment, the results section would benefit if the authors would focus on summarizing their main findings first, and discuss the limitations of the study in a second stage with a focus on their implications of the obtained results, rather than first discussing experimental conditions/limitations as results followed by reporting the actual findings.

In summary, I have enjoyed seeing these results and am looking forward to see the revised manuscript published.

SPECIFIC COMMENTS:

Overall:

o The main findings are dilute throughout the manuscript and difficult to grasp. Parts in the conclusion section remain vague too. I suggest to summarize the main goals and questions of the study as specific as possible at the end of the introduction and to state the core findings as specific as possible in the conclusions section.

o While the manuscript title is focused primarily on the photochemical aging of the emissions, a substantial part of the manuscript discusses primary emissions (Fig 2+3), operating/experimental conditions (Fig 4+5) and only the second part of figures (Fig 6-11) and results actually addresses the aging and chemistry question. In my view, some of the initial figures (e.g. 4+5) could be moved to the SI along with their text in favor of clarity of the manuscript; the implications of the determined losses in Fig 4+5 should

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then be referred to discussing the actual results, i.e. for example, the authors might address how do particle/vapor losses influence the observed decay of compounds as a function of OH exposure in their experiments. Alternatively, Figure S1, S3 and S4 could fit well with the main text, as they summarize the primary emissions composition, which is relevant for any following discussion of emissions aging. Further remarks to help clarity and focus are listed later on.

Abstract, Introduction & Methods:

o L20/ Abstract: suggest to specify here which oxidation flow reactor is used in this study; suggest to use "PEAR OFR" throughout

o L21 vs L 28 and other occasions/ Abstract: The authors mix between "gaseous organic compounds" and "volatile organic compounds"; suggest they try to harmonize the language

o L27/ Abstract: specify based on which analysis the acetic fragmentation is investigated

o L30 / Abstract and other occasions: the authors use the more generic term "polycyclic aromatic compounds (PACs)" rather than polycyclic aromatic hydrocarbons (PAHs) which has been used in previous related work and is also mentioned in e.g., L75. I suggest to specify and/or define for non-specialists, why the authors refer to PACs in some cases but PAHs in others. This should also take into account the limitations of their instrumentation to effectively distinguish between PACs and PAHs. In my understanding, frequently only fragments of PACs can be detected with PTR-ToF-MS or AMS, however, they are assumed to be and referred to as PAHs in the manuscript.

o L36 / Abstract: suggest to specify which scale is "fresh", "shortly aged", and "long-term aged" in the context of this study

o L54: Is there a difference between "fresh" and "unaged"? Otherwise, I suggest the authors rephrase to read "fresh, i.e. not atmospherically aged"

C3

o L60/61: The authors may include in this section of SOA-precursor discussion that removing aromatic hydrocarbons from wood burning emissions by use of e.g. catalytic converters can drastically reduce SOA formation, as recently presented by Pieber et al., 2018; also changing appliance operation and modifying combustion phases to conditions that emit less aromatic hydrocarbons might have this effect; Figure S3+S4 are valuable indicators in this context.

o L87: suggest to provide some references for previous RWC OFR studies in addition to the mentioned smog chamber experiments; e.g. Bruns et al. 2015, Czeck et al. 2017, Pieber et al. 2018, etc.

o L132: "In addition" . . . "additional"; language is redundant. Suggest to remove one of the two.

o L133-134: Ozone and butanol-d9 metrics in volumetric flows does not provide any information on concentration levels; could the authors in addition or instead specify the mixing ratios?

o L134: "formed" should probably read "forms"

o L135: "depended" should probably read "depends"

o L135: "H2O" should probably read "H2O vapor"

o L143: "OH concentration" should read "24-hour average global OH concentration"

o L146: was butanol-d9 mixing ratio included in this equation and what is its relative contribution to the total OHR external?

o L148: suggest the authors present the main results of OHR external analysis in one brief sentence in this paragraph, and mention its implications for the results and conclusions later on.

o L150ff: suggest the author present the main results of particle and LVOC loss estimates in 1-2 brief sentences in the main text here and move the remaining text on this

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topic from the results section to the SI, discussing it in the main text only as a limitation of the study including its implications for conclusions (as reasoned above). I suggest also to define what LVOCs refers to in the context of this article.

o Line 160/161: I suggest to keep all information in one paragraph, rather than starting a new paragraph here.

o L167: suggest to define semi-VOCs in this context.

o L168: "isotope labelled" should probably read "isotopically labelled"

o L173: suggest to replace "after the PEAR" with "after the PEAR, i.e. at its outlet"

o L187: the author refer to this instrument as "AMS" throughout the manuscript; I suggest to change this to SP-HR-ToF-AMS on all occasions, starting from the abstract, as is done for all other instrumentation (e.g. PTR-ToF-MS).

o L189: Why did the authors choose to use the "Improved-Ambient method" for this laboratory data set?

o L200: Suggest to compare also with Bruns et al., 2015 who have used this method beforehand for an intercomparison of spectra from OFR and smog chambers including RWC.

o L205: Suggest to replace "residential wood combustion" with RWC

o L209 (from L186 onwards): as noted in the next comments; please add important information on AMS data analysis in the main text.

o Some text is repetitive or split into different locations (partially found in main text, partially in duplicate SI), while other text is grouped together into subchapters which are not entirely logical. I suggest to make the overall language more concise and shorten the text, while keeping all relevant information in the main text. E.g. some suggestions:

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• L170 (main text): I suggest to relabel this as "Online aerosol particle and gasphase measurements" to avoid ambiguity." It may be beneficial to split the subsection 2.4 into three sections for each instrument, and then make further separate paragraphs for any AMS information aggregated as a) experimental/calibration/raw data correction, b) PMF analysis, c) HR fitting or PAH fitting.

• L186 onwards (main text): relevant AMS operating conditions (e.g. size-cut off) and data corrections (RIE=1.4 for OA, CO₂-interference correction, CO₂ gasphase correction) should be mentioned in the main text; I suggest to move information from SI (Section S5) entirely to the main text, but shorten the paragraph by avoiding redundancies (e.g. "The AMS data was analysed using the standard analysis tools SQUIRREL v1.62A and PIKA v1.22D adapted in Igor Pro 8 (Wavemetrics)." is currently stated double. With regards to the RIE=1.4, please mention that this is valid for OA. With regards to the CO₂-interference correction, please mention the magnitude of interference and potential impacts on the determined O/C ratios. What was the level of inorganic nitrate to OA in the primary and secondary emissions? With regards to CO₂ gasphase-correction, please mention whether this was done by standard measurements of particle-filtered air during the experiment or external calibration with gaseous CO₂.

• L190 onwards (main text): I suggest to make a new paragraph with all information relevant to PMF, see comments above.

Results:

o L210: Suggest to relabel as "results and discussion", given the separate section entitled "conclusions" in L540

o Section 3.1.: Is there any information on the temperatures during these different combustion phases available?

o L228: "constantly" should probably read "continuously"; "from the diluted flue gas"

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should probably read "in the diluted flue gas".

o L232: "primary aerosol" is certainly technically correct if referring to aerosol as particles plus their surrounding gas, however, it may quickly become confusing as often "aerosol" is used when referring to the particle phase only. I suggest to replace "primary aerosol" with "primary emissions" here.

o L233: suggest to specify the value of protonation efficiency (proton affinity) here

o L230: suggest to state the limitations of both, FTIR and PTR-ToF-MS, here briefly, e.g. for PTR-ToF-MS, rather than point out alkanes specifically, it should be noted that any molecules with proton affinity lower than that of water (in H₃O⁺ mode) can not be protonated and hence detected; further, I suggest to mention based on which criteria 127 molecular formulas were identified and how many ions remained unidentified. For the FTIR, it would be informative to give a brief reasoning why only 27 compounds can be detected and quantified, rather than only refer to the table in SI.

o L233: fragmentation does not necessarily limit the quantification but rather the identification; suggest to rephrase

o L236: suggest to introduce the later used abbreviation "ArHC" here at its first occasion

o L243: suggest to replace "significant" by "statistically significant" here

o L259: ArHC are also discussed earlier, but the abbreviation is only introduced in L259; suggest to revise and use and define ArHC earlier on

o L265: Suggest to add that previous studies (e.g. Pieber et al. 2018), demonstrated that removing ArHC from the emissions mix substantially reduces their SOA formation.

o Figure 7 and 8: where do O/C and H/C ratios of other wood burning OFR studies fall in comparison to the obtained results (e.g. add data from Bruns et al., 2015, Czech et al. 2017, Pieber et al., 2018, and similar data from other research groups as available).

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o L371: Replace "consequent" with "subsequent"

Conclusions

o L556: "Notably, small, acidic" should probably read "Notably, small acidic" (i.e. without comma)

o L565: given that the presented manuscript discusses OFR-experiments, I suggest to cite and discuss also other OFR studies with RWC rather than only smog chamber experiments; e.g. Czech et al. 2017, Bruns et al. 2015, Pieber et al. 2018: how do those PAM OFR studies compare in OH exposure with the here presented PEAR OFR study?

o L564-566: The authors conclude: "Based on this work, different transformation pathways for RWC exhaust under photochemical conditions can be roughly outlined: the initial pathways consisting of functionalisation and condensation from gaseous precursors are followed by more particulate-phase-driven chemistry consisting of heterogeneous oxidation and fragmentation." The authors need to discuss their limitations of differentiating between gas-phase oxidation, heterogeneous chemistry and particle-phase-driven chemistry owing to their experimental set-up in the discussion of the results and the presentation of their conclusions.

o L569 onwards: this information is quite generic and could be omitted and replaced with more specific conclusions in my point of view; otherwise it does not add additional value to the manuscript.

Technical Comments:

o Formatting of units (e.g. L/min vs L min⁻¹), figures (e.g. legends are sometimes to be found left, right or centered) and tables (e.g. horizontal lines in tables, as well as table dimensions), in particular in the SI is inconsistent. While this is of course not critical with regards to the scientific quality of the work, it would help the reader to follow the presented research work more easily and hence enjoy the results more.

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Supporting Information

o All information provided in the SI should also be noted in the main text; all information provided in the SI should be described with the references such that the document can be read independently, etc.

• E.g., Table S1: please add reference for the OH constant used.

• E.g. Table S2.1: please add reference for the "OHR external" definition. Is CH₄ negligible or why was it not included in the analysis?

REFERENCES

Bruns et al. 2015, DOI: 10.5194/amt-8-2315-2015 Czech et al. 2017, DOI: 10.1016/j.atmosenv.2017.03.040 Pieber et al. 2018, DOI: 10.1021/acs.est.8b04124

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-1078>, 2019.