Response to Reviewers

23/11/21

Response to Reviewers of:

NO_3 chemistry of wildfire emissions: a kinetic study of the gas-phase reactions of furans with the NO_3 radical by Newland et al., 2021, submitted to ACP

General Response

We thank the reviewers for giving up their time to make insightful comments, helping to clarify and improve our manuscript. The reviewers recognise the importance of the results presented, and recommend publication in ACP after some minor changes. All changes to the manuscript are in line with the reviewers' comments and suggestions.

Responses to each reviewer are given below. Responses to specific points raised by each reviewer are given separately beneath that point. Reviewers' comments are bold and italic, the authors' comments are inset in plain type.

Major changes

Many of the reviewers' concerns are focused on the experiments using α-terpinene as a reference compound, and the recommendation of a NO_3 rate coefficient larger than the three previous determinations (which we note are not in agreement). Reviewer 1 raised the possibility that we had overlooked the potential for the α-terpinene+NO_2 reaction to impact our results under the experimental conditions employed. This was correct. Having performed experiments with α-terpinene+NO_2, we obtained a rate coefficient in agreement with that previously determined by Atkinson et al. (1984). Further details of the NO_2 experiments with α-terpinene and several of the furans are given in response to specific comments below. However, using this value for $k(\alpha$-terpinene+$NO_2)$, with the measured NO_2 (FTIR), to correct the relative rate calculations led to disagreement between our experimental results. The experiment with α-terpinene and 2,5-dimethylfuran gave a rate coefficient relative to $k(2,5$-dimethylfuran+$NO_3)$ of about 2.3, giving a rate coefficient for $k(\alpha$-terpinene+$NO_3)$ of about 2.5×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, based on our determination of $k(2,5$-dimethylfuran+$NO_3)$. Whereas, the experiment using 2,3-dimethyl-2-butene as a reference compound, after correction gives a rate relative to 2,3-dimethyl-2-butene of about 2.8, yielding a value for $k(\alpha$-terpinene+ $NO_3)$ of 1.6×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, in line with that reported by Atkinson et al. (1985).

In light of the disagreement between our results and the reported values, and since the manuscript is not explicitly about α-terpinene, it was merely one of several reference compounds, it seems prudent to remove the experiments using α-terpinene as a reference from the manuscript. We will continue to explore the system, which is clearly important atmospherically, interesting from a chemistry standpoint, and important as a reference compound with one of the largest NO_3 reaction rate coefficients known.

The recommended 2,5-dimethylfuran and pyrrole rate coefficients are still tied to at least three reference compounds.

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It should be noted that the removal of the α-terpinene experiments has reduced the recommended rate coefficients of the furans slightly.

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Data Presentation / Availability

Figure 2 is now a six panel plot containing relative rate plots for all experiments for all six compounds (furan, 2-methylfuran, 2,5-dimethylfuran, furfural, pyrrole, α-angelicalactone).

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The SI now contains an additional six concentration-time plots, with the same setup as Figure 1.

All of the data (raw output from the FTIR, and concentration-time data) will be made available at https://data.eurochamp.org with a doi.

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Anonymous Referee #1

A relative rate study is reported, which considers the reactions of NO₃ with a series of furans and related compounds, which are known to be important components of biomass burning emissions. The experiments were carried out in the large CNRS-ICARE chamber, using N₂O₅ decomposition as the source of NO₃, with the rate coefficients being mainly determined relative to those of a series of alkenes of comparable reactivities. The target compounds include furan, 2-methylfuran, 2,5-dimethylfuran, furan-2-aldehyde, 5-methyl-2(3H)-furanone, 2(5H)-furanone and pyrrole. In the case of 5-methyl-2(3H)-furanone, this is the first reported determination. A rate coefficient for the reaction of NO₃ with the reactive monoterpene, alpha-terpinene, is also reported which is higher than previous absolute and relative rate determinations.

This paper considers an important topic, where new and confirmatory kinetic data are required, and the paper is clearly presented and written. I have one major comment on the experimental set-up and its interpretation, and some minor comments, which are outlined below. The major comment relates to the possible impact of NO₂ chemistry in the system, particularly for the α-terpinene rate coefficient determination, but which should probably also be checked in other cases where the current and previous results differ. I have submitted this review promptly, and I hope this will give the authors time to consider this and make adjustments, if required.

Major Comment

The NO₃ source employed (N₂O₅ decomposition) produces an equivalent amount of NO₂, and additional NO₂ is likely formed as a product of the NO₃-initiated organic chemistry (i.e., from decomposition of nitro-oxy oxy radicals). Given the timescale of the experiments (0.5 – 2 hours), and the lack of reaction partners for NO₂, the potential reaction of NO₂ with the unsaturated organics needs to be considered and assessed, to confirm that the assumption of NO₃ being the only reagent is valid (i.e., Eq. (E1)).

NO₂ has previously been shown to react only very slowly with monoalkenes, but systematically more rapidly with conjugated dienes – and with further increases in reactivity resulting from alkyl substitution and in cyclohexadiene rings (Atkinson et al., 1984; Niki et al., 1986; Ohta et al., 1986; Jenkin et al., 2005; Bernard et al., 2013). The rate coefficient reported for α-terpinene (1-isopropyl-4-methyl-cyclohexa-1,3-diene: 6.5×10^{-18} cm³ molecule⁻¹ s⁻¹) is therefore one of the highest measured to date (Atkinson et al., 1984). The lifetime of NO₂ with respect to reaction with 3 ppm alpha-terpinene is therefore about 0.5 hours, such that some supplementary removal of α-terpinene by this reaction is likely to have occurred under the conditions employed in the present work. In contrast, the alkene reference compound, 2,3-dimethyl-2-butene, reacts much more slowly with NO₂ (1.5×10^{-20} cm³ molecule⁻¹ s⁻¹). As a result, this interference may contribute to the present k(NO₃) determination for α-terpinene being higher than all previous determinations. The previous relative rate studies either corrected for NO₂ reaction (Atkinson et al., 1985) or employed flowing systems with short residence times (Berndt et al., 1996). The authors therefore need to check for this potential interference (which presumably would be a very straightforward experiment) and make corrections if required.

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We thank the reviewer for pointing out this potential interference in our experiments and providing the comment early to give us time to check these interferences experimentally.

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In response to this comment we have conducted experiments looking at the NO$_2$ reaction with alpha-terpinene, furan, 2,5-dimethylfuran, and pyrrole. The experiments were performed with initial NO$_2$ mixing ratios of roughly 5 ppmv, similar to the maximum amount of NO$_2$ observed during the NO$_3$ experiments reported in the manuscript. The rate coefficient $k(\alpha\text{-terpinene} + NO_2)$ was determined by a
130   fit to the measured α-terpinene mixing ratio constrained by [NO$_2$] (Figure 1 of response). The value obtained for the rate coefficient is $(5.8\pm0.8) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}. This is in agreement with the value obtained by Atkinson et al. (1984) of $(6.5\pm1.4) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}. For furan, 2,5-dimethylfuran, and pyrrole, the derived rate coefficients were all indistinguishable from zero under the experimental conditions employed, and can all be said to be $< 2.0 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1}. This is now discussed in the
135   manuscript – see additional text below. However, the alpha-terpinene experiment is not reported, as these experiments have now been removed from the manuscript, see 'Major Changes' above.
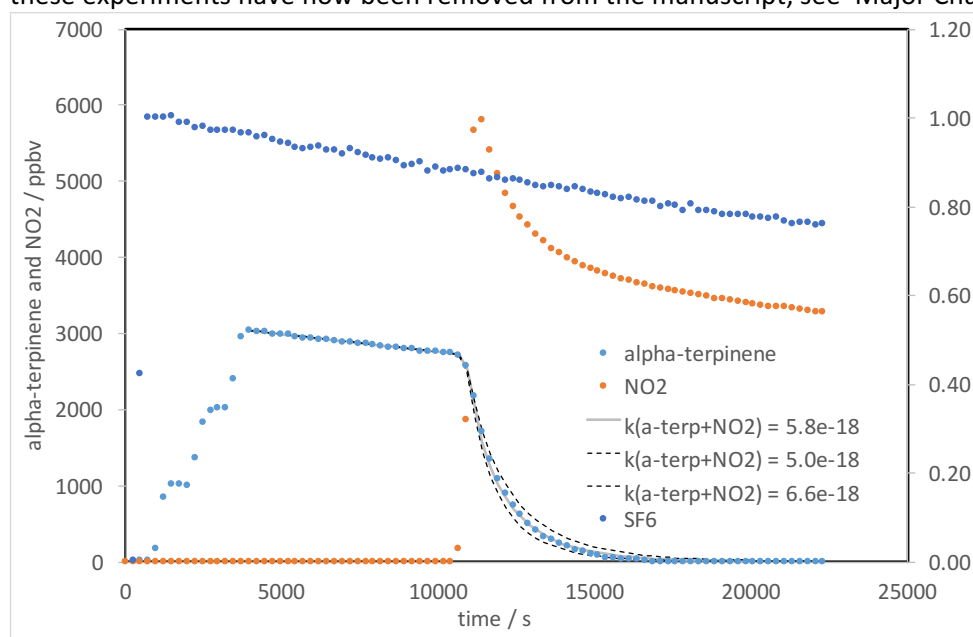

Figure 1 Experiment to determine $k(\alpha\text{-terpinene} + NO_2)$

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"A further potential interference with the current experimental setup, is the reaction of NO_2 with the compounds used. Rate coefficients have previously been measured for reaction of NO_2 with a number of unsaturated compounds here (Atkinson et al., 1984; Bernard et al., 2013). For conjugated dienes, these values can be large enough (~10^{-18} cm^3 molecule^{-1} s^{-1}) to provide a significant loss under the experimental

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conditions employed here. NO_2 is formed during these experiments from the decomposition of N_2O_5, with the NO_2 mixing ratio typically increasing up to roughly 3 ppmv through the experiment. Separate experiments were performed to look at the potential reaction of NO_2 with furan, 2,5-dimethylfuran and pyrrole. For all three compounds, their loss in the presence of NO_2 (allowing for dilution) was indistinguishable from zero, allowing an upper limit of < 2×10^{-20} cm^3 molecule^{-1} s^{-1} to be placed on their

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$k(NO_2)$ rate coefficients."

Minor comments

155 **Abstract: The common names furfural, α-angelicalactone and γ-crotonolactone are generally used for furan-2-aldehyde, 5-methyl-2(3H)-furanone and 2(5H)-furanone throughout the manuscript. It might be useful to include the common names in the abstract summary (i.e., as done on line 54).**

These names have been added in the abstract.

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Line 70: Please further clarify whether the N_2O_5 sample was introduced "continually" (i.e., repeatedly in aliquots) or "continuously" (i.e., without interruption in a constant flow throughout the experiment).

The reviewer is correct, the sample was added continuously. This has been clarified in the text, which
165   now reads:

"The reaction was then initiated by continuously introducing an N_2O_5 sample, held in a trap at ~ 235 K with air flow of (2.5 – 5) L/min through it, for the duration of the experiment."

170 **Lines 79-83: Cyclohexane (used as the reference for γ-crotonolactone) needs to be included in the materials list. Its rate coefficient should also be included in Table 2.**

This information has been added to the materials list and Table 2.

175 **Line 101: It would be helpful to have some explanation of why the rate of alkene and furan loss rates increase with time during the experiment (Fig. 1). It is not clear from the information given. At what point was the N_2O_5 flow added? It also would be good to have similar plots for other studied compounds in the Supplement.**

The VOCs were monitored for at least thirty minutes after addition, prior to the beginning of the N_2O_5
180   addition, to ascertain wall loss rates of the VOCs. The N_2O_5 addition was then continuous during the experiments. The trap slowly warms throughout the experiment, potentially increasing the rate of

addition of N_2O_5. When there are multiple VOCs in the chamber, as the experiment progresses, the NO_3 sink is reduced, as VOCs are removed. Therefore, even at a fixed rate of addition, the NO_3 concentration and hence the VOC loss rate of the slower reacting VOCs (cyclohexene in Figure 1) will noticeably increase through the experiment.

The SI now contains an additional six concentration-time plots, with the same setup as Figure 1 – see **Data Presentation / Availability** above.

Line 113: Terminology: The term "rate(s)" is used incorrectly in many places where "rate coefficient(s)" should be used. As the authors are of course aware, a reaction rate (dimension: concentration/time) is the product of the rate coefficient and reagent concentration(s) – i.e., "k" is a rate coefficient, not a rate.

This has been corrected throughout the manuscript, on lines 17, 18, 119, 120, 126, 127, 128, 143, 181, 203, 208, 211, 212, 227, 230, Table 4, 255, and 300.

Line 138: Note that there is also a direct source of HO_2 from the reaction of NO_3 with α-terpinene. Like other conjugated cyclohexadienes, a minor H abstraction channel occurs to form a substituted cyclohexadienyl radical, followed by its reaction with O_2 to form p-cymene and HO_2 (Berndt et al., 1996).
Lines 134-150. Because the NO_3 + HO_2 reaction also forms OH, it might be worth mentioning that this is (presumably) uncompetitive under the experimental conditions.

The following lines have been added to the paragraph to acknowledge this potential HO_2 source.

"An additional minor source of HO_2 during the experiments will be H abstraction reactions by NO_3. These will produce RO_2 that can react to form RO radicals which may yield HO_2 following abstraction of an H atom by O_2. The rate coefficient of H abstraction by NO_3 is generally expected to be negligible relative to that of the NO_3 addition pathway. For α-terpinene, Berndt et al. (1996) measured a yield of p-cymene, the aromatic product of the H abstraction pathway, of 6 %."

Line 206, Table 3: a-terpinene entries should be "α-terpinene".

These have been changed.

Line 215: The derived values of k(NO_3) for 2,5-dimethylfuran and pyrrole are highlighted as being significantly smaller using α-terpinene as the reference. But, inspection of Table 3 suggests that the values obtained using 2,3-dimethyl-2-butene are further from the average in each case, the highest and lowest of the sets respectively.

We agree that this was not made clear in the text / table. The $k(NO_3)$ values in Table 3 were calculated using the recommended value of $k(\alpha$-terpinene+$NO_3)$ from this manuscript. Using the $k(\alpha$-terpinene+$NO_3)$ value from the database (McGillen et al., 2020) gave the smaller values for 2,5-

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dimethylfuran and pyrrole mentioned in the text. With the removal of the α-terpinene experiments, these lines have now been removed.

Line 224. Replace "TME" by "2,3-dimethyl-2-butene".

Replaced.

Line 227, Table 4: "Kind et al. (2006)" or "Kind et al. (1996)"?

The reviewer is correct, this should be Kind et al. (1996) throughout Table 4 and has been corrected.

Line 347: Berndt et al. (1996) reference is missing.

This reference has been added. In addition, on lines 151 and 270 the reference was given as Berndt et al. (1996) when it should have been Berndt et al. (1997). This has been changed.

General comments

The manuscript presents a relative kinetic study in chamber simulation of a series of furans and relative compounds with NO_3 radical, major oxidant in the atmosphere by night. The studied compounds are furan, 2-methyl furan, 2,5-dimethylfuran, furan-2-aldehyde, 5-methyl-2(3H)-furanone, 2(5H)-furanone and pyrrole which are known to be emitted in the atmosphere during biomass burning.

This study reports for the first time rate coefficients for two furanones (α-angelicalactone and γ-crotonolactone) and investigate rate coefficients for the others compounds witch present few rate constant determinations in the literature. Although new kinetic studies are mandatory to complete and improve kinetic data bases the manuscript needs significant improvements before being published in ACP. The recommendations listed here after must absolutely be taken into consideration.

Major comments

1) As the paper includes a relative kinetic study I would expect a detailed presentation of the experimental conditions, analysis of data, results and discussion. However, there is a certain number of information missing from the manuscript (and/or SI) to allow a proper evaluation of the quality of the data. My main comment is that relative rate plots and time series of concentrations are missing for the majority of the compounds. The plots are needed for example to investigate the presence of an eventual secondary chemistry or products interference. This is of particular interest for the compounds for which the rate constants obtained are not in agreement with the literature.

- please present relative rate plots and time series of concentrations for compounds of interest (VOC, reference compound and NO_2) for 2,5-dimethyl furan, pyrrole, furfural, γ-crotonolactone, α-terpinene;
- please present relative rate plots and time series of concentrations for reference compound and NO_2 for α-angelicalactone;
Although there is no need to include all the time series and plots in the manuscript I suggest to complete the manuscript by including time series of concentration and relative rate plots for compounds for which this is the first rate constant determination (α-angelicalactone) or/and those experiencing fast reactivity (e.g 2,5-dimethylfuran or pyrrole). Representative plots that are not shown in the manuscript must be included in SI for all compounds.

Figure 2 is now a six panel plot containing relative rate plots for all experiments for all six compounds (furan, 2-methylfuran, 2,5-dimethylfuran, furfural, pyrrole, α-angelicalactone).

The SI now contains an additional six example concentration-time plots, with the same setup as Figure 1.

All of the data (raw output from the FTIR, and concentration-time data) will be made available at https://data.eurochamp.org with a doi.

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2) The technique used for monitor VOCs is an in situ IRTF.
- The absorption bands used for reference compounds are missing. Please add a table with the missing information.

These have been added to Table 1.

- The technique is not selective and reactants as well as the products of reaction are expected to absorb IR light and be presented on the absorption spectra at the level of concentration used here. Some of the products have absorption bands that may interfere with the reactant bands and thus perturb the data analysis. Is this the case? Can you comment on that?

The reviewer is right that products may have absorption bands that overlap with those being used to follow the reactants. This is generally not a problem for analysis if the reactant bands are either sharp peaks, as is the case for most of the furans, or if there is only a partial overlap. It is only really if the reactant peaks are broad and the product peaks have a very similar profile, that analysis becomes more challenging. As presented in Table 1, all of the compounds used have a number of possible absorptions which could be used if there is an interference with either a reference, or with a product of the compound or reference. If a compound had multiple absorption features, all were checked for the analysis even if the primary absorption feature appeared to have no interference.

- Generation of NO₃ via the thermal dissociation of N₂O₅ implies the presence of N₂O₅, NO₂ and HNO₃ (depending of the purity of the N₂O₅ synthesis) in the chamber. IRTF allows also to monitor these species. Please add information about the levels of these species in the experiments.

The following text has been added to Section 2.4 (Analysis). NO_2 concentrations are now also discussed later in Section 2.4 concerning its potential interference with the calculated relative rate coefficients.

"N_2O_5 was not present at detectable levels (by FTIR) during most of the experiments. The only experiments in which N_2O_5 concentrations built up in the chamber, were those with the slowest reacting VOCs, i.e. furfural and γ-crotonolactone. NO_2 concentrations increased throughout all experiments, typically up to 2 – 3 ppmv. The NO_2 is initially produced from the decomposition of N_2O_5, and later potentially by the loss of NO_2 from nitrated VOCs / nitrated radicals. HNO_3 concentrations increased throughout the experiments, typically up to 3 – 4 ppmv. This could be either due to impurities in the N_2O_5 sample, or from H abstraction reactions of NO_3. It is not thought that this level of HNO_3 will cause any interference in the rate coefficient determinations."

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3) Although α-terpinene is a compound of interest in this work, there is very few information regarding this compound in the manuscript:

- The title and introduction of the paper are focused mainly on furans

- No information regarding the data analysis is presented (absorption bands in Table 1, absorption spectra in SI). Please complete

- The compound is used as reference compound in two experiments (2,5-dimethylfuran, pyrrole) but the recommended rate and uncertainties are not present in Table 2. Please complete.

- No concentration profiles, no relative rate plots are presented. Please complete.

- Not included in Figure 3 neither in table S1. Please complete.

- No discussion or explanation is given on the faster rate constant regarding the previous rate constant determinations. I would expect further discussion as previous values are in good agreement within the uncertainties.

The experiments using α-terpinene as a reference have now been removed from the manuscript, with justification as given in the opening statement above.

It is noted that we mistakenly presented the literature rate coefficients in Table 4 from Fouqueau et al. (2020), where they were given relative to k(2,3-dimethyl-2-butene+NO$_3$) = 5.5 $\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, rather than 5.7 $\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, the recommendation from McGillen et al. (2020) used elsewhere in our manuscript.

It is also noted that, as discussed in Fouqueau et al. (2020), the two previous relative rate determinations (Atkinson et al., 1985 and Berndt et al., 1996) are not in good agreement. The recommended rate coefficients normalised to k(2,3-dimethyl-2-butene + NO$_3$) = 5.7$\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, are (1.81±0.47)$\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al. 1985) and (1.02±0.06)$\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (Berndt et al., 1996). And much of the uncertainty attributed to the rate coefficient of Atkinson et al. is related to the uncertainty of the rate coefficient of the reference. When assessing the values and stated uncertainties for the relative rate coefficient k(α-terpinene+NO$_3$)/k(2,3-dimethyl-2-butene+NO$_3$): Atkinson (3.18±0.13), Berndt (1.796±0.1), it becomes clear that there is a large discrepancy between these measurements. The value of (1.2±0.3)$\times10^{-10}$ cm^3 molecule^{-1} s^{-1} determined by Fouqueau et al. (2020) using an absolute method, lies in between the two relative rate measurements.

-α-terpinene was used with 90% of purity without further purification. Can you specify the nature of the impurity and discuss impact on the rate constant?

The α-terpinene sample was used as provided by Sigma-Aldrich. Stated impurities are 1,4-cineole and 1,8-cineole. As discussed above, in the FTIR each compound has a unique absorption signature. So these impurities would only be a potential problem if they were to have very similar absorption features to α-terpinene.

Furthermore, if cineole was causing an interference, it a reported k(NO₃) of 1.7e-16, i.e. roughly six orders of magnitude smaller than α-terpinene. As such, a significant interference would make the derived rate coefficient smaller than expected, rather than larger as observed in our experiments.

In my opinion the data regarding this compound should be further presented and discuss or the authors should take in consideration to remove it from the manuscript.

4) While authors have investigated a possible OH generation and thus reactions of VOC of interest with OH no other sinks in the experiments were considered or discuss. The generation of NO₃ radicals by thermal dissociation of N₂O₅ has indeed the advantage to work in a O₃ free environment but implies large amounts of NO₂. I agree with the first referee, NO₂ may be possible sink for the studied compounds in the experimental conditions presented here (large concentrations of VOC, and N₂O₅). Authors should investigate this possible path for all compounds but especially for rate constants found higher that the already published ones (pyrrole, 2,5-dimethylfuran and α-terpinene).

Experiments have been performed to examine NO₂ reaction with α-terpinene, furan, 2,5-dimethyl furan, and pyrrole in response to reviewer 1's comments. It was concluded that the reaction rate coefficient is $< 2.0 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} for the latter three compounds. Please see the discussion above for further details.

Minor comments

Furan -2-aldehyde, 5 methyl-2(3H)-furanone and 2(H)-furanone are used either by their scientific names (eg. abstract, table 1) or by their common names (furfural, α-angelicalactone, γ-crotonolactone) (eg. Materiels, Table 3) which is difficult to follow. For clarity, please homogenize.

The common names are now used throughout the manuscript. When mentioned in the abstract and in the introduction, the scientific name is given in brackets after the common name.

Line 43: The sentence "Furan type compounds are removed from the atmosphere by reaction with the major oxidants OH, NO₃ and O₃" should be introduce earlier (line 34) for clarity.

The introduction is ordered by first, a discussion of sources of furans to the atmosphere, and second a discussion of their sinks. There is admittedly a brief discussion of furan oxidation prior to discussion of the oxidants, the purpose of which is to introduce the source of 2-furanones (i.e. production in the atmosphere from furan oxidation).

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Experimental

More information about the experiments is needed in my opinion.

Line 62: The authors mention that the experiments were conducted with the chamber operated at a slight overpressure to compensate from" removal of air sampling and to prevent ingress of outside air to the chamber". The reason for "air sampling" is unclear as the only instrument mentioned for these experiments is an in situ IRTF. Please clarify.

It is true that removal of air through sampling was minimal. An ozone monitor was running during the experiments which will remove a very small amount of air.

Line 67: Specify the order of introduction of VOCs (VOC of interest followed by Reference VOC?), continuous injection of N_2O_5, …

There was no set order of introduction of VOCs. If a reference spectrum was required for one of the VOCs then this was added first and the reference spectrum taken. The VOCs were then monitored for at least half an hour prior to the beginning of the continuous addition of N_2O_5 (see discussion on this point in answer to review 1 above) to ascertain wall loss rates.

Line 74: Please specify the time and spectral resolution for the IR spectra

The spectral resolution was 0.25 cm^{-1}. As stated, each scan consisted of 30 or 60 co-additions. These took a time of 2 or 4 minutes. The text has been amended accordingly and now reads:

"Each scan was comprised of either 30 or 60 co-additions, taking a total of 2 or 4 minutes respectively, depending on the expected rate of loss of the VOCs, with a spectral resolution of 0.25 cm^{-1}."

Materials

For clarity, please differentiate interest VOC from reference VOC.

This has been added.

Results and discussion

Table 3: A number of experiments are missing. Please complete.

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It is not clear to what the reviewer is referring in Table 3. We note that the number of repeats was missing for some of the compounds in Table 3 and have now completed this, we assume that this is to what the reviewer refers.

445   ***Table 4: For α-terpinene: information are missing regarding previous studies: i) for Atkinson et al., et Berndt et al. please specify the type of study. For Fouqueau et al., 2020 please specify the study and method used.***

The α-terpinene information has now been removed.

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SI

Table S1: for clarity: replace "NA" by "-"; reorganize the table (e.g. by Compound 1 or Reference)

This has been corrected and the table has been ordered by Compound 1.

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