

We thank the reviewer for this thorough feedback, which has been very useful in improving the composition and preciseness of the manuscript. In the following comments we provide point-by-point responses to the questions and comments 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.

**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.

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.

The entire text was revised to improve clarity of the manuscript, shorten the text, and improve language where necessary. Some information was moved to the supplementary information in order to better emphasize the core findings in the manuscript text. The tables and figures have been reformatted where necessary for better consistency in formats. We also added a paragraph in the Results & discussion section which summarizes the main findings as requested by the reviewer.

**SPECIFIC COMMENTS:****Overall:**

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.

The goals of the manuscript are now stated more clearly at the end of Introduction. We included a chapter in the beginning of the Results and discussion to give an outline of the contents and major findings in the result:

“This study comprehensively characterises the chemical properties of RWC exhaust at different atmospheric aging times by combining extensive information gathered from gas-phase and particulate phase chemical analyses. In this section, we first discuss the dynamic combustion conditions and the characteristics of primary emissions from logwood stoves utilized with different fuels, which define the starting point for the aging experiments. Next, the aging conditions in the PEAR OFR are evaluated in order to validate the atmospheric relevance of the results. Finally, we assess the changes in the gaseous and particulate OA during the aging process under a variety of different oxidant concentrations. The observations of changes both in bulk- and molecular level aerosol chemical composition demonstrate that the major transformation pathway of OA changes from initial gas phase functionalisation followed by condensation to the transformation of the particulate OA by heterogeneous oxidation reactions and fragmentation. The study shows a linear dependency between OH exposure and organic aerosol oxidation state. Furthermore, OH-exposure-dependencies of specific OA constituents, such as nitrophenols, carboxylic acids and PACs, are established.“

We also thoroughly revised the Conclusion section, where needed.

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 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.

We consider presentation of the primary emission contents important for throughout understanding of the aging process and products, but the focus of this manuscript is indeed in the secondary products formed in the aging exhaust. Thus, as proposed by the reviewer, revised Figure S3 was implemented in the main text, replacing previous, more general Figure 3. Furthermore, information on the LVOC fate, including previous Figures 4 and 5, was transferred to Supplementary section S2.2.

### **Abstract, Introduction & Methods:**

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

Revised as suggested by the referee. The reactor is now referred to as “the PEAR OFR” throughout the manuscript.

- 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

We harmonized the language by using “organic gaseous compounds (OGC)” throughout the manuscript when the volatility of the compound/group was not mentioned.

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

The following sentence was added into the abstract:

“Aging led to an increase in acidic fragmentation products in both phases, as measured by the IDTD-GC-ToFMS for the particulate and PTR-ToF-MS for the gaseous phase.”

- 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.

We chose to use the term “PAC” due to it covering also substituted polycyclic aromatic compounds. It is also suitable in cases where the parent compound is not known. The use of the terms (PAC/PAH) in the manuscript was revised to be more uniform (e.g. “*X-substituted PAC*” instead of “*X-substituted PAH*”).

Analysis of all PACs, including the substituted PAHs, was done in similar manner. Fortunately, fragmentation of the PACs is minor in both PTR-ToF-MS (Gueneron et al., 2015) and AMS (Herring et al., 2015). With the AMS, the PAC with  $m/z < 300$  are seen as the original molecular ion, while for larger PAC only the possible fragments are observed in the spectra (< 5 % of AMS signal; Herring et al. 2015). PACs are known to give intense signatures in AMS for both single and double charged molecular ions (Herring et al., 2015; Dzepina et al., 2007) due to delocalization of the charge, which is an asset when considering the extent of possible fragmentation. For the HR-PAH analysis, the quantification by the P-MIP-method (Herring et al., 2015) is done by considering also the main fragmentation and isotopic patterns of the PACs, which enables precise molecular identification likewise for substituted and for hydrocarbon PACs.

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

During revision, this sentence was removed from the abstract, which now states, more broadly, that “The observed continuous transformation of OA composition throughout a broad range of OH exposures indicates that the entire atmospheric lifetime of the emission needs to be explored --“

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

In this situation there is no difference. Revised.

- 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.

This is a good notion, and now also included in the Introduction:

“-- removal of these [aromatic] compounds either via improved combustion conditions or for example catalytic cleaning have been shown to be efficient in lowering the SOA potential of RWC emissions (Czech et al., 2017; Pieber et al., 2018). “

It is now also mentioned in the results section 3.2.1 to highlight the importance of aromatic compounds to SOA formation.

- 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.

References to previous OFR studies are now also included.

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

We have removed the extra “additional” as suggested.

- 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?

Ozone mixing ratios are available in Table 1 and now also included in the Methods-section, together with the butanol-d9 mixing ratios.

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

Corrected.

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

Corrected.

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

Corrected.

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

Corrected.

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

Butanol-d9 was not included in the initial OHR<sub>ext</sub> calculations. We thank the reviewer for pointing this out, as naturally the additional OH tracer consumes radicals as well. The OHR<sub>ext</sub> by butanol-d9 varied from 7–17

$s^{-1}$ , corresponding to 1 – 7 % of total  $OHR_{ext}$ . Its importance was highest on the experiments with otherwise lower  $OHR_{ext}$ , and minor (1 %) on the experiments with e.g. lower DR (and higher  $OHR_{ext}$ ).

$OHR_{ext}$  by butanol-d9 is now included in the discussion about  $OHR_{ext}$  and in the consideration of the reaction pathways in the PEAR OFR, including e.g. Table S4 and Figs. S6, S10 and S11.

- 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.

We now present the main  $OHR_{ext}$  results already in the Methods Section 2.2:

“Due to the differences in the emission concentrations during logwood combustion also the  $OHR_{ext}$ , and consequently  $OH_{exp}$ , vary also within a batch (Fig. S9). Average  $OHR_{ext}$  was in the range 130 – 1300  $s^{-1}$  with the highest contributions from CO, NO, and unsaturated hydrocarbons (Fig. S5).”

- 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 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.

Discussion of LVOC fate from chapter 3.3.1. was divided into main text Section 2.2. and SI Section S2.2. as suggested. We rephrased the whole paragraph, which now also better defines the meaning of “LVOC” in this context, i.e.: “The fate of the gaseous organic compounds capable of irreversible condensation under the present experimental conditions, i.e., low-volatility organic compounds (LVOC), was estimated based on Palm et al. (2016)”.

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

Corrected as suggested.

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

Section was revised to note that majority of the compounds can be classified as semi- or intermediately volatile (saturation mass concentrations between 0.3 -  $3 \times 10^6$ ), to highlight that these compounds may exist in both phases under the experimental conditions.

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

Corrected.

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

Revised to “ -- were monitored at the outlet of the PEAR OFR”

- 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).

AMS is now referred to as SP-HR-TOF-AMS throughout the manuscript.

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

The commonly used "Aiken-Ambient" method is systematically biased low (Aiken et al., 2008), with larger biases observed for alcohols and simple diacids. The Aiken-Ambient method underestimates the CO<sup>+</sup> and especially H<sub>2</sub>O<sup>+</sup> produced many oxidized species. The Improved-Ambient method uses specific ion fragments as markers to correct for molecular functionality-dependent systematic biases and reproduces known O:C and (H : C) ratios of individual oxidized standards within 28 % (13 %) of the known molecular values (Canagaratna et al., 2015).

- 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.

Bruns et al. (2015) applied the PMF as a tool for separation of POA/SOA components and created a two-factor solution by first finding the mass spectra for POA, and then assuming the rest as SOA (or aged-POA). In other words, spectra for SOA is not given nor were different oxidation pathways segregated. One important difference between PMF factors by Bruns et al. (2015) and those present here, is that in Bruns et al. the exhaust from the batch was first mixed in a chamber before aging in a PAM OFR, while in this manuscript the measurement of the exhaust was dynamic, and the factors are also tied to the combustion periods of batchwise combustion with the POA factors being separated by the combustion phases.

References to previous RWC studies utilizing similar factorization methods are now included in Section 2.5:

"Similar method have been used previously for example for the assessment of RWC generated POA and SOA in a chamber (Bruns et al., 2015a; Tiitta et al., 2016) and in an OFR (Bruns et al., 2015a) or for time-resolved analysis of RWC OA emission constituents (Elsasser et al., 2013; Czech et al., 2016)."

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

Replaced as suggested.

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

Information of the AMS operating conditions was moved to the Material and methods Section S2.5.

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:

- L170 (main text): I suggest to relabel this as "Online aerosol particle and gas-phase 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.

We split the section 2.4 into two sections, namely, 2.4 for the gas phase measurements, 2.5. for the particulate-phase. AMS section now contains three paragraphs which are related to (1) data correction, (2) PMF-analysis, and (3) HR-PAH analysis.

- L186 onwards (main text): relevant AMS operating conditions (e.g. size-cut off) and data corrections (RIE=1.4 for OA, CO<sub>2</sub>-interference correction, CO<sub>2</sub> 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.

Information of the AMS operating conditions was moved to the main text (Section 2.5) and the repetitive parts removed or rephrased; see specific comments for rephrased sections below.

- With regards to the RIE=1.4, please mention that this is valid for OA.

For biomass burning emissions, RIE of 1.4 agrees with the OA mass concentrations with stated  $\pm 38$  % uncertainty of AMS (Bahreini et al., 2009; Xu et al. 2018). This is now stated in Section 2.5 discussing AMS analysis.

- With regards to the CO<sub>2</sub>-interference correction, please mention the magnitude of interference and potential impacts on the determined O/C ratios.

A CO<sub>2</sub>-AMS interference calibration value of 0.3 % ( $a=0.003$ ) of the NO<sub>3</sub> concentration was determined by NO<sub>3</sub>NH<sub>4</sub> calibration and corrected via the fragmentation table according to Pieber et al. (2016). Without correction, maximum effect on O:C value was 5 %, with typical values lying under 1 %. This is now stated in the Section 2.5 on AMS analyses.

- What was the level of inorganic nitrate to OA in the primary and secondary emissions?

The concentrations of inorganic NO<sub>3</sub> in the emissions are available in Table S7. The ratio of NO<sub>3</sub>-to-OA varied between 0.02 (masonry heater, age 1.5 eqv.d) and 1.1 (chimney stove, age 0.6 eqv.d), but cannot be tied to atmospheric age. As stated in the previous answer, the effect of nitrate to the AMS analysis was small.

- With regards to CO<sub>2</sub> gas phase-correction, please mention whether this was done by standard measurements of particle-filtered air during the experiment or external calibration with gaseous CO<sub>2</sub>.

The time-dependent gas-phase CO<sub>2</sub><sup>+</sup> subtraction was applied. It was conducted using the online HEPA filter measurement technique of gas-phase CO<sub>2</sub> for corrections. This information was added to the Material and methods Section 2.5 on AMS analysis.

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

The information considering PMF was separated into its own paragraph, as suggested by the reviewer.

## **Results:**

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

Corrected.

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

Unfortunately, no measured temperature information is available from the current study. The time-dependent temperature patterns during batchwise logwood combustion and their effects on emission characteristics have been established earlier by e.g. Czech et al., (2016) and Kortelainen et al., (2018). Section 3.1 was modified to not give an impression that we have exact measured temperature data available from these experiments.

- L228: "constantly" should probably read "continuously"; "from the diluted flue gas" should probably read "in the diluted flue gas".

Corrected.

- 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.

This sentence was revised to "-- OGC in the primary emissions --" to highlight that here we discuss the gaseous phase of the primary emissions.

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

Mention of the exact proton affinity of water ( $691 \text{ kJ mol}^{-1}$ ) that sets apart the detectable compounds is now included.

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  $\text{H}_3\text{O}^+$  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.

The sentence about PTR limitations is now revised, including e.g. the limiting protonation affinity, as suggested. The identification of compounds by PTR-MS was done based on the high-resolution  $m/z$  and previously reported compounds found from RWC as in previous work (Hartikainen et al. 2018) as stated on Section 2.4. Molecular formula could be allocated to majority of the compounds, although precise identification of higher  $m/z$  compounds is innately not possible.



The organic compounds measured with the FTIR were limited to those calibrated to the particular instrument used in this study. The sentence describing the measured components in the manuscript Section 3.2.1 now states that “-- FTIR was calibrated for 27 typical combustion-derived compounds --”

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

True. The sentence is rephrased.

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

Introduction of the abbreviation is now included already in Section 3.2.1.

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

Done.

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

ArHC is now defined already in the Section 3.2.1 when discussing primary OGC emissions.

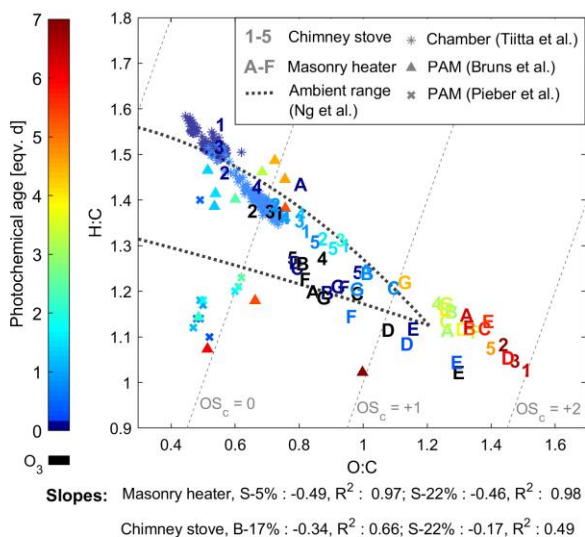
- L265: Suggest to add that previous studies (e.g. Pieber et al. 2018), demonstrated that removing ArHC from the emissions mix substantially reduces their SOA formation.

A notion that " removal of ArHC from the flue gas either by improving combustion conditions or using e.g. catalytic cleaning has been noted to decrease also the resulting SOA formation (Bruns et al., 2016; Hartikainen et al., 2018; Pieber et al., 2018). “ were added to Section 3.2.1, as suggested.

- 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).

The O<sub>S</sub>C of highly aged particulate OA observed here is lower than previously measured for RWC exhaust with a PAM OFR (Bruns et al., 2015, Pieber et al., 2018), where the exhaust from batchwise combustion was mixed prior to aging in the PAM. While this approach is reasonable as the exhaust exists as a mixture also in the atmosphere, the resulting O:C and H:C ratios (see the van Krevelen-diagram below (Fig. 6 in the revised manuscript)) indicate worse agreement with the ambient range when compared to compositions obtained by the PEAR OFR (presented in this work) or previously measured in a chamber (Tiitta et al., 2016). This can also be due to differences in the combustion technologies and protocols or differences in the aging conditions.

Comparison of the O:C and H:C ratios of the particulate OA to previous studies in the Section 3.5.1 is now expanded. The results of aging of RWC exhaust by PAM OFR (by Bruns et al., 2015 and Pieber et al., 2018) are included also in the van Krevelen diagram (previously Fig. 8, now Fig. 6). Values from Czech et al. (2017) were not included in the van Krevelen diagram due to different combustion source (pellet boiler with notably higher initial oxidation states) but are included in the discussion on O<sub>S</sub>C on Section 3.5.1.



Regarding the gaseous phase (Previous Fig. 7, now Fig. 5), OFR studies reporting gaseous compounds from RWC extensively are scarce and direct comparison of O:C and H:C ratios is not possible due to e.g. differences in the analyzed and reported compounds. Previously, Bruns et al. (2017) have reported emission factors for primary and secondary exhaust for 65 compounds measured with a PTR-MS. Although these compounds differ slightly from those considered here, the main compounds (aromatics and carbonyls with highest concentrations) are included. The changes during aging reported by Bruns et al. (2017) follow the phenomena observed here: both O:C and H:C ratios increase by photochemical exposure. The  $\Delta\text{H:C}/\Delta\text{O:C}$  during the five chamber experiments in Bruns et al. (2017) are in the range of 0.34 - 0.81 at final exposure of 1.9-2.3 eqv.d, which is similar to the changes observed here. This is now noted also in Section 3.4.

- L371: Replace "consequent" with "subsequent"

Corrected.

## Conclusions

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

Corrected.

- 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?

The photochemical exposures were in the ranges 0.5-2.5 eqv.d in Pieber et al. (2018) and ~18 eqv.h in Czech et al. (2017) who discuss pellet burning. To our knowledge, highest OH exposures for RWC exhaust in a PAM have been reported by Bruns et al. (2015), where the exposure was 2.5-10 eqv.d for the flaming phase of RWC. The conclusions section was overall revised, including rephrasing of this paragraph and addition of references to OFR studies, which are now also otherwise better noted in this work.

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.

Limitations in differentiating between gas-phase oxidation, heterogeneous chemistry and particle phase -driven chemistry certainly exist. In addition, it should be noted that the different oxidation processes are likely overlapping. The sentence in question was aimed to simply give a rough outline of the major oxidation mechanisms, and is based on the following facts observed in this study: (1) for RWC-exhaust, short OH-exposures are sufficient to functionalize gaseous precursors and lead to their condensation into particulate phase, which consequently dominates the overall OA transformation until the SOA precursors have been depleted; (2) continuing aging in the presence of OH-radicals leads to further oxidation of particulate organic aerosol, which is likely explained by heterogenous reactions between gas-phase oxidants and particles. However, related to the second fact it is also possible that particulate phase oxidation occurs via evaporation and homogeneous gas-phase oxidation followed by recondensation, as discussed by for example Tiitta et al. (2016). Third, it should not be omitted that in an OFR utilized with high OH-radical concentrations, the gaseous phase precursors may receive higher oxidation state before condensation, e.g. due to several fast functionalization reactions in the gas phase, which would be a topic for further studies. Nevertheless, the comparison of similar OH-exposure in a smog chamber (low OH-radical concentrations) and the PEAR OFR (high OH-radical concentrations) give fairly similar OA oxidation states, as stated e.g. in Section 3.5.1. and shown in Figure 6 (van Krevelen -diagram). This indicates that the utilized high OH-concentrations do not lead to any severe artefacts in terms of OA composition.

We have revised the text in the Conclusions section to better reflect on the limitations and the observations on which the conclusions are based upon.

- 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.

This last, concluding paragraph considers the potential uses of these results, especially the importance of the consideration of different atmospheric aging stages for OA. The aim of the section in question is to emphasize the need for similar consideration of also other OA sources as a point toward future studies, pointing also towards the potential importance of aging towards both environmental and health related effects.

We have revised this final section of the Conclusions section, which now reads:

“--this study highlights the importance of also higher exposure levels towards chemical transformation of OA. Due to the potentially long atmospheric lifetimes of OA, long-term aging is also important to consider in large-scale atmospheric models, which typically estimate SOA formation and characteristics based on short-term aging experiments. The

consideration of only the first stage of gas-phase functionalization and condensation may lead to underestimated oxygenation of the long-transported OA, while specific compound groups, such as nitrophenols or substituted-PACs, can be overestimated. In general, the potential health and climate effects of aerosols are to a large extent determined by their composition, which depends on their sources and the levels of atmospheric aging. Thus, the characterisation of aerosol emissions from different sources and their atmospheric transformation at different exposure levels would be crucial for assessment of the overall environmental effects of ambient air pollution.”

### **Technical Comments**

- Formatting of units (e.g. L/min vs L min<sup>-1</sup>), 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.

The notations for units were corrected. Tables were made more consistent with e.g. no horizontal lines, and the figures were revised for better coherency, with similar formatting of figures of similar type (e.g. scatterplots Figs. 9-10 or timeseries in Figs. S6 and S10-S11).

### **Supporting Information**

- 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.

All portions of SI are noted in the main text and clarification and references included in the text where needed.

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

Reference included.

- E.g. Table S2.1: please add reference for the "OHR external" definition. Is CH<sub>4</sub> negligible or why was it not included in the analysis?

Reference to the OHR<sub>ext</sub> is now included on Table S2.1. Methane (CH<sub>4</sub>) is included in the analysis (6<sup>th</sup> compound from the bottom of the Figure S2), although its share in the total OHR<sub>ext</sub> is minor (< 0.025 %) due to its low OH reactivity.

### **REFERENCES**

Bruns et al. 2015, DOI: 10.5194/amt-8-2315-2015 Czech et al. 2017, DOI:

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