Nighttime measurements of HO$_x$ during the RONOCO project and analysis of the sources of HO$_2$

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We would like to thank the reviewers for their constructive comments on the manuscript and recommendation for publication. We have improved the manuscript in a number of areas, as suggested by the reviewers, and provide detailed responses to the comments below. The reviewers' comments are given in italics. Changes to the manuscript are given in red.

Review #1

1.1

The authors should clarify throughout the manuscript that their measurements of HO$_2$ include a small interference from RO$_2$ radicals and should be labeled as HO$_2$* rather than HO$_2$ to avoid confusion, including Figures 4, 7, 8, and 15. This would also be consistent with the presentation of their data (as HO$_2$*) in Stone et al. (2014b).

We acknowledge that the measurements should be labelled HO$_2^*$. The manuscript has been changed accordingly. HO$_2^*$ is defined on page 3009, and HO$_2$ measurements are referred to as HO$_2^*$ thereafter. Tables 4 and 5, and Figures 4, 7, 8, and 15 and their captions have been updated.

1.2   Pages 3008-3009

Although the RO$_2$ interference with HO$_2$ measurements has been quantified in the ground based instruments as described in Whalley et al. (2013), it appears that this has yet to be done for the aircraft instrument with only the interference due to ethene quantified and the rest calculated using the MCM. What was the distribution and calculated detection efficiencies of the different peroxy radicals calculated for the campaign conditions that led to the conclusion that only 15% of RO$_2$ radicals were detected by their instrument?

Whalley et al. (2013) describe in detail interference tests for three FAGE cells of varying design, one of which is comparable to that used in the aircraft measurements described in this work. In addition, interference tests have been conducted specifically for the aircraft FAGE instrument for ethene-derived peroxy radicals and are given by Stone et al. (2014). The

results of Whalley et al. indicate that the chemistry responsible for the observed interferences is well described by the MCM. MCM-based models are able to reproduce the observed interferences once the interference has been characterised for a single peroxy radical, since the level of interference is dependent on the efficiency of mixing of NO into the sampled air and the residence time of the sampled air in the FAGE cell. Both of these parameters are constrained in the model from experiment. Accordingly, the interferences presented in this work, as described by Stone et al. (2014), are determined relative to that for the ethene-derived peroxy radical using known chemistry.

The interference from the ethene-derived peroxy radical was determined experimentally, and was found to be (39.7 ± 4.8) % for a 1:1 mixture of HO_2 and RO_2. Stone et al. used a box model constrained to the temperature, pressure, and [NO] in the aircraft FAGE detection cell, with a detailed MCM-based chemistry scheme, to calculate the potential RO_2-based interference in the RONOCO HO_2 measurements. The model run time was varied until the model-predicted interference from ethene-derived RO_2 radicals was equal to the experimentally determined interference, thereby tuning the model to the conversion efficiency of HO_2 to OH. The model was initialised with equal concentrations of HO_2 and RO_2 so that an interference factor, f (i.e. the fractional increase in 'HO_2' signal upon addition of RO_2 to the system), could be calculated for every RO_2 species in the model. The greatest interference was calculated to come from isoprene-derived RO_2 (e.g. 57 % from $HC(O)C(O)O_2$), followed by RO_2 species derived from aromatic compounds and C_2 to C_5 alkenes.

The interference factors were applied to model-predicted RO_2 speciation and concentrations for the RONOCO flights. Model-predicted RO_2 species were dominated by CH_3O_2 (33 %; $f = 1.1$ %) and HO_2 (24 %; $f = 0.0$ %), with smaller contributions from RO_2 derived from *iso*-butene (12 %; $f = 0.5$ %), *cis*-2-butene and *trans*-2-butene (10 %; $f = 0.05$ %), and isoprene (2 %; $f = 7.6$ %). RO_2 species with high interference factors are a minor component of the total RO_2.

A plot of modelled HO_2 (no interference) vs modelled HO_2* ($HO_2 + f$*RO_2) was best described by HO_2* $= [1.15 \times HO_2] + 2 \times 10^5$ cm^{-3}. The potential interference in the FAGE measurements of HO_2 during RONOCO was calculated using this equation.

The following sentences have been added to the manuscript to clarify the discussion:

P3008 L18:

"Whalley et al. (2013) show that the chemistry responsible for the observed interferences is well known, and that a model using the Master Chemical Mechanism (MCM, version 3.2: Jenkin et al., 1997; Saunders et al., 2003; Bloss et al., 2005, via http://mcm.leeds.ac.uk/MCM) can reproduce the interferences once tuned to the conversion efficiency of HO_2 to OH in the FAGE detection cell. Accordingly, Stone et al. (2014b) have applied the results of the ethene-derived RO_2 interference testing in a modelling study to assess the effect of the interference on the HO_2 measurements made during the RONOCO and SeptEx campaigns."

P3008 L25:

"The model run time was varied until the model-predicted interference from ethene-derived RO_2 radicals was equal to the experimentally determined interference, thereby tuning the model to the conversion efficiency of HO_2 to OH."

P3009 L8:

"The interference factors were applied to model-predicted RO_2 speciation and concentrations for the RONOCO flights. Model-predicted RO_2 species were dominated by CH_3O_2 (33 %; $f =$ 1.1 %) and HO_2 (24 %; $f = 0.0$ %), with smaller contributions from RO_2 derived from *iso*-butene (12 %; $f = 0.5$ %), *cis*-2-butene and *trans*-2-butene (10 %; $f = 0.05$ %), and isoprene (2 %; $f = 7.6$ %). RO_2 species with high interference factors were a minor component of the total RO_2."

1.3   Page 3011

The authors state that the LOD reported in Table 4 are for an averaging time of 1 min, while on pages 3007-3008 a 5 min time average is state for these LOD. Stone et al. (2014b) lists these LODs for 4-5 min averages.

We thank the reviewers for highlighting this error. The averaging time is 5 minutes. The averaging time has been included in the table caption to make it clearer, and the main text has been changed as follows:

P3011 L27:

"Table 4 summarises the OH and HO_2* measurements during RONOCO and SeptEx and gives the instrument's average 1σ limit of detection for a 5 minute averaging period."

1.4 Page 3014

The authors present the OH and HO₂ measurements as a function of altitude, but calculate what appear to be average rates in Figures 11-14. This should be clarified in the text. Did the authors observed an altitude dependence of these rates? A figure that illustrates the measured concentrations of ozone, NO₃ and alkenes as a function of altitude would be useful.

Average rates of production are presented in Figures 11 to 14. This has been made clearer in the text:

P3017, L12: "The rates of reaction and rates of instantaneous production of HO_2 presented hereafter are average values for individual flights, seasons, or times of day."

The figure captions for Table 6 and Figures 11-14 have been amended to read "average rates of reaction" or "average rates of instantaneous production of HO_2" as appropriate.

No altitude dependence of the rates of reaction of O_3 and NO_3 with the alkenes measured, or of the rate of production of HO_2, was observed.

A figure illustrating the altitude profiles of NO_3, O_3 and two selected alkenes (*trans*-2-butene and propene, which are dominant in reactions of oxidants with the alkenes measured during RONOCO, and in production of HO_2) is shown below (Figure 1) and will be included in the manuscript as Figure 3 (numbering of subsequent figures and references to them have been updated).

The new figure is introduced:

P3006 L19:

"Table 3 also highlights the unusual chemical conditions encountered during flight B537 on 20th July 2010, discussed further in Sect. 4.1. Nighttime altitude profiles of NO_3, O_3, *trans*-2-butene, and propene (the latter two being illustrative of the alkenes measured) are given in Fig. 3."
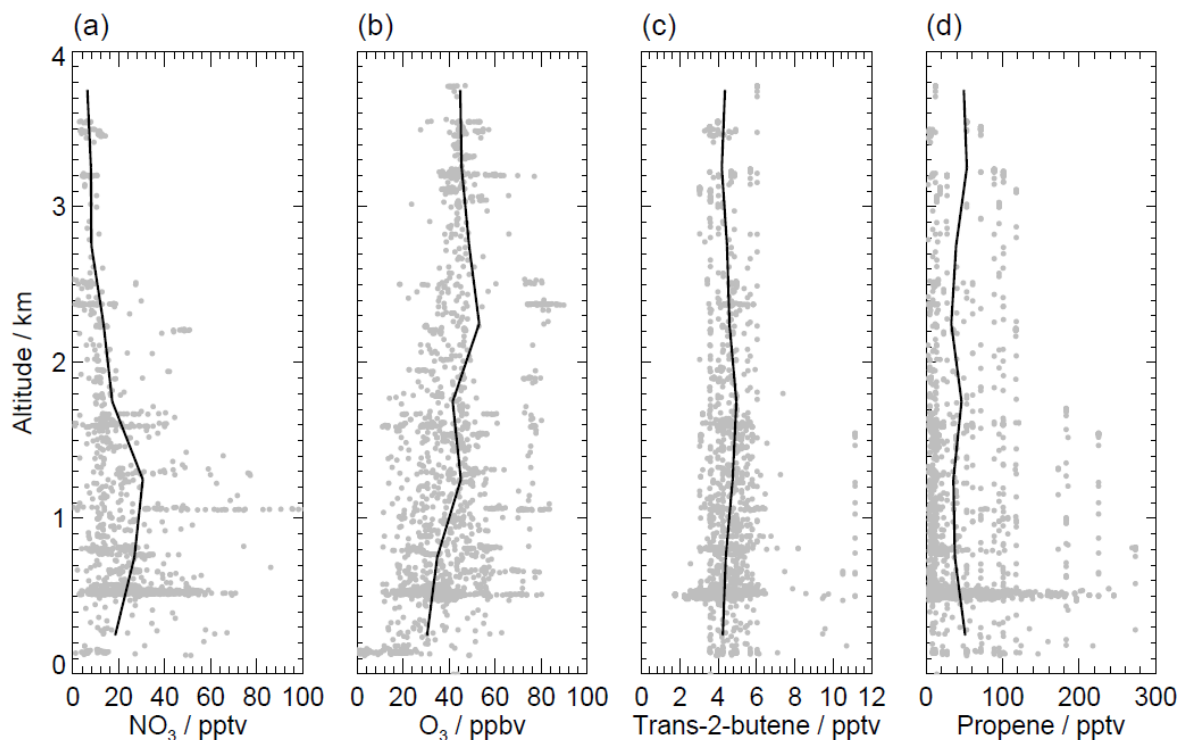
Figure 1. Nighttime altitude profiles of a) NO_3; b) O_3; c) Trans-2-butene; d) Propene, showing 60 second data (grey points) and mean values in 500 m altitude bins (solid black lines).

Review #2

2.1 P2999 L21

The oxidising capacity of the atmosphere is described as its "ability" to remove trace gases. While capacity is a physical and quantifiable characteristic of a system, ability is not. Please reword.

The authors acknowledge that "ability" is not suitable. The sentence contributes nothing further to the preceding sentence, so it has been removed.

2.2 P3008 L23-26

Why were equal concentrations of HO_2 and RO_2 used to constrain the model? The sentence "the model was run until the model interference … matched the interference measured in the

interference experiments" is clumsy. Please re-word and state how the model was tuned to get it to match.

Equal concentrations of HO_2 and RO_2 were used to initialise the model calculations used to determine RO_2 interferences. The experimental determination of RO_2 interference used equal concentrations of HO_2 and RO_2, and compared the 'HO_2' signal to experiments in which no RO_2 radicals were present. The fractional increase in the observed signal on addition of RO_2 to the system thus represents the fractional RO_2 interference. The model calculations were performed to replicate the experimental method, with the model tuned to the observed increase in 'HO_2' signal on inclusion of the RO_2 species by varying the reaction time (representing the extent of mixing of NO and residence time in the detection cell) until the modelled interference matched the experimental observations.

The sentence has been reworded as follows:

P3008 L25 to P3009 L1:

"The model run time was varied until the model-predicted interference from ethene-derived RO_2 radicals was equal to the experimentally-determined interference, thereby tuning the model to the conversion efficiency of HO_2 to OH."

Please see Sect 1.2 for further discussion of this section of the manuscript.

2.3   P3008 L28

"interference measurements described above". There is no description of the so-called interference experiments, only a citation to Whalley.

The sentence has been changed (see Sect. 1.2 of this document), and "interference measurements described above" has been removed. The aircraft instrument experiments, which have not been published elsewhere, are mentioned briefly after the reference to Whalley et al.

2.4   P3009 L14

After describing the corrections for HO_2 and deriving alkene dependent correction factors for the HO_2 measurements the authors then state that the correction (on average 14 %) was not made. If they trust the correction, they should apply it to the data.

Correction of the observations of HO_2^* to determine HO_2 relies on the model calculated RO_2 speciation and RO_2 concentrations, and would thus make HO_2 a combination of observations and model products. In order to avoid this we report the HO_2^* as observed, as is the case for other groups (e.g. Lu et al., 2012; Griffith et al., 2013), and apply the interference to the modelled HO_2 (as described in Stone et al., 2014), maintaining independence of the observed data from the modelled data.

The manuscript has been changed as follows:

P3009 L14:

"The HO_2 measurements made during RONOCO and SeptEx were not adjusted since speciated RO_2 measurements were not available. The measurements are hereafter referred to as HO_2^*."

2.5   P3011 L10

Wall losses of NO_3 and N_2O_5 were determined prior to and after each flight. What was the variability in this parameter and how large the correction factor? The total uncertainty in the NO_3 measurement is given as 11 %. This seems too low, especially considering that the NO_3-transmission of the aircraft inlet is unknown.

As described in detail by Kennedy et al. (2011) potential changes to the transmission efficiency caused by ageing or build-up of particulates on the PFA surface were investigated by determining the pseudo first order loss rate of NO_3 onto the instrument's internal surface, $k_{NO3\ loss}$, prior to and following each flight. For each flight the measured rate coefficient was found to equal that measured in the laboratory ($0.27\ \text{s}^{-1} \pm 0.02\ \text{s}^{-1}$), within error, indicating negligible change to the PFA surface.

High flow rates through channels 1 and 2 ensure short residence times (380 ms in channel 1 and 170 ms in channel 2). The calculated transmission efficiencies of NO_3 into channels 1 and 2 are $T_1 = 90\ \% \pm 1.5\ \%$ and $T_2 = 96\ \% \pm 0.7\ \%$, respectively.

The transmission efficiency of N_2O_5 into channel 1, T_0, depends upon direct loss of N_2O_5 to the walls of the inlet and wall losses of NO_3 produced by thermal dissociation. The loss rate of N_2O_5 to the walls of the inlet was found to be considerably slower than that for NO_3 ($k_{N2O5\ loss} = 0.042\ \text{s}^{-1} \pm 0.004\ \text{s}^{-1}$). The short residence time in the inlet (<0.02 s) ensures that direct losses of N_2O_5 are within the error of ambient N_2O_5 measurements and can be

neglected. Accordingly T_0 is determined by loss of NO_3 following thermal dissociation. For a residence time of 250 ms between the preheater and the detection cell T_0 is calculated to be equal to 93 % ± 6 %.

The manuscript has been changed as follows:

"In addition, wall losses of NO_3 and N_2O_5 were determined before and after each flight to account for changes in the surface properties of the inlet and detection cell walls, which were found to be negligible."

2.6   P3015 L17

Is the value of 0.6 (equation5) valid for all VOCs ? The authors should consider giving some examples of F_RO for a few different alkenes.

The calculation follows the method employed in the MCM, a near-explicit state-of-the-art organic chemistry mechanism, in which each peroxy radical is assumed to react with all other peroxy radicals at a single, collective rate. The branching ratios to RO, $RC(O)CH_3$, and RCH_2OH, and ROH, are determined by the structure of the peroxy radical. The value of 0.6 for primary and secondary RO_2 (excluding CH_3O_2, see below) is based on the mean of the values of the self-reactions of $C_2H_5O_2$, i-$C_3H_7O_2$, neo-$C_5H_{11}O_2$, c-$C_5H_{11}O_2$, $CH_2{=}CHCH_2O_2$, $HOCH_2CH_2O_2$, $CH_3OCH_2O_2$, $CH_3C(O)CH_2O_2$, and $CH_2ClCH_2O_2$, which range between 0.5 and 0.75, and is the best estimate using currently-available data. Nitrooxyalkyl peroxy radicals are assumed to react in the same manner as the RO_2 species listed above. CH_3O_2 is treated separately in the MCM, with a branching ratio of 0.330 to the non-terminating (RO) channel. Note that Equation 5 refers to the reactions of nitrooxyalkyl peroxy radicals produced from NO_3 + alkene reactions, and therefore does not include CH_3O_2, which is produced in the reactions of O_3 with alkenes.

Some examples of F_{RO} have been given in the manuscript as follows:

P3015 L18:

"where RO_2 represents all peroxy radicals. Average values of F_{RO} for the NO_3 + alkene reactions range between 0.50 for *trans*-2-pentene- and 1-pentene-derived RO_2 species and 0.61 for ethene-derived RO_2 species."

P3016 L19:

"…F_{RO} is the fraction of RO_2 radicals that react to produce RO radicals, and F_{HO2} is the fraction of RO radicals that react to produce HO_2 radicals, which is equal to 1 for all the alkenes studied. Average values of F_{RO} for the O_3 + alkene reactions range between 0.54 for 1-pentene-derived RO_2 species and 0.64 for 1-butene- and *trans*-2-pentene-derived RO_2 species."

2.7   P3017 L24

"the seasonal difference in NO_3 concentrations may have been the result of lower temperatures." As the temperatures, the equilibrium constants and NO_2 levels are known this statement can be confirmed and quantified.

We have calculated $K_{eq}[NO_2] = [N_2O_5]/[NO_3]$ for summer and winter:

$K_{eq}[NO_2]_{summer} = 4.8$

$K_{eq}[NO_2]_{winter} = 29.6$

$[N_2O_5]/[NO_3]_{summer} = 3.4$

$[N_2O_5]/[NO_3]_{winter} = 18.1$

Though $K_{eq}[NO_2]$ is not equal to $[N_2O_5]/[NO_3]$ in either season, both $K_{eq}[NO_2]$ and $[N_2O_5]/[NO_3]$ increase between summer and winter, supporting the hypothesis that the decreased concentrations of NO_3 during winter are attributable to the change in the N_2O_5-NO_3 equilibrium.

The manuscript has been changed to reflect this:

P3017 L24 to P3018 L1:

"This seasonal difference in NO_3 concentrations is attributable to the lower mean nighttime temperature in winter (277.7K) compared to summer (286.7 K) which disfavours NO_3 in the thermal equilibrium $N_2O_5 \rightleftharpoons NO_3 + NO_2$. $K_{eq}[NO_2]$, which determines $[N_2O_5]/[NO_3]$, is calculated to be 4.8 in summer and 29.6 in winter."

2.8   P3021

The authors calculate the rate of HO_2 production assuming that the losses of NO_3 are completely accounted for by the alkenes measured. Based on this assumption, the authors should also be able to calculate the steady-state mixing ratios of NO_3 as the production term (via O_3 and NO_2) is known. They will find that the NO_3 concentrations calculated this way

are too high as the true overall loss rate is actually not known. Indeed on page 3023 the authors show that the model used also over-predicts NO₃. The authors then state that the discrepancy between modelled and measured NO₃ helps to explain the model overprediction of the role of NO₃ in HO₂ generation. I'm not sure if this is correct. If the model does not account for the losses of NO₃ with hydrocarbons that were not measured it will generate more N₂O₅ (as the model NO3 lifetime increases) and thus underestimate the rate of oxidation of VOCs by NO₃ and thus also UNDERpredict the rate of RO₂ production.

We acknowledge that calculating steady-state mixing ratios of NO_3 using NO_3 + alkenes as the sole loss mechanism would indeed lead to overprediction of NO_3 concentrations compared to the measured values. However, we aim to highlight the relative importance of NO_3 and O_3 in the production of HO_2 during summer and winter, and to compare the calculations to the results of the modelling study by Stone et al. (2014), rather than focussing on the absolute rates of production of HO_2. Both the modelling study and the current work use observed values of $[O_3]$ to calculate rates of reaction between O_3 and alkenes and subsequent rates of production of HO_2, so the contribution of O_3 + alkenes to production of HO_2 is equivalent in Stone et al. and in the current work. Since the model overpredicts the observed NO_3 concentrations by 80 % on average, and is constrained to observed values of $[O_3]$, the model is expected to predict an enhanced role for NO_3 relative to that of O_3 in production of HO_2, compared to calculations based entirely on the observations.

The manuscript has been changed to highlight the relative importance of NO_3 and O_3 in production of HO_2:

P3024, L6 to L12:

"These results are in general agreement with the results of the analysis presented in Sect. 6.1, though the model predicts a more important role for NO_3 (80 % of RO_x radical production, which is 7.2 times the contribution from O_3 + alkenes) than is predicted by the analysis based on the observations (69 % of HO_2 radical production during summer, which is 2.1 times the contribution from O_3 + alkenes). The model predicts a relatively small role for O_3 in both summer and winter. The model is constrained to measured values of O_3, but overpredicts NO_3...."

2.9 P3023 L15

Data from flight B537 were excluded owing to atypical observations of HO_2, NO_3, O_3 and "other chemical species". What does atypical mean? Sometimes "atypical" events can be a better test of our understanding of chemical processes than analysis of only the data that we a priori expect to find.

In this instance atypical refers to the high concentrations of HO_2, NO_3, O_3, CO, aerosol surface area, and aerosol organic fraction compared to the values measured in other flights, as described in Sect. 4.1 (P3013, L5 to L10). We agree that this flight offers a good opportunity to investigate the atmospheric chemistry sampled, which is why we have used it as a small case study in the current work, highlighting the observed correlation between HO_2* and NO_3 and including the analysis of the production of HO_2 during this individual flight. Model results constrained to measurements of long-lived species made during flight B537 were found to be outliers from the rest of the data, and were excluded to enable analysis of the data without the influence of this flight. A modelling study dedicated to interpreting the chemistry observed during B537 would be valuable.

2.10 P3026 L29

"and others" is not a useful reference.

The reference has been changed to include other publications, and "and others" has been removed:

"Alkene ozonolysis also plays a significant role in nocturnal oxidation in agreement with Salisbury et al. (2001), Geyer et al. (2003), Ren et al. (2003a), Emmerson et al. (2005), Ren et al. (2006), and Volkamer et al. (2010)."

References

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