We thank the referee for the critical review and suggestions, which are much appreciated. The specific comments are addressed one by one in the following. The corresponding changes in the manuscript are highlighted in a marked-up version accordingly. Here, we structure our responses in the following scheme:

Referee's comments/questions in bold font.
Author's response in regular font.
Proposed changes in italic font.

Section 4.1.2. The authors parameterize measured wall losses using simple equations. How does this parameterization compare against theoretical considerations or other efforts to quantify wall losses using chemical information? There are a number of papers that have investigated vapor wall loss and developed a number of parameterizations (e.g., Yeh and Ziemann, Ye et al. 2016, McVay et al. 2014 to name a few). These are estimated using C*, which in itself is related to molecular weight by the ideal gas law. How do these relate to the functions described here? And why the square root of the vapor pressure? Some context and description of previous parameterizations would be helpful.
I can see how this is a valid approach for the toluene system, but is it the intention of the authors to use this more broadly for other systems? If so, I would think that it may be necessary to discuss this in more detail and how this parameterization compares to other forms (as noted in comment above). This parameterization seems very simple compared to previous efforts to characterize wall loss rates, but I may not be aware of all of the various efforts.
https://www.tandfonline.com/doi/full/10.1080/02786826.2016.1195905
https://www.tandfonline.com/doi/full/10.1080/02786826.2015.1068427
https://pubs.acs.org/doi/10.1021/es502170j

Our intention is not to present a mathematical wall loss model, but rather to parameterize the wall losses under our studied conditions and for the toluene photooxidation system. We selected the parameters to rely on easily accessible input-values for straight-forward usage. Following your suggestions, we added an explicit explanation and justified that the reason of the square root was to improve the fit of the parameterization. Furthermore, we made the link between our parameters and the previous studies more explicit.

Old version (section 4.1.2, 2nd paragraph):
The dependence of the measured wall loss rates of the studied oxygenated compounds on their molecular properties is shown in Fig. 5. The most influential parameter was the vapor pressure, which has already been shown previously to be inversely related to wall losses in Teflon chambers (Yeh and Ziemann, 2015; Zhang et al., 2015). In addition, we found a dependency on the molecular weight of the compounds, which is similar to other studies where partitioning to walls increased with the carbon number of the molecule (Matsunaga and Ziemann, 2010; Yeh and Ziemann, 2015). Finally, the wall loss was also influenced by the degree of functionalization and oxygenation (Lumiaro et al., 2021; Matsunaga and Ziemann, 2010; Yeh and Ziemann, 2015), considered in this study in terms of the oxygen-to-carbon ratio (O:C ratio). Here, we propose a parameterization for the wall loss rate ($R^2 = 0.80$) as given in Eq. (5):

New version (section 4.1.2, 2nd paragraph):
The dependence of wall losses on molecular properties has been investigated and described for other Teflon chambers by sophisticated gas-wall partitioning models, which are for example based on the ideal gas law or on related parameters such as the saturation concentration (e.g. Matsunaga and Ziemann, 2010; Ye et al., 2016; Yeh and Ziemann, 2015; Zhang et al., 2015). These models also reveal fundamental relationships, such as an inverse link between wall loss rates and vapor pressure, and an increase in wall losses with increasing carbon number and molecular size as well as with an increasing degree of functionalization. Building onto these findings, we developed a simple parameterization that is based on readily accessible parameters and expresses the wall losses of the toluene photooxidation products as first order processes with a fixed rate constant. We tested several fundamental molecular properties alone

and in combination for their ability to describe the empirical loss rates. The most influential parameter was the vapor pressure. We obtained the best fit ($R^2 = 0.80$) when also including the molecular weight and oxygen-to-carbon ratio (O:C ratio) and reducing the impact of the vapor pressure by taking its square root (Fig. 5). We therefore propose the parameterization for the wall loss rate given in Eq. (7):

Based on another comment by reviewer 2, we also included a statement describing the limitations of the presented parameterization with regard to ambient conditions (temperature, humidity). There, we also addressed the experimental duration, which is short in our cases and therefore enables us to assume fixed first order loss rates. In the „best practice" section that we added based on a suggestion by reviewer 2, we also stress the need to re-assess wall losses for other VOC precursors, longer experiments, and changing conditions.

Added text (end of section 4.1.2)*:*
It should be noted that the presented wall loss rates as well as their parameterization are valid only for dry conditions and a temperature of 298 K, but may differ if experimental conditions change (Grosjean, 1985; Zhang et al., 2015). Furthermore, both the time frame over which we determined the wall losses empirically and the conducted photooxidation experiments were limited to three to four hours. On longer time scales, desorption processes, wall saturation, and equilibrium between the gas phase and the chamber walls need to be taken into account more specifically (Yeh and Ziemann, 2015; Zhang et al., 2015).

Added text (within new section 4.1.4):
Wall losses need to be re-assessed (i) for experiments operated at different temperatures, (ii) for experiments performed in humid air, (iii) for new VOC photooxidation systems with different compound structures and properties, (iv) for new chambers when the Teflon body was replaced (see below), and (v) for longer periods of time and more complex wall interactions if the experimental duration is increased.

<u>Minor comments</u>

Lines 101-112: This is a very nice discussion about the utility of derivatization. Can the authors point to some relevant studies on the aromatic systems that have used derivatization to quantify the yields of aldehydes, acids, etc.? I think this would be helpful to place in context why derivatization is a powerful technique and relevant to the studied toluene system.

We added a few examples to show more specifically in which kinds of studies these derivatization techniques have been used.

Old version (Introduction, 2nd-to-last paragraph):
[description of techniques ...]. These derivatization techniques can also be used in combination to cover a broad range of compounds with diverse functionalities (Pindado Jiménez et al., 2013; White et al., 2014; Yu et al., 1998).

New version (Introduction, 2nd-to-last paragraph):
[description of techniques ...]. These derivatization techniques have been used, for example, to analyze gaseous and particulate oxygenated products formed in the photooxidation of aromatic compounds (e.g. Gómez Alvarez et al., 2007; White et al., 2014), monoterpenes (e.g. Jang and Kamens, 1999; Yu et al., 1998), or VOC mixtures (e.g. Pindado Jiménez et al., 2013) in laboratory studies. By combining silylation and oxime formation, a broad range of compounds with diverse functionalities can be covered (Pindado Jiménez et al., 2013; White et al., 2014; Yu et al., 1998).

For the sake of consistency, we did the same for the PTR-ToF-MS part in the introduction.

Added sentence (Introduction, 4th paragraph):
PTR-MS is selective to compounds with higher proton affinity than water and commonly applied to quantify airborne VOC and their photooxidation products (e.g. Müller et al., 2012; Zaytsev et al., 2019).

The following paper was added to the bibliography:

Müller, M., Graus, M., Wisthaler, A., Hansel, A., Metzger, A., Dommen, J., and Baltensperger, U.: Analysis of high mass resolution PTR-TOF mass spectra from 1,3,5-trimethylbenzene (TMB) environmental chamber experiments, Atmospheric Chem. Phys., 12, 829–843, https://doi.org/10.5194/acpd-11-25871-2011, 2012.

Concerning the derivatization, please note that we improved Figures S6 and S7 by labelling the panels and adapting the captions accordingly.

Old version of captions (Fig. S6 + S7):
Upper graph: derivatization of [...]. Lower graph: typical [...]

New version of captions (Fig. S6 + S7):
(a) Derivatization of [...]. (b) Typical [...]

Lines 125-132: I would also point towards papers that have studied the SOA and product yields from the second generation products (e.g., cresol, Schwantes et al. 2017). This would be relevant to the discussion that follows about multi-generational formation of glyoxal.

We added some example studies in which the secondary chemistry of some channels was evaluated, and also added information to the discussion of multi-generational glyoxal formation.

Added sentence after outline of primary chemistry (Sect. 2, end of 1st paragraph):
The follow-up chemistry of major toluene products such as the cresols, benzaldehyde, or the different dicarbonyls has been the subject of previous laboratory studies (e.g. Atkinson et al., 1980; Liu et al., 1999; Majer et al., 1969; Olariu et al., 2002; Schwantes et al., 2017).

Old version glyoxal + methylgyloxal part (2nd parapraph Sect. 2):
The dicarbonyl products glyoxal and methylglyoxal occur not only in the primary chemistry of toluene but also as secondary products in most channels (Atkinson et al., 1980; Bloss et al., 2005; Wagner et al., 2003). Although their primary production is typically dominant (Gómez Alvarez et al., 2007; Volkamer et al., 2001), a contribution from secondary sources to their observed concentrations cannot be fully dismissed.

New version glyoxal + methylgyloxal part (2nd parapraph Sect. 2):
The dicarbonyl products glyoxal and methylglyoxal occur not only in the primary chemistry of toluene but are also formed as secondary products in most channels (Atkinson et al., 1980; Bloss et al., 2005; Wagner et al., 2003), especially in the breakdown of other dicarbonyls (Liu et al., 1999). Although primary production is typically dominant (Gómez Alvarez et al., 2007; Volkamer et al., 2001), secondary sources contribute to a fraction of the observed concentrations of glyoxal and methylglyoxal.

The following papers were added to the bibliography:

Liu, X., Jeffries, H. E., and Sexton, K. G.: Atmospheric Photochemical Degradation of 1,4-Unsaturated Dicarbonyls, Environ. Sci. Technol., 33, 4212–4220, https://doi.org/10.1021/es990469y, 1999.

Majer, J. R., Naman, S.-A. M. A., and Robb, J. C.: Photolysis of aromatic aldehydes, Trans. Faraday Soc., 65, 1846–1853, https://doi.org/10.1039/TF9696501846, 1969.

Line 154: This is very impressive temperature range I may have missed this in the text, but what are the dimensions of the containment room? How quickly does it take to reach the desired temperature set point? Is it possible to do dynamic temperature changes during experiments? My take is that this system is about the same size as that described by Osseiran et al. and contained in a similar temperature-controlled vessel. Is that correct? As a note, it might be nice to have a picture of the chamber in a TOC graphic to get a sense of the scale.
https://www.sciencedirect.com/science/article/abs/pii/S1001074220301170

It is true that we did not specify the dimensions of the containment room in the text, and that this would be useful information for the reader. Our setup is quite different than the system described by Osseiran et al., as we do not use a temperature-controlled vessel which is more or less tightly enclosing the chamber. Instead, we placed the chamber into a climatized cabinett which is entirely temperature-controlled and about 3x4x5 m in size. As the room is so much larger than the chamber itself, we feel that this would be difficult to capture in a small picture in a TOC graphic. We added the dimensions of the climatized cabinett to the text.

The temperature set point is reached reasonably fast, depending on the exact set point. During this work, we only ran test experiments between 5 °C and 35 °C, which could all be reached within about half an hour. For -25 °C (the lowest-possible temperature), for sure it would take a longer time. It is not possible to do dynamic temperature changes during experiments, only one set point can be defined.

Old version (beginning Sect. 3):
The BATCH Teflon chamber was located in a temperature-controlled room (Hans Zettner GmbH), in which the temperature could be adjusted between -25 °C and 35 °C with a stability of ±1 K (DeLonghi, HCS 2550 FTS and Dixell, XR170C).

New version (beginning Sect. 3):
The BATCH Teflon chamber was located in a temperature-controlled room (Hans Zettner GmbH, 3×4×5 m), in which the temperature could be adjusted between -25 °C and 35 °C with a stability of ±1 K (DeLonghi, HCS 2550 FTS and Dixell, XR170C).

We also added the dimensions of the containment room and the chamber itself to the overview graphic of the laboratory setup.

[see Figure 2]

Line 168: Is this the footprint of the Teflon chamber? Can the third dimension be provided to get a sense of the full size at max volume (300 L)?

Yes, we referred to the footprint of the chamber. We adapted the formulation and changed the structure of the sentence to make this clearer. We also added information about the third dimension as suggested.

Old version (Sect. 3.1):
The BATCH Teflon chamber was made from UV-transparent fluorinated ethylene propylene (FEP). We constructed the pillow-shaped bag by folding a single sheet of a 50 μm thick FEP film (Chemours, 200A FEP100) and heat-sealing (Dieck, UM 802) the three open sides. Excluding the heat-sealed areas, the empty chamber was 140×110 cm in size. It could be filled to approximately 300 L, in which case the surface-area-to-volume ratio was about SA:V = 0.1 cm^{-1}. To reduce the risk of leaks, only one connector was installed at the front side of the chamber and used both as inlet (during filling) and outlet (during ongoing experiments). The chamber was suspended in a metal scaffold, with the two short sides being used as top and bottom ends. It was not further stabilized into a specific shape, so that it remained flexible and fully collapsible, and could be operated in batch mode.

New version (Sect. 3.1):
The BATCH Teflon chamber was made from UV-transparent fluorinated ethylene propylene (FEP). We constructed the pillow-shaped bag by folding a single sheet of a 50 μm thick FEP film (Chemours, 200A FEP100) and heat-sealing (Dieck, UM 802) the three open sides. Excluding the heat-sealed areas, the empty and flattened chamber was 140×110 cm in size. It was suspended in a metal scaffold, with the two short sides being used as top and bottom ends. It was not further stabilized into a specific shape, so that it remained flexible and fully collapsible, and could be operated in batch mode. The chamber could be filled to approximately 300 L, in which case the surface-area-to-volume ratio was about SA:V = 0.1 cm^{-1}. When it was inflated, it expanded to a maximum of about 100 cm in the third dimension. To reduce the risk of leaks, only one connector was installed at the front side of the chamber and used both as inlet (during filling) and outlet (during ongoing experiments).

We furthermore added the dimensions of the chamber and the information that it's inflatable to the overview graphic of the laboratory setup, hoping that this improves clarity.

[see Figure 2]

Line 250: Perhaps useful to note the estimated mass that could be collected on the SPME fibers for a typical experiment (e.g., the toluene system)?

During the calibration, we injected 17 compounds simultaneously into the chamber. For the highest calibration level (5 ppbv), this sums up to a total mixing ratio of 85 ppbv of oxygenated products. But even under these circumstances, we did not see any saturation effect. As the loss of toluene in the experiments is much lower, we expect that the fibre is well capable of collecting the entire product mass formed in the experiments.
We feel that line 250 is too early to address this (e.g. since the calibration has not been described at this point), but we instead elaborated this point a bit more in the results/discussion part (section 4.2.1), where we so far only mentioned the linearity of the calibration curves. We now included the implication for the experiments.

Old version (1st paragraph, Sect. 4.2.1):
The calibration curves are shown exemplary for the ring-retaining first generation products in Fig. 7. No saturation effect is apparent in these curves, indicating that the calibration interval between c = 0 − 12.3×10^{10} molecules cm^{-3} is still within the linear range of the SPME fibre. [...]

New version (1st paragraph, Sect. 4.2.1):
The calibration curves are shown exemplary for the ring-retaining first generation products in Fig. 7. No saturation effect is apparent in these curves, indicating that the calibration interval between c = 0 − 12.3×10^{10} molecules cm^{-3} is still within the linear range of the SPME fibre. As all tested toluene products were injected jointly during the calibration, the total mixing ratio of the products reached about 85 ppbv for the highest calibration level. During the NO$_x$-free photooxidation experiments, the loss of toluene and hence the maximum production of oxygenated compounds (as C$_7$ equivalents) was by about a factor of 4 or more lower than that, so that the sampling capacity of the fibre was likely not exceeded. [...]

Line 256-262: Later in the text, the authors note that the stability of ISTDs were tracked for a week using PTR-ToF-MS. I would include that discussion here.

We moved the sentence "To validate the temporal stability of the permeation source, the enriched outflow was monitored over a period of one week by PTR-ToF-MS." from the Results/Discussion section (4.2.2) to the Method section (3.2.1). With the previous sentence missing, we added some context to the following sentence in the Results/Discussion section.

Old version methods (3.2.1, ISTD parapraph):
These ISTDs were added into the transfer line between the chamber and the SPME-GC-MS sampling cell by means of a customized permeation source (for details, see Supplement S3.3 and Fig. S5). Phenol-d_6 was used to correct [...]

New version methods (3.2.1, ISTD parapraph):
These ISTDs were added into the transfer line between the chamber and the SPME-GC-MS sampling cell by means of a customized permeation source (for details, see Supplement S3.3 and Fig. S5). To validate the temporal stability of the permeation source, the enriched outflow was monitored over a period of one week by PTR-ToF-MS. Phenol-d_6 was used to correct [...]

Old version results/discussion (4.2.2):
In the present setup, the comparability of different samples, of different experiments, and of the experimental period and the on-line calibration was maintained by the added ISTDs. To validate the temporal stability of the permeation source, the enriched outflow was monitored over a period of one week by PTR-ToF-MS. The RSDs of the PI-normalized responses were as low as 5 % for phenol-d_6 and 6 % for acetophenone-d_8, confirming the suitability of the setup for on-line ISTD addition. Hence, the variability of the ISTD responses measured by SPME-GC-MS (Fig. 8) is indicative for changes in the preparation of the derivatization efficiency, the performance of the GC-MS, and most importantly fibre effects.

New version results/discussion (4.2.2):
In the present setup, the comparability of different samples, of different experiments, and of the experimental period and the on-line calibration was maintained by the added ISTDs. The PTR-ToF-MS data showed that the ISTDs in the permeation source outflow were stable over the course of one week, with RSDs of 5 % and 6 % for the PI-normalized responses of phenol-d_6 and 6 % for acetophenone-d_8 respectively. Hence, the variability of the ISTD responses measured by SPME-GC-MS (Fig. 8) is indicative for changes in the preparation of the derivatization efficiency, the performance of the GC-MS, and most importantly fibre effects.

Lines 382-385: Was there an order that experiments were conducted? I.e., were NOx-free experiments conducted prior to those where NO was injected? If not, is there uncertainty associated with possible NOx sources from the walls? Previous studies have shown that walls act as a NOx source once NO or NO2 are introduced as reactants (e.g., Rohrer et al.), so I feel that this should be referenced here. https://acp.copernicus.org/articles/5/2189/2005/acp-5-2189-2005.html

Yes, the NO_x-free experiments were conducted first (see e.g. Figure 8). We agree that this should be mentioned specifically. We therefore added a statement and also included the proposed citation.

Added text (Sect. 3.3):
[description of evaluated NO_x-free experiments …]. These experiments were performed first to avoid the risk for contamination and wall sources of NO_x (e.g. Rohrer et al., 2005).

Accordingly, the paper was added to the bibliography.

Rohrer, F., Bohn, B., Brauers, T., Brüning, D., Johnen, F.-J., Wahner, A., and Kleffmann, J.: Characterisation of the photolytic HONO-source in the atmosphere simulation chamber SAPHIR, Atmospheric Chem. Phys., 5, 2189–2201, https://doi.org/10.5194/acp-5-2189-2005, 2005.

Line 419: Do wall losses include possible line losses?

Yes. In the manuscript, we describe how we minimized these losses by heating the transfer line („To maintain comparable conditions between the experiments and to reduce losses, the transfer line from the chamber to the sampling cell (~ 6 m length, 6 mm inner diameter) was temperature-controlled to 50 °C", l. 254-255 in original version). We furthermore expect near-equilibrium between the sample flow and the line walls, as it is not a static system like the chamber interior. We considered such "steady-state line losses" in the calibration, which we performed from the chamber ("To account for losses in the transfer line, the extraction from the sampling cell, and the on-line ISTD addition, we calibrated the analytes determined by SPME-GC-MS directly from within the chamber.", l. 287-288 in original version).

[no change made]

Line 502: For consistency with the previous comparison, I would recommend phrasing that the experimental photolysis rate is "21% higher" than the calculated value.

We agree that the rewording serves consistency, and therefore implemented the change as suggested.

Original version (Sect. 4.1.1, 1st paragraph):
[…] is 1.21-fold higher [...]

New version (Sect. 4.1.1, 1st paragraph):
[…] is 21 % higher [...]

Line 525-527: This sentence tends to suggest that HONO is not contributing, but this is a little speculative without HONO or measurements of NO / NO2 at low detection limits. I would suggest leaning on the conclusion that H2O2 is the main source of OH radicals and leave out the mention of HONO.

As suggested we deleted the statement concerning HONO.

Old version (4.1.1, OH radical paragraph):
We did not observe any product formation in a test run without H_2O_2 addition, confirming H_2O_2 photolysis as the main source of OH radicals, rather than for example the release of HONO from chamber walls which would produce both OH radicals and NO.

New version (4.1.1, OH radical paragraph):
We did not observe any product formation in a test run without H_2O_2 addition, confirming H_2O_2 photolysis as the main source of OH radicals.

Lines 529-531: Here, and elsewhere, it would also be helpful to see the photolysis and OH lifetimes for each species. This would help the reader to gauge how much loss of these species might be expected after they are formed relative to OH or other processes and complement the loss distributions shown in Fig. 11.

We would like to point out that the rate constants for the wall losses, photolysis rates, and OH radical reactions are listed for each species in the SI (Tables S1, S7, S8) and referenced in the main text accordingly.

However, we understand that a direct comparison and overview would be helpful for the reader. We therefore added a figure showing the absolute and normalized first order rate constants for all three loss processes for each of the compounds in the Supplement (new Figure S12). We prefer showing the loss rates rather than the lifetimes, because for some compounds, absorption cross sections are not available from the literature so that we could not compile photolysis rates (see Table S1). Since in these cases, the loss rate is likely small (meaning that the lifetime is long), it seems to us more intuitive and realistic to exclude them from loss rate plots than from lifetime plots. Also, as conditions change during the experiments, especially with regard to irradiation and OH radical production, we feel that lifetimes could perhaps be misleading.

As additional information to show the extent of the losses (at least for two exemplary species), we included the relative change from the measured to the fully loss-corrected mixing ratios in the other two figures in the Supplement S7 (previously S12 + S13, now S13 + S14).

Added figure in Supplement:

[see Figure S12]

Introductory text (in SI, S7):
The absolute and relative importance of wall losses, photolysis, and OH radical reactions is shown for each of the analysed compounds in Fig. S12.

Caption Fig. S12:
Figure S12: Loss processes for each of the analysed toluene photooxidation products. (a) First order loss rates. For the OH radical reactions, we used the mean OH radical concentration of [OH] = 4.89 $\times 10^6$ molecules cm^{-3} for obtaining pseudo first order rates. (b) Normalization of the first order loss rates for each individual compound. Note that we could not compile any photolysis rates for (nitromethyl)benzene (NMB), p-methylcatechol (PMC), and p-hydroxybenzaldehyde (PHB), and assumed zero photolytic loss in these cases (marked with stars). Photolysis is only relevant during chamber irradiation, and the assumed OH radical concentration likewise only applies to the irradiated time period.

We added the following sentence to the discussion of the losses.

Added sentence (Sect. 4.3.1, 1st paragraph):
An overview of the first order rate constants of all three loss processes for each of the analysed compounds is provided in Fig. S12.

Due to the addition of Figure S12, we changed the previous Figures S12 and S13 to Figures S13 and S14, and changed the references in the main text and the Supplement S7 accordingly.
In these figures, we included an additional panel, showing a comparison of the relative change from the measured to the fully loss-corrected mixing ratios for both instruments. We updated the caption, and described the calculation of this relative change in the text above.
Note that we also adapted the colour scheme of Figures S13 and S14 by swapping the purple and black colour to better match the designated colours for the losses in the new Figure S12.

[See Fig. S13 + S14]

Main text (4.3.1, last paragraph) old version:
[…] for different compounds and experiments (see Supplement S7 with Fig. S12 and S13). [...]

Main text (4.3.1, last paragraph) new version:
[…] for different compounds and experiments (see Supplement S7 with Fig. S13 and S14). [...]

Old version (SI S7):
In order to evaluate and validate the loss correction procedure at the two instruments, we compared the measured and the loss-corrected data sets obtained by SPME-GC-MS and PTR-ToF-MS. Since the extent of the loss corrections depends on the non-corrected concentrations, we selected experiments in which the measured data of the two instruments agreed particularly well. We show this comparison for benzaldehyde as a compound with no known spectral interference and high photolytic losses (Fig. S12), and for o-cresol as one of the C_7H_8O isomers and a compound with a high reactivity towards OH radicals and a relatively high wall loss rate (Fig. S13). The loss-corrected data are in good agreement.

New version (SI S7):
In order to evaluate and validate the loss correction procedure at the two instruments, we compared the measured and the loss-corrected data sets obtained by SPME-GC-MS and PTR-ToF-MS. We show this comparison for benzaldehyde as a compound with no known spectral interference and high photolytic losses (Fig. S13), and for o-cresol as one of the C_7H_8O isomers and a compound with a high reactivity towards OH radicals and a relatively high wall loss rate (Fig. S14). Figures S13 and S14 include not only the time series of the measured data and the individual losses for both instruments (Fig. S13b and S14b), but also the direct comparison of the relative change associated with the loss corrections (Fig. S13a and S14a). This relative change was calculated as the difference between the loss-corrected data and the measured data divided by the measured data, and makes it possible to compare the extent of the loss corrections even in view of slightly different measured initial mixing ratios. The relative changes obtained by the two instruments are in good agreement for both compounds.

Addition to caption for both Fig. S13 and S14:
[…] (a) The relative change between the measured and fully loss-corrected mixing ratio for each sample. (b) Absolute raw and corrected mixing ratios. Error bars in both panels are the instrumental quantification error.

Figure 8: It is somewhat difficult to see the dark grey bars relative to the lighter grey bars. Perhaps using a different color would help? Or, dotted vertical lines could indicate new experiments?

We agree that the dark grey and light grey bars were difficult to distinguish. As suggested, we now use dotted vertical lines for new experiments, and additional bars for those experiments where a new fibre was inserted. We adapted the caption accordingly.

[see Figure 8]

Old version of caption:
[…] The grey vertical bars indicate the start of a new experiment. The insertion of a new SPME fibre is illustrated in dark grey. […]

New version of caption:
[…] The dotted vertical lines indicate the start of a new experiment. The insertion of a new SPME fibre is illustrated with additional dark grey bars. […]

Lines 752-753: This may be the case for chamber studies, but previous studies investigating field observations of isomer distributions (e.g., C8-aromatics, propanal / acetone) have applied isomer-specific sensitivities to interpret PTR signals in very complex mixtures (e.g., biomass burning, Koss et al.). This is also a technique currently used in other mass spectrometers with significant variability in isomer sensitivities (e.g., I-CIMS, Xiong et al.) https://acp.copernicus.org/articles/15/11257/2015/ https://acp.copernicus.org/articles/15/11257/2015/18/3299/2018/

The reviewer is correct, and we apologize for this oversight. We deleted the sentence.

Old version (Sect. 4.2.3 last paragraph):
This is particularly valuable for modelling and for gaining insights into chemical mechanisms. To the best of our knowledge, this study marks the first demonstration of a correction of the sum signal based on both the abundance and the sensitivity of the individual isomers. Rather than performing a separate weighted calibration for each time segment assigned to a specific SPME-GC-MS sample, we used a fixed relative abundance of the C_7H_8O isomers for the weighted calibration and the experimental data.

New version (Sect. 4.2.3 last paragraph):
This is particularly valuable for modelling and for gaining insights into chemical mechanisms. Rather than performing a separate weighted calibration for each time segment assigned to a specific SPME-GC-MS sample, we used a fixed relative abundance of the C_7H_8O isomers for both the weighted calibration and the experimental data.

In the method part, we instead cited the Koss study, but included an equation for our calculation as it was slightly different.

Old version (Sect. 3.2.2 last paragraph):
To highlight the benefit of the combined analytical instrumentation, we aimed to resolve the C_7H_8O isomers also in the PTR-ToF-MS signal. Therefore, we performed separate calibrations for each of the three cresol isomers and benzyl alcohol. These calibrations were conducted on-line from the BATCH Teflon chamber analogously to the joint PTR-ToF-MS calibration. All compounds were analysed at the protonated mass of m/z 109.0626, yet the instrumental response of each of the isomers was derived individually. For analyzing the sum signal during the photooxidation experiments, we calculated the weighted sensitivity for each of the isomers as the product of its instrumental sensitivity and its relative abundance. The relative abundances were derived as fixed values from the formation yields as determined with the SPME-GC-MS data (Sect. 4.3.2). The sum of these weighted sensitivities was used as the weighted calibration factor for the m/z 109.0626 signal (Table S6). From the correctly quantified sum signal, we extracted the concentrations of the individual C_7H_8O isomers using the same fixed relative abundances.

New version (Sect. 3.2.2 last paragraph):
To highlight the benefit of the combined analytical instrumentation, we aimed to resolve the C_7H_8O isomers also in the PTR-ToF-MS signal. In a first step, we compiled a weighted calibration similar to e.g. the work by Koss et al. (2018). Therefore, we performed separate calibrations for each of the three cresol isomers and benzyl alcohol. These calibrations were conducted on-line from the BATCH Teflon chamber analogously to the joint PTR-ToF-MS calibration. All compounds were analysed at the protonated mass of m/z 109.0626, yet the instrumental response of each of the isomers was derived individually. For analyzing the sum signal during the photooxidation experiments, we calculated the weighted sensitivity for each of the isomers as the product of its

instrumental sensitivity and its relative abundance. The relative abundances were derived as fixed values from the formation yields as determined with the SPME-GC-MS data (Sect. 4.3.2). According to Eq. (2), the sum of these weighted sensitivities was used as the weighted calibration factor for the m/z 109.0626 signal (Table S6). From the correctly quantified sum signal, we later extracted the experimental concentrations of the individual C_7H_8O isomers using the same fixed relative abundances.

$$weighted\ calibration\ factor = \sum_i weighted\ sensitivity_i = \sum_i sensitivity_i \times relative\ abundance_i \qquad (2)$$

We added the Koss paper to the bibliography:

Koss, A. R., Sekimoto, K., Gilman, J. B., Selimovic, V., Coggon, M. M., Zarzana, K. J., Yuan, B., Lerner, B. M., Brown, S. S., Jimenez, J. L., Krechmer, J., Roberts, J. M., Warneke, C., Yokelson, R. J., and de Gouw, J.: Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment, Atmospheric Chem. Phys., 18, 3299–3319, https://doi.org/10.5194/acp-18-3299-2018, 2018.

As we added the equation in the method part (Sect. 3.2.2, Eq. 2), we also changed the numbering of the following equations accordingly.

[see following equations]

<u>Further note</u>

As part of this manuscript, we present a weighted calibration for the mass *m/z* 109.0626 at the PTR-ToF-MS, assigned to the chemical structure C_7H_8O. In the original preprint, we considered the three cresol isomers as well as benzyl alcohol. During the review of the preprint, we improved the assignment. As the PTR-ToF-MS does not show any signal for benzyl alcohol at this mass due to fragmentation, we decided that the inclusion of benzyl alcohol within the weighted calibration can be misleading. In particular, the difference between the averaged and weighted calibration factor is disproportionately large when including zero-sensitivity compounds. Therefore, we suggest the following modifications:

- to change the calculation and interpretation of the weighted PTR-ToF-MS calibration to include only the three cresol isomers, using their individual sensitivities and relative abundances (0.74:0.04:0.22 for the *o/m/p* isomer, respectively).
- to compare the sum signal at *m/z* 109.0626 against the sum of the three cresol isomers (no longer including benzyl alcohol) at the SPME-GC-MS accordingly (Fig. 9).
- to not evaluate and show any PTR-ToF-MS time series of benzyl alcohol (Fig. 10), as (i) it is not measurable at *m/z* 109.0626 and would no longer be represented in the weighted calibration, and (ii) we prefer not to analyse the unspecific *m/z 91.0522* fragment.

While the PTR-ToF-MS cresol data is not a major part of the manuscript, it is nevertheless addressed in a few different sections. We suggest to make all necessary changes for consistency, as outlined in the following:

<u>Abstract:</u>

Old version:
For the cresols and benzyl alcohol, we compiled a weighted calibration factor for the PTR-ToF-MS, taking into account isomer-specific sensitivities as well as the relative distribution as determined by the SPME-GC-MS. The weighted calibration improved the instrumental agreement to 15 %, whereas the PTR-ToF-MS overestimated the sum of the isomers by 25 % compared to the SPME-GC-MS concentrations when using the averaged calibration factor.

New version:
For the cresols, we compiled a weighted calibration factor for the PTR-ToF-MS, taking into account isomer-specific sensitivities as well as the relative distribution as determined by the SPME-GC-MS. The weighted calibration improved the instrumental agreement to 14 %, whereas the PTR-ToF-MS overestimated the sum of the isomers by 31 % compared to the SPME-GC-MS concentrations when using the averaged calibration factor.

<u>Methods (last paragraph 3.2.2):</u>

Old version:
[…] All compounds were analysed at the protonated mass of m/z 109.0626, yet the instrumental response of each of the isomers was derived individually. For analyzing the sum signal during the photooxidation experiments, we calculated the weighted sensitivity for each of the isomers as the product of its instrumental sensitivity and its relative abundance. The relative abundances

were derived as fixed values from the formation yields as determined with the SPME-GC-MS data (Sect. 4.3.2). [...] From the correctly quantified sum signal, we later extracted the experimental concentrations of the individual C_7H_8O isomers using the same fixed relative abundances.

New version:
[...] All compounds were analysed at the protonated mass of m/z 109.0626, yet the instrumental response of each of the isomers was derived individually. For analyzing the sum signal during the photooxidation experiments, we calculated the weighted sensitivity for each of the isomers as the product of its instrumental sensitivity and its relative abundance. Since benzyl alcohol did not have any signal at this mass (Table S6), only the cresols isomers were included in the weighted calibration. Their relative abundances were derived as fixed values from the formation yields as determined with the SPME-GC-MS data (Sect. 4.3.2). [...] From the correctly quantified sum signal, we later extracted the experimental concentrations of the individual cresol isomers using the same fixed relative abundances.

Results (section 4.2.3):

➤ 2nd paragraph:

Old version 2nd paragraph:
[...] Benzyl alcohol did not show any signal on m/z 109.0626 and thus did not contribute to the sum signal. Instead, it fragmented to m/z 91.0522, which is in accordance with the literature (Yeoman et al., 2021) and probably indicates the formation of the benzyl radical after abstraction of water from the protonated molecule. The isomer-specific calibration was performed with relative abundances of 0.71 for o-cresol, 0.04 for m-cresol, 0.21 for p-cresol, and 0.04 for benzyl alcohol (Sect. 4.3.2). As o-cresol is by far the most abundant isomer, its contribution to the weighted calibration factor on m/z 109.0626 was as high as 87 %. Overall, considering the relative abundances and the specific sensitivities of the individual isomers led to a 1.47-fold increase of the calibration factor compared to the non-weighted calibration (Table S6).

New version 2nd paragraph:
[...] Benzyl alcohol did not show any signal on m/z 109.0626 and thus did not contribute to the sum signal and was excluded from the weighted calibration. Instead, it fragmented to m/z 91.0522, which is in accordance with the literature (Yeoman et al., 2021) and probably indicates the formation of the benzyl radical after abstraction of water from the protonated molecule. As this fragment is unspecific, we did not evaluate it further. The isomer-specific calibration was performed with relative abundances of 0.74 for o-cresol, 0.04 for m-cresol, and 0.22 for p-cresol (Sect. 4.3.2). As o-cresol is by far the most abundant isomer, its contribution to the weighted calibration factor on m/z 109.0626 was as high as 87 %. Overall, considering the relative abundances and the specific sensitivities of the individual isomers led to a 1.15-fold increase of the calibration factor compared to the non-weighted calibration (Table S6).

➤ Figure 9:

In Figure 9, the first panel now shows a comparison of the sum of the three cresol isomers, not of all C_7H_8O isomers, changing both the x and y data. The caption was adapted accordingly.

[See Fig 9]

Old caption:
[…] In case of the cresol isomers and benzyl alcohol, the non-weighted and weighted calibrations for the sum of the isomers are distinguished. Error bars represent the quantification error of the respective instruments. Error bars of the sum of the C_7H_8O isomers (cresols and benzyl alcohol) at the SPME-GC-MS are the weighted sum of the individual errors. […]

New caption:
[…] In case of the cresol isomers, the non-weighted and weighted calibrations for the sum of the isomers are distinguished. Error bars represent the quantification error of the respective instruments. Error bars of the sum of the cresol isomers at the SPME-GC-MS are the weighted sum of the individual errors. […]

➢ 3rd paragraph:

Old version 3rd paragraph:
[…] For the cresol isomers and benzyl alcohol, the weighted calibration improved the coherence between the two instruments from 25 % to 15 % deviation. […]

New version 3rd paragraph:
[…] For the cresol isomers, the weighted calibration improved the coherence between the two instruments from 31 % to 14 % deviation. […]

➢ 4th paragraph:

Old version 4th paragraph:
[…] Rather than performing a separate weighted calibration for each time segment assigned to a specific SPME-GC-MS sample, we used a fixed relative abundance of the C_7H_8O isomers for both the weighted calibration and the experimental data. This is a reasonable assumption, as their sinks in the BATCH Teflon chamber (wall losses, photolysis, secondary OH radical reactions) agree within 26 % (Tables S1, S7, S8). The experimental SPME-GC-MS data confirm that the variability of the isomeric distribution over the course of the conducted experiments is only 17 % and hence within the quantification error. In addition to the simplicity of implementation, the adoption of a fixed relative abundance also makes the PTR-ToF-MS results less susceptible to the random error of the SPME-GC-MS data.

New version 4th paragraph:
[…] Rather than performing a separate weighted calibration for each time segment assigned to a specific SPME-GC-MS sample, we used a fixed relative abundance of the cresol isomers for both the weighted calibration and the experimental data. This is a reasonable assumption, as their sinks in the BATCH Teflon chamber (wall losses, photolysis, secondary OH radical reactions) agree within 16 % (Tables S1, S7, S8). Accordingly, the isomeric distribution derived from the formation yields (including loss corrections) is equal to the average isomeric distribution calculated from the measured concentrations (excluding loss corrections). The variability of the isomeric distribution in the experimental SPME-GC-MS data is only 13 % and hence within the quantification error. In addition to the simplicity of implementation, the adoption of a fixed relative abundance also makes the PTR-ToF-MS results less susceptible to outliers and the random error of the SPME-GC-MS data.

➢ Figure 10:

In Figure 10, benzyl alcohol was excluded. The caption was adapted accordingly.

[See Fig 10]

Old version caption:
Figure 10: Time series of the cresol isomers and benzyl alcohol by SPME-GC-MS and PTR-ToF-MS. [...] In the depicted experiment, the sum of the isomers agrees exceptionally well between the two instruments, while the measured isomeric distribution deviates slightly from the fixed relative abundance. Toluene products in this figure include o-cresol (OCR), m-cresol (MCR), p-cresol (PCR), and benzyl alcohol (BOH).

New version caption:
Figure 10: Time series of the cresol isomers by SPME-GC-MS and PTR-ToF-MS. [...] Toluene products in this figure include o-cresol (OCR), m-cresol (MCR), and p-cresol (PCR).

Conclusion:

Old version:
We calibrated the main first generation products of toluene for both instruments, and found good agreement for the ring-retaining products (the cresol isomers, benzyl alcohol, benzaldehyde). We further demonstrated that the sensitivity of the PTR-ToF-MS for different structural isomers can vary substantially. For the cresols and benzyl alcohol, we therefore applied a weighted calibration factor based on the determined isomer-specific sensitivities and the distribution of the isomers as obtained by the SPME-GC-MS data. This led to an improved instrumental agreement, and [...]

New version:
We calibrated the main first generation products of toluene for both instruments, and found good agreement for the cresol isomers and benzaldehyde. We further demonstrated that the sensitivity of the PTR-ToF-MS for different structural isomers can vary substantially. For the cresols, we therefore applied a weighted calibration factor based on the determined isomer-specific sensitivities and the distribution of the isomers as obtained by the SPME-GC-MS data. This led to an improved instrumental agreement, and [...]

Supplement:

➢ Table S6

In the table, we differentiated the cresol isomers and benzyl alcohol more explicitly, showing plainly that benzyl alcohol is not incorporated into the weighted calibration. We still list its zero sensitivity at *m/z* 109.0626, as we believe this to be of interest to the community. For the weighted calibration, we updated all the values. Note that also the non-weighted values now appear different, as we performed the isomer-specific calibrations at a slightly later point and scaled them to the previously recorded sum signal, which is now composed of three instead of

four compounds. We also changed the caption of the table, specifying the relative abundances as well as changing the mentions of the C_7H_8O isomers to only the cresol isomers.

[see Table S6]

Old version caption:
[…] For the C_7H_8O isomers, we derived a weighted sensitivity by multiplying the recorded sensitivity with the relative abundance as determined by SPME-GC-MS. The weighted calibration factor for the sum signal was obtained from the sum of these weighted isomer-specific sensitivities. When evaluating individual C_7H_8O isomers, we adopted the error and LOD of the weighted sum of the isomers.

New version caption:
[…] For the cresol isomers, we derived a weighted sensitivity by multiplying the recorded sensitivity with the relative abundance as determined by SPME-GC-MS (0.74 for o-cresol, 0.04 for m-cresol, and 0.22 for p-cresol). The weighted calibration factor for the sum signal was obtained from the sum of these weighted isomer-specific sensitivities. When evaluating individual cresol isomers, we adopted the error and LOD of the weighted sum of the isomers.

➢ Section S7

In Section S7, we changed the wording in the introductory text and the caption of Figure S14, and updated the displayed PTR-MS data in Figure S14.

[see Fig. S14]

Old version text:
[…] for o-cresol as one of the C_7H_8O isomers […]

New version text:
[…] for o-cresol as one of the cresol isomers […]

Old version caption:
[…] The mixing ratio of o-cresol at the PTR-ToF-MS was calculated from the weighted calibration and the fixed relative abundance of the C_7H_8O isomers (0.71 for o-cresol).

New version caption:
[…] The mixing ratio of o-cresol at the PTR-ToF-MS was calculated from the weighted calibration and the fixed relative abundance of 0.74 for o-cresol.