

# Nighttime measurements of HO<sub>x</sub> during the RONOCO project and analysis of the sources of HO<sub>2</sub>

H.M. Walker et al.

We would like to thank the reviewers for their constructive comments which have helped to improve the manuscript. We have modified 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<sub>2</sub> include a small interference from RO<sub>2</sub> radicals and should be labeled as HO<sub>2</sub>\* rather than HO<sub>2</sub> to avoid confusion, including Figures 4, 7, 8, and 15. This would also be consistent with the presentation of their data (as HO<sub>2</sub>\*) in Stone et al. (2014b).*

We acknowledge that the measurements should be labelled HO<sub>2</sub>\*. The manuscript has been changed accordingly. HO<sub>2</sub>\* is defined on page 3009, and HO<sub>2</sub> measurements are referred to as HO<sub>2</sub>\* 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<sub>2</sub> interference with HO<sub>2</sub> 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<sub>2</sub> 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  $(39.7 \pm 4.8)$  % for a 1:1 mixture of HO<sub>2</sub> and RO<sub>2</sub>. 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<sub>2</sub>-based interference in the RONOCO HO<sub>2</sub> measurements. The model run time was varied until the model-predicted interference from ethene-derived RO<sub>2</sub> radicals was equal to the experimentally determined interference, thereby tuning the model to the conversion efficiency of HO<sub>2</sub> to OH. The model was initialised with equal concentrations of HO<sub>2</sub> and RO<sub>2</sub> so that an interference factor,  $f$  (i.e. the fractional increase in 'HO<sub>2</sub>' signal upon addition of RO<sub>2</sub> to the system), could be calculated for every RO<sub>2</sub> species in the model. The greatest interference was calculated to come from isoprene-derived RO<sub>2</sub> (e.g. 57 % from HC(O)C(O)O<sub>2</sub>), followed by RO<sub>2</sub> species derived from aromatic compounds and C<sub>2</sub> to C<sub>5</sub> alkenes.

The interference factors were applied to model-predicted RO<sub>2</sub> speciation and concentrations for the RONOCO flights. Model-predicted RO<sub>2</sub> species were dominated by CH<sub>3</sub>O<sub>2</sub> (33 %;  $f = 1.1$  %) and HO<sub>2</sub> (24 %;  $f = 0.0$  %), with smaller contributions from RO<sub>2</sub> 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<sub>2</sub> species with high interference factors are a minor component of the total RO<sub>2</sub>.

A plot of modelled HO<sub>2</sub> (no interference) vs modelled HO<sub>2</sub>\* (HO<sub>2</sub> +  $f^*$ RO<sub>2</sub>) was best described by  $\text{HO}_2^* = [1.15 \times \text{HO}_2] + 2 \times 10^5 \text{ cm}^{-3}$ . The potential interference in the FAGE measurements of HO<sub>2</sub> 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<sub>2</sub> to OH in the FAGE detection cell. Accordingly, Stone et al. (2014b) have applied the results of the ethene-derived RO<sub>2</sub> interference testing in a modelling study to assess the effect of the interference on the HO<sub>2</sub> 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<sub>2</sub> radicals was equal to the experimentally determined interference, thereby tuning the model to the conversion efficiency of HO<sub>2</sub> to OH.”

P3009 L8:

“The interference factors were applied to model-predicted RO<sub>2</sub> speciation and concentrations for the RONOCO flights. Model-predicted RO<sub>2</sub> species were dominated by CH<sub>3</sub>O<sub>2</sub> (33 %;  $f = 1.1$  %) and HO<sub>2</sub> (24 %;  $f = 0.0$  %), with smaller contributions from RO<sub>2</sub> 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<sub>2</sub> species with high interference factors were a minor component of the total RO<sub>2</sub>.”

### 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 inconsistency. 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<sub>2</sub>\* measurements during RONOCO and SeptEx and gives the instrument’s average 1 $\sigma$  limit of detection **for a 5 minute averaging period.**”

## 1.4 Page 3014

*The authors present the OH and HO<sub>2</sub> 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 observe an altitude dependence of these rates? A figure that illustrates the measured concentrations of ozone, NO<sub>3</sub> 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<sub>2</sub> 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<sub>2</sub>” as appropriate.

No significant altitude dependence of the rates of reaction of O<sub>3</sub> and NO<sub>3</sub> with the alkenes measured, or of the rate of production of HO<sub>2</sub>, was observed.

A figure illustrating the altitude profiles of NO<sub>3</sub>, O<sub>3</sub> 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<sub>2</sub>) 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 20<sup>th</sup> July 2010, discussed further in Sect. 4.1. **Nighttime altitude profiles of NO<sub>3</sub>, O<sub>3</sub>, *trans*-2-butene, and propene (the latter two being illustrative of the alkenes measured) are given in Fig. 3.**”

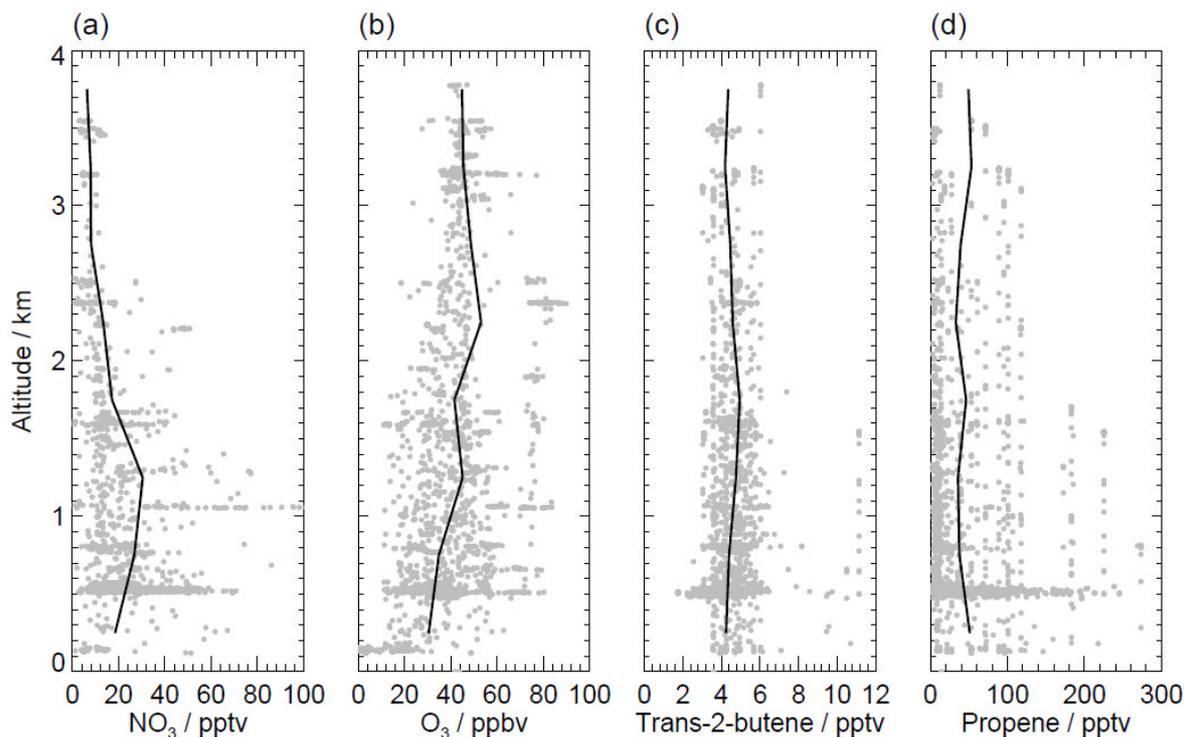


Figure 1. Nighttime altitude profiles of a)  $\text{NO}_3$ ; b)  $\text{O}_3$ ; c) Trans-2-butene; d) Propene, showing 60 second data (grey points) and mean values in 500 m altitude bins (solid black lines).

## 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  $\text{HO}_2$  and  $\text{RO}_2$  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<sub>2</sub> and RO<sub>2</sub> were used to initialise the model calculations used to determine RO<sub>2</sub> interferences. The experimental determination of RO<sub>2</sub> interference used equal concentrations of HO<sub>2</sub> and RO<sub>2</sub>, and compared the ‘HO<sub>2</sub>’ signal to experiments in which no RO<sub>2</sub> radicals were present. The fractional increase in the observed signal on addition of RO<sub>2</sub> to the system thus represents the fractional RO<sub>2</sub> interference. The model calculations were performed to replicate the experimental method, with the model tuned to the observed increase in ‘HO<sub>2</sub>’ signal on inclusion of the RO<sub>2</sub> 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<sub>2</sub> radicals was equal to the experimentally-determined interference, thereby tuning the model to the conversion efficiency of HO<sub>2</sub> to OH.”

Please see Sect 2.1.2 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. 1.6 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<sub>2</sub> and deriving alkene dependent correction factors for the HO<sub>2</sub> 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<sub>2</sub>\* to determine HO<sub>2</sub> relies on the model calculated RO<sub>2</sub> speciation and RO<sub>2</sub> concentrations, and would thus make HO<sub>2</sub> a combination of observations and model products. In order to avoid this we report the HO<sub>2</sub>\* 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<sub>2</sub> (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<sub>2</sub> measurements made during RONOCO and SeptEx were not adjusted since speciated RO<sub>2</sub> measurements were not available. The measurements are hereafter referred to as HO<sub>2</sub>\*.”

## 2.5 P3011 L10

*Wall losses of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> 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<sub>3</sub> measurement is given as 11 %. This seems too low, especially considering that the NO<sub>3</sub>-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<sub>3</sub> onto the instrument's internal surface,  $k_{\text{NO}_3 \text{ loss}}$ , 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<sub>3</sub> 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<sub>2</sub>O<sub>5</sub> into channel 1,  $T_0$ , depends upon direct loss of N<sub>2</sub>O<sub>5</sub> to the walls of the inlet and wall losses of NO<sub>3</sub> produced by thermal dissociation. The loss rate of N<sub>2</sub>O<sub>5</sub> to the walls of the inlet was found to be considerably slower than that for NO<sub>3</sub> ( $k_{\text{N}_2\text{O}_5 \text{ loss}} = 0.042 \text{ s}^{-1} \pm 0.004 \text{ s}^{-1}$ ). The short residence time in the inlet (<0.02 s) ensures that direct losses of N<sub>2</sub>O<sub>5</sub> are within the error of ambient N<sub>2</sub>O<sub>5</sub> measurements and can be

neglected. Accordingly  $T_0$  is determined by loss of  $\text{NO}_3$  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  $93 \% \pm 6 \%$ .

The manuscript has been changed as follows:

“In addition, wall losses of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  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,  $\text{RC(O)CH}_3$ , and  $\text{RCH}_2\text{OH}$ , and ROH, are determined by the structure of the peroxy radical. The value of 0.6 for primary and secondary  $\text{RO}_2$  (excluding  $\text{CH}_3\text{O}_2$ , see below) is based on the mean of the values of the self-reactions of  $\text{C}_2\text{H}_5\text{O}_2$ , *i*- $\text{C}_3\text{H}_7\text{O}_2$ , *neo*- $\text{C}_5\text{H}_{11}\text{O}_2$ , *c*- $\text{C}_5\text{H}_{11}\text{O}_2$ ,  $\text{CH}_2=\text{CHCH}_2\text{O}_2$ ,  $\text{HOCH}_2\text{CH}_2\text{O}_2$ ,  $\text{CH}_3\text{OCH}_2\text{O}_2$ ,  $\text{CH}_3\text{C(O)CH}_2\text{O}_2$ , and  $\text{CH}_2\text{ClCH}_2\text{O}_2$ , 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  $\text{RO}_2$  species listed above.  $\text{CH}_3\text{O}_2$  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  $\text{NO}_3 + \text{alkene}$  reactions, and therefore does not include  $\text{CH}_3\text{O}_2$ , which is produced in the reactions of  $\text{O}_3$  with alkenes.

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

P3015 L18:

“where  $\text{RO}_2$  represents all peroxy radicals. **Average values of  $F_{RO}$  for the  $\text{NO}_3 + \text{alkene}$  reactions range between 0.50 for *trans*-2-pentene- and 1-pentene-derived  $\text{RO}_2$  species and 0.61 for ethene-derived  $\text{RO}_2$  species.**”

P3016 L19:

“... $F_{RO}$  is the fraction of  $RO_2$  radicals that react to produce RO radicals, and  $F_{HO_2}$  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 NO<sub>3</sub>. The authors then state that the discrepancy between modelled and measured NO<sub>3</sub> helps to explain the model overprediction of the role of NO<sub>3</sub> in HO<sub>2</sub> generation. I'm not sure if this is correct. If the model does not account for the losses of NO<sub>3</sub> with hydrocarbons that were not measured it will generate more N<sub>2</sub>O<sub>5</sub> (as the model NO<sub>3</sub> lifetime increases) and thus underestimate the rate of oxidation of VOCs by NO<sub>3</sub> and thus also UNDERpredict the rate of RO<sub>2</sub> production.*

We acknowledge that calculating steady-state mixing ratios of NO<sub>3</sub> using NO<sub>3</sub> + alkenes as the sole loss mechanism would indeed lead to overprediction of NO<sub>3</sub> concentrations compared to the measured values. However, we aim to highlight the relative importance of NO<sub>3</sub> and O<sub>3</sub> in the production of HO<sub>2</sub> 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<sub>2</sub>. Both the modelling study and the current work use observed values of [O<sub>3</sub>] to calculate rates of reaction between O<sub>3</sub> and alkenes and subsequent rates of production of HO<sub>2</sub>, so the contribution of O<sub>3</sub> + alkenes to production of HO<sub>2</sub> is equivalent in Stone et al. and in the current work. Since the model overpredicts the observed NO<sub>3</sub> concentrations by 80 % on average, and is constrained to observed values of [O<sub>3</sub>], the model is expected to predict an enhanced role for NO<sub>3</sub> relative to that of O<sub>3</sub> in production of HO<sub>2</sub>, compared to calculations based entirely on the observations.

The manuscript has been changed to highlight the relative importance of NO<sub>3</sub> and O<sub>3</sub> in production of HO<sub>2</sub>:

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<sub>3</sub> (80 % of RO<sub>x</sub> radical production, **which is 7.2 times the contribution from O<sub>3</sub> + alkenes**) than is predicted by the analysis based on the observations (69 % of HO<sub>2</sub> radical production during summer, **which is 2.1 times the contribution from O<sub>3</sub> + alkenes**). **The model predicts a relatively small role for O<sub>3</sub> in both summer and winter.** The model is constrained to measured values of O<sub>3</sub>, but overpredicts NO<sub>3</sub>....”

## 2.9 P3023 L15

*Data from flight B537 were excluded owing to atypical observations of HO<sub>2</sub>, NO<sub>3</sub>, O<sub>3</sub> 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<sub>2</sub>, NO<sub>3</sub>, O<sub>3</sub>, 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<sub>2</sub>\* and NO<sub>3</sub> and including the analysis of the production of HO<sub>2</sub> 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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Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Bohn, B., Brauers, T., Chang, C. C., Häsel, R., Hu, M., Kita, K., Kondo, Y., Li, X., Lou, S. R., Nehr, S., Shao, M., Zeng, L. M., Wahner, A., Zhang, Y. H., Hofzumahaus, A.: Observation and modelling of OH and HO<sub>2</sub> concentrations in the Pearl River Delta 2006: a missing OH source on a VOC rich atmosphere, *Atmos. Chem. Phys.*, 12, 1541-1569, 2012.

1 **Nighttime measurements of HO<sub>x</sub> during the RONOCO**  
2 **project and analysis of the sources of HO<sub>2</sub>**

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28

## 29 **Abstract**

30 Measurements of the radical species OH and HO<sub>2</sub> were made using the Fluorescence Assay  
31 by Gas Expansion (FAGE) technique during a series of nighttime and daytime flights over  
32 the UK in summer 2010 and winter 2011. OH was not detected above the instrument's 1σ  
33 limit of detection during any of the nighttime flights or during the winter daytime flights,  
34 placing upper limits on [OH] of 1.8 × 10<sup>6</sup> molecule cm<sup>-3</sup> and 6.4 × 10<sup>5</sup> molecule cm<sup>-3</sup> for the  
35 summer and winter flights, respectively. HO<sub>2</sub> reached a maximum concentration of 3.2 × 10<sup>8</sup>  
36 molecule cm<sup>-3</sup> (13.6 pptv) during a nighttime flight on 20<sup>th</sup> July 2010, when the highest  
37 concentrations of NO<sub>3</sub> and O<sub>3</sub> were also recorded. Analysis of the rates of reaction of OH, O<sub>3</sub>,  
38 and the NO<sub>3</sub> radical with measured alkenes indicates that the summer nighttime troposphere  
39 can be as important for the processing of VOCs as the winter daytime troposphere. Analysis  
40 of the instantaneous rate of production of HO<sub>2</sub> from the reactions of O<sub>3</sub> and NO<sub>3</sub> with alkenes  
41 has shown that, on average, reactions of NO<sub>3</sub> dominated nighttime production of HO<sub>2</sub> during  
42 summer, and reactions of O<sub>3</sub> dominated nighttime HO<sub>2</sub> production during winter.

43

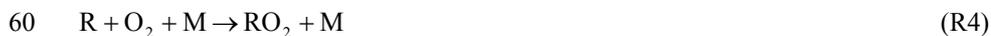
## 44 **1 Introduction**

45 Trace gases emitted into the atmosphere, including pollutants and greenhouse gases, are  
46 removed primarily by oxidation. The hydroxyl radical, OH, is the most important oxidising  
47 species in the daytime troposphere, reacting with numerous species including volatile organic  
48 compounds (VOCs), CO, SO<sub>2</sub>, and long-lived anthropogenic halogenated compounds. ~~The  
49 oxidising capacity of the atmosphere, that is its ability to remove trace gases, is determined  
50 by the concentration of OH.~~ During the day, primary production of OH (i.e. initialisation of  
51 the radical chain) occurs predominantly via photolysis of ozone at λ ≤ 340 nm followed by  
52 reaction of the resulting electronically excited oxygen atom, O(<sup>1</sup>D), with water vapour. The  
53 OH-initiated oxidation of VOCs leads to the production of the hydroperoxy radical, HO<sub>2</sub>, and  
54 together the two radicals form the HO<sub>x</sub> family. A key reaction in the conversion of OH to  
55 HO<sub>2</sub> is the reaction with CO:

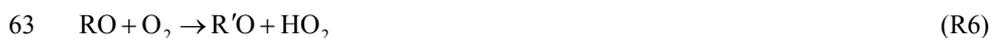


58 Reaction of OH with VOCs results in the production of organic peroxy radicals, RO<sub>2</sub>:

**Comment [HW1]:** See reviewers' comments Sect 2.1



61 Reactions of  $\text{HO}_2$  and  $\text{RO}_2$  with  $\text{NO}$  propagate the  $\text{HO}_x$  radical chain, regenerating  $\text{OH}$ :



65 The production of  $\text{OH}$  through photolysis of ozone (and other species at longer wavelengths)  
66 is limited to daylight hours, and oxidation of trace gases at night proceeds through alternative  
67 mechanisms. Two mechanisms are known to initiate  $\text{HO}_x$  radical chemistry and oxidation  
68 chemistry at night: ozonolysis of alkenes, and reactions of the nitrate radical,  $\text{NO}_3$ , with  
69 alkenes.

70 Reactions of ozone with alkenes occur via addition of ozone to the double bond to form a  
71 five-membered ring called a primary ozonide. The primary ozonide decomposes to form one  
72 of two possible pairs of products, each pair consisting of a carbonyl compound and a  
73 vibrationally- and rotationally-excited carbonyl oxide termed a Criegee intermediate (CI).  
74 The simplest gas-phase CI,  $\text{CH}_2\text{OO}$ , and the alkyl-substituted  $\text{CH}_3\text{CHOO}$ , have been  
75 observed directly by photoionisation mass spectrometry (Taatjes et al., 2008; Beames et al.,  
76 2012; Taatjes et al., 2012; Welz et al., 2012; Beames et al., 2013; Taatjes et al., 2013; Stone  
77 et al., 2014a), by infrared absorption spectroscopy (Su et al., 2013), and by microwave  
78 spectroscopy (Nakajima and Endo, 2013, 2014). Excited CIs may be stabilised by collision  
79 with surrounding molecules (Donahue et al., 2011; Drozd and Donahue, 2011), or may  
80 undergo isomerisation or decomposition to yield products including  $\text{OH}$ ,  $\text{H}$ , and subsequently  
81  $\text{HO}_2$  (Paulson and Orlando, 1996; Kroll et al., 2001a; Kroll et al., 2001b; Kroll et al., 2002;  
82 Johnson and Marston, 2008). Stabilised CIs (SCIs) are known to react with a variety of  
83 compounds, including  $\text{H}_2\text{O}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ , and a variety of organic compounds (e.g. Mauldin III  
84 et al., 2012; Taatjes et al., 2012; Ouyang et al., 2013; Taatjes et al., 2013; Stone et al., 2014a;  
85 Taatjes et al., 2014). There is experimental evidence for the formation of  $\text{OH}$  from thermal  
86 decomposition of SCIs, on a much longer timescale than the decomposition or isomerisation  
87 of excited CIs (Kroll et al., 2001a; Kroll et al., 2001b). The  $\text{OH}$  produced through these  
88 ozonolysis mechanisms will proceed to oxidise other VOC species. Criegee intermediates  
89 formed in the ozonolysis of alkenes are known to be an important source of  $\text{HO}_x$  during the

90 day and at night (Paulson and Orlando, 1996; Donahue et al., 1998; Kanaya et al., 1999;  
91 Salisbury et al., 2001; Geyer et al., 2003; Ren et al., 2003a; Heard et al., 2004; Harrison et al.,  
92 2006; Ren et al., 2006; Sommariva et al., 2007). The gas-phase ozonolysis of unsaturated  
93 VOCs, and in particular the role and subsequent chemistry of the Criegee intermediate, have  
94 been reviewed in detail by Johnson and Marston (2008), Donahue et al. (2011), Vereecken  
95 and Francisco (2012), and Taatjes et al. (2014).

96 Another key nighttime oxidant, NO<sub>3</sub>, is formed primarily by reaction of NO<sub>2</sub> with ozone.  
97 NO<sub>3</sub> reacts with a range of species in the troposphere, and its reaction with alkenes is known  
98 to be an important nighttime oxidation mechanism (Salisbury et al., 2001; Geyer et al., 2003;  
99 Sommariva et al., 2007; Emmerson and Carslaw, 2009; Brown et al., 2011). The reaction  
100 between NO<sub>3</sub> and an alkene proceeds primarily via addition to a double bond, to form a  
101 nitrooxyalkyl radical, R-ONO<sub>2</sub>. At atmospheric pressure, the main fate of the nitrooxyalkyl  
102 radical is reaction with O<sub>2</sub> (Berndt and Böge, 1994) to produce a nitrooxyalkyl peroxy  
103 radical, O<sub>2</sub>-R-ONO<sub>2</sub>. The nitrooxyalkyl peroxy radical can react with NO<sub>2</sub>, HO<sub>2</sub>, RO<sub>2</sub>, NO  
104 and NO<sub>3</sub>, of which the latter two reactions lead to formation of the nitrooxyalkoxy radical,  
105 O-R-ONO<sub>2</sub>. The nitrooxyalkoxy radical can undergo isomerisation, decomposition, or  
106 reaction with O<sub>2</sub>. Reaction with O<sub>2</sub>, analogous to the reaction of organic alkoxy radicals,  
107 yields HO<sub>2</sub>:



109 Thus, nighttime oxidation of hydrocarbons by NO<sub>3</sub> leads to production of HO<sub>2</sub>. Reaction of  
110 HO<sub>2</sub> with NO (Reaction (R7)), O<sub>3</sub> and NO<sub>3</sub> can generate OH:



113 Atkinson and Arey (2003) published a detailed review of tropospheric degradation of VOCs,  
114 including reaction with O<sub>3</sub> and NO<sub>3</sub>. A comprehensive review of nighttime radical chemistry  
115 is given by Brown and Stutz (2012).

116 The oxidising capacity of the nocturnal troposphere is thought to be controlled by the  
117 reactions described above, with a limited role for OH and HO<sub>2</sub> due to the absence of their  
118 photolytic sources. Oxidation of VOCs at night can have significant effects on daytime air  
119 quality and tropospheric ozone production (Brown et al., 2004; Brown et al., 2006; Wong and  
120 Stutz, 2010; Brown et al., 2011). Several field measurement campaigns have involved  
121 nighttime measurements of OH, HO<sub>2</sub>, RO<sub>2</sub>, and NO<sub>3</sub> (see Table 1), and have highlighted the

122 importance of the vertical profile of nighttime radical concentrations and chemistry (Geyer  
123 and Stutz, 2004a, b; Stutz et al., 2004; Volkamer et al., 2010), but prior to the current work  
124 there had been no aircraft-based studies of nighttime chemistry involving measurements of  
125 both  $\text{NO}_3$  and  $\text{HO}_2$ , to enable vertical profiling of the lower atmosphere and full evaluation of  
126 the nocturnal radical budget. Table 1 gives details of some previous measurements and  
127 modelling of nighttime  $\text{HO}_x$  concentrations in polluted or semi-polluted environments.  
128 Highlights from these studies are discussed here, with particular attention paid to those  
129 involving measurements of  $\text{HO}_x$ ,  $\text{NO}_3$ , and  $\text{O}_3$ , and in which the contributions made by  $\text{O}_3$   
130 and  $\text{NO}_3$  to nighttime radical chemistry have been considered.

131 Geyer et al. (2003) report radical measurements and modelling from the 1998 Berliner Ozone  
132 Experiment (BERLIOZ). Measurements of  $\text{NO}_3$ ,  $\text{RO}_2$ ,  $\text{HO}_2$  and  $\text{OH}$  were made by matrix  
133 isolation electron spin resonance (MIESR), chemical amplification (CA), and laser-induced  
134 fluorescence (LIF) spectroscopy at a site approximately 50 km from Berlin.  $\text{HO}_2$  was  
135 detected at night with concentrations frequently as high as  $5 \times 10^7$  molecule  $\text{cm}^{-3}$   
136 (approximately 2 pptv), and an average concentration of  $1 \times 10^8$  molecule  $\text{cm}^{-3}$  over one hour  
137 (02:00 to 03:00) of nocturnal measurements during an intensive period of the study (Holland  
138 et al., 2003).  $\text{OH}$  was usually below the limit of detection of the LIF instrument  
139 ( $3.5 \times 10^5$  molecule  $\text{cm}^{-3}$ ). Modelling revealed that nitrate radical reactions with terpenes  
140 were responsible for producing 53 % of  $\text{HO}_2$  and 36 % of  $\text{OH}$  radicals in the night, with  
141 ozonolysis accounting for production of the remaining 47 % of  $\text{HO}_2$  and 64 % of  $\text{OH}$   
142 radicals. A positive linear correlation between  $\text{RO}_2$  and  $\text{NO}_3$  was observed and was  
143 reproduced by the model.

144 Reactions of  $\text{O}_3$  with alkenes were found to be responsible for the majority of formation of  
145  $\text{OH}$  during the winter PUMA (Pollution of the Urban Midlands Atmosphere) campaign (a  
146 low photolysis urban environment) (Heard et al., 2004; Emmerson et al., 2005; Harrison et  
147 al., 2006). Measurements of  $\text{OH}$ ,  $\text{HO}_2$  and  $\text{RO}_2$  were unavailable at night, but model-  
148 predicted values of these radicals were used to calculate that 90 % of nighttime initiation via  
149  $\text{HO}_2$  was from  $\text{O}_3$  reactions. Without measurements of  $\text{NO}_3$  during the campaign, there was  
150 no estimate of its contribution to radical initiation.

151 Modelling results from the MCMA-2003 (Mexico City) field campaign (Volkamer et al.,  
152 2010) indicate that nighttime radical production at roof-top level (approximately 16 m above  
153 the ground) was dominated by ozonolysis of alkenes, and that reactions of  $\text{NO}_3$  with alkenes  
154 played only a minor role. The measurement site was located in a polluted urban environment,

155 with high levels of NO, NO<sub>2</sub> and O<sub>3</sub>. NO<sub>3</sub> was observed at a maximum concentration of 50  
156 pptv during the night at a mean height above the ground of 70 m. Roof-top level  
157 concentrations of NO<sub>3</sub> were estimated using a linear scaling factor calculated from the  
158 observed O<sub>3</sub> vertical gradient, and were found to be, on average, 3 times lower than the  
159 concentrations measured at 70 m. This predicted vertical gradient accounts for the relative  
160 unimportance of NO<sub>3</sub> reactions in radical initiation at roof-top level. Propagation of RO<sub>2</sub>  
161 radicals to HO<sub>2</sub> and OH, by reaction with NO<sub>3</sub>, was found to be negligible.

162 The 2006 Texas Air Quality Study (TexAQS) involved a series of nighttime flights onboard  
163 the NOAA P-3 aircraft over Houston, Texas, and along the Gulf Coast (Brown et al., 2011).  
164 Loss rates and budgets of NO<sub>3</sub> and highly reactive VOCs were calculated, but there were no  
165 measurements of OH, HO<sub>2</sub> and RO<sub>2</sub> during the flights. Budgets for NO<sub>3</sub> show that it was lost  
166 primarily through reactions with unsaturated VOCs, but the contribution to NO<sub>3</sub> loss through  
167 reaction with peroxy radicals was uncertain because of the lack of direct measurements of  
168 RO<sub>2</sub> during the flights. NO<sub>3</sub> dominated VOC oxidation, being 3 to 5 times more important  
169 than O<sub>3</sub>.

170 In summary, NO<sub>3</sub> and O<sub>3</sub> have both been found to dominate radical initiation in the nighttime  
171 troposphere, and in some situations the two mechanisms were found to be equally important.  
172 The relative importance of O<sub>3</sub>- and NO<sub>3</sub>-initiated oxidation depends on the availability of  
173 NO<sub>3</sub>, which is determined by the amount of NO<sub>x</sub> present in the atmosphere and the ratio of  
174 NO to NO<sub>2</sub>, and the concentration and species distribution of VOCs (Bey et al., 2001; Geyer  
175 et al., 2003). A modelling study by Bey et al. (2001) suggests that nocturnal radical initiation  
176 is driven by alkene ozonolysis in urban environments or in environments with low NO<sub>x</sub>  
177 concentrations, while both O<sub>3</sub> and NO<sub>3</sub> contribute to radical initiation in rural environments  
178 with moderate NO<sub>x</sub> levels. It is expected that NO<sub>3</sub> dominates nocturnal radical initiation in air  
179 masses containing sufficient NO<sub>2</sub> and O<sub>3</sub> for NO<sub>3</sub> production while being deprived of NO  
180 (e.g. air masses downwind of urban areas). Geyer and Stutz (2004b) have found that the  
181 effects of suppressed mixing in the nocturnal boundary layer can also control whether NO<sub>3</sub> or  
182 O<sub>3</sub> dominates nighttime radical chemistry.

183 In this paper we report airborne measurements of OH and HO<sub>2</sub> made during the RONOCO  
184 (ROle of Nighttime chemistry in controlling the Oxidising Capacity of the atmosphere) and  
185 SeptEx (September Experiment) projects in 2010 and 2011. The rates of reaction between O<sub>3</sub>,  
186 NO<sub>3</sub>, and OH with the alkenes measured during the flights are investigated. Analysis of  
187 radical production from the nighttime reactions of O<sub>3</sub> and NO<sub>3</sub> with alkenes is also given.

188 Comparisons are made between the daytime and nighttime chemistry studied, and between  
189 the summer and winter measurement periods. Details and results of a box modelling study,  
190 and comparison to the observations, are given by Stone et al. (2014b).

191

## 192 **2 Details of the RONOCO and SeptEx fieldwork**

193 RONOCO is a NERC-funded consortium project aimed at improving our understanding of  
194 the mechanisms and impact of nocturnal oxidation chemistry over the UK. The RONOCO  
195 fieldwork consisted of two measurement campaigns, in July 2010 and January 2011. An  
196 additional fieldwork period, SeptEx, was conducted in September 2010. The RONOCO and  
197 SeptEx flights were conducted onboard the BAe-146 research aircraft operated by the Facility  
198 for Airborne Atmospheric Measurements (FAAM). Both field measurement campaigns were  
199 based at East Midlands Airport (52.8° N, 1.3° W) in the UK. During RONOCO the majority  
200 of the flying took place at night, with occasional flights beginning or ending in daylight hours  
201 to study chemical behaviour at dusk and dawn. Flights during SeptEx were mainly during the  
202 day, providing a useful comparison to the nocturnal chemistry.

203 Flights were conducted between altitudes of 50 m and 6400 m, above the UK and the North  
204 Sea. Figure 1 shows the flight tracks during the summer, SeptEx, and winter measurements  
205 coloured by altitude. Measurements of OH and HO<sub>2</sub> were made using the University of Leeds  
206 aircraft-based Fluorescence Assay by Gas Expansion (FAGE) instrument. A suite of  
207 supporting measurements, including CO, O<sub>3</sub>, NO, H<sub>2</sub>O, VOCs, NO<sub>3</sub>, and HCHO, were made  
208 during the flights and have been used in the current work. Table 2 summarises the techniques  
209 used to measure these species.

210 Air mass histories for each flight have been calculated using the UK Met Office Numerical  
211 Atmospheric-dispersion Modelling Environment (NAME). NAME is a three-dimensional  
212 Lagrangian particle dispersion model (Jones et al., 2007) which is run here using the UK  
213 Meteorological Office's Unified Model meteorological fields. Model 'particles', restricted to  
214 a 300 m deep layer from the surface, were released along the flight path and were tracked  
215 backwards through the modelled atmosphere. Model particle densities were integrated over  
216 24 h periods, beginning at 24, 48, 72, and 96 hours before each flight. The resulting  
217 'footprint' maps show the regions where the measured air has been in contact with the  
218 surface over the 4 days preceding a flight. An example is shown in Fig. 2, which shows  
219 model particle densities integrated over the 24 hour period beginning 48 hours prior to flight

220 B535. The majority of the summer flights were characterised by air masses originating from  
221 the west and south west of the UK, having Atlantic or continental European influences. The  
222 SeptEx flights were predominantly influenced by air masses from the north-east, east, and  
223 south-east of the UK, with northern European influences. The winter flights were mainly  
224 characterised by air masses arriving from the west of the UK, bringing Atlantic influences.

225 Table 3 gives mean and maximum mixing ratios of CO, O<sub>3</sub>, NO, and NO<sub>2</sub> measured during  
226 RONOCO and SeptEx. The mean mixing ratios of NO measured during the summer  
227 RONOCO flights are much lower than ground-based nighttime measurements (e.g. 1.0 ppbv  
228 during TORCH (Emmerson and Carslaw, 2009), 0–20 ppbv during PMTACS-NY, (Ren et  
229 al., 2006)), but are comparable with previous airborne nighttime measurements (e.g.  
230 < 30 pptv during TexAQS (Brown et al., 2011)). Mean values of NO up to 14 pptv were  
231 reported by Salisbury et al. (2001) for semi-polluted air masses sampled at Mace Head. These  
232 comparisons indicate that the RONOCO and SeptEx flights enabled sampling of air masses  
233 generally removed from the influence of NO in fresh surface emissions. Table 3 also  
234 highlights the unusual chemical conditions encountered during flight B537 on 20<sup>th</sup> July 2010,  
235 discussed further in Sect. 4.1. Nighttime altitude profiles of NO<sub>3</sub>, O<sub>3</sub>, trans-2-butene, and  
236 propene (the latter two being illustrative of the alkenes measured) are given in Fig. 3.

Comment [HW2]: See Reviewers'  
Comments Sect 1.4

237

### 238 3 Experimental

#### 239 3.1 The Leeds FAGE aircraft instrument

240 The University of Leeds Aircraft FAGE instrument has been described in detail by Commane  
241 et al. (2010). A brief description is given here. The instrument, which was designed  
242 specifically for use onboard the FAAM BAe-146 research aircraft (Floquet, 2006), is housed  
243 in two double-width 19 inch aircraft racks, with the inlet, detection cells, and pump set being  
244 separate to the two racks. Ambient air is sampled through a 0.7 mm diameter ‘pinhole’ into a  
245 cylindrical inlet (length = 50 cm, diameter = 5 cm) which extends through a window blank on  
246 the starboard side of the aircraft.

247 Downstream of the inlet are two low pressure fluorescence cells positioned in series, the first  
248 for detection of OH and the second for detection of HO<sub>2</sub>. During the RONOCO and SeptEx  
249 flights the pressure inside the cells ranged from 1.9 Torr at ground level to 1.2 Torr at 6 km.

250 Laser light at  $\lambda \sim 308$  nm is generated by a diode-pumped Nd:YAG-pumped tunable  
251 Ti:Sapphire laser (Photonics Industries DS-532-10 and TU-UV-308nm) and delivered to the  
252 fluorescence cells via optical fibres, on an axis perpendicular to the gas flow. A small fraction  
253 of the Ti:Sapphire second harmonic ( $\lambda = 462$  nm) is directed to the probe of a wavemeter to  
254 enable measurement of the laser wavelength to within 0.001 nm. A UV photodiode is  
255 positioned opposite the laser input arm on each fluorescence cell to measure laser power.

256 The sampled air forms a supersonic gas expansion beam in which the rate of collision  
257 between OH radicals and ambient air molecules is reduced. The OH fluorescence lifetime is  
258 therefore extended to several hundred nanoseconds, significantly longer than the laser pulse,  
259 so that the measured signal can be temporally discriminated from laser scattered light. OH is  
260 excited from its ground state,  $X^2\Pi_i(v'' = 0)$ , to its first electronically excited state,  
261  $A^2\Sigma^+(v' = 0)$ , at  $\lambda \sim 308$  nm. The resulting on-resonance fluorescence is detected by a UV-  
262 sensitive channel photomultiplier tube on an axis perpendicular to both the gas flow and the  
263 laser light. HO<sub>2</sub> is detected by titration with an excess of NO (Reaction (R7)), the resulting  
264 OH being detected as described.

265 The FAGE instrument was calibrated prior to and following each field measurement period,  
266 using a well-established method (Edwards et al., 2003; Faloona et al., 2004; Commane et al.,  
267 2010). Light at  $\lambda = 184.9$  nm from a mercury pen-ray lamp photolyses water vapour in a flow  
268 of synthetic air inside an aluminium flow tube, generating OH and HO<sub>2</sub> at known  
269 concentrations. The aircraft FAGE instrument's limit of detection (LOD) for OH and HO<sub>2</sub> is  
270 determined by the instrument's sensitivity and the standard deviation of the background  
271 signal. During the RONOCO and SeptEx fieldwork the  $1\sigma$  LOD for a 5 minute averaging  
272 period ranged between  $0.64$  and  $1.8 \times 10^6$  molecule  $\text{cm}^{-3}$  for OH and between  $5.9$  and  
273  $6.9 \times 10^5$  molecule  $\text{cm}^{-3}$  for HO<sub>2</sub>.

### 274 **3.2 RO<sub>2</sub>-based interference in FAGE measurements of HO<sub>2</sub>**

275 It has recently been shown that reaction of alkene-derived  $\beta$ -hydroxyalkyl peroxy radicals,  
276 RO<sub>2</sub>, with NO inside the HO<sub>2</sub> detection cell, can lead to interference in FAGE HO<sub>2</sub>  
277 measurements (Fuchs et al., 2011; Whalley et al., 2013). The magnitude of the interference  
278 depends on the parent alkene, the residence time and mean temperature inside the cell, and  
279 the amount of NO injected. The interference therefore depends on the chemical environment  
280 and differs between FAGE instruments. In view of this, the University of Leeds ground-based

281 and aircraft FAGE instruments have been tested for RO<sub>2</sub> interference. A thorough description  
282 of the ground-based experimental method and results, and the results of a modelling study,  
283 are given by Whalley et al. (2013). The strongest interference in the aircraft instrument  
284 measurements was observed for ethene-derived RO<sub>2</sub>, amounting to an increase of 39.7 ± 4.8  
285 % in the observed HO<sub>2</sub> signal, with a cell pressure of 1.8 Torr, an estimated detection cell  
286 temperature of 255 K (obtained from rotational excitation spectra performed previously), and  
287 [NO]<sub>cell</sub> = 10<sup>14</sup> molecule cm<sup>-3</sup>.

288 ~~Whalley et al. (2013) show that the chemistry responsible for the observed interferences is~~  
289 ~~well known, and that a model using the Master Chemical Mechanism (MCM, version 3.2:~~  
290 ~~Jenkin et al., 1997; Saunders et al., 2003; Bloss et al., 2005, via~~  
291 ~~http://mcm.leeds.ac.uk/MCM) can reproduce the interferences once tuned to the conversion~~  
292 ~~efficiency of HO<sub>2</sub> to OH in the FAGE detection cell. Accordingly,~~ Stone et al. (2014b) have  
293 applied the results of the ethene-derived RO<sub>2</sub> interference testing in a modelling study to  
294 assess the effect of the interference on the HO<sub>2</sub> measurements made during the RONOCO  
295 and SeptEx campaigns. A box model using a detailed ~~MCMaster Chemical Mechanism~~  
296 scheme was used to calculate a total potential interference in the RONOCO HO<sub>2</sub>  
297 measurements. The model was constrained to the conditions in the detection cell (1.8 Torr,  
298 255 K, [NO] ~ 10<sup>14</sup> molecule cm<sup>-3</sup>). Equal concentrations of HO<sub>2</sub> and ∑RO<sub>2</sub> (sum of all  
299 peroxy radicals in the MCM generated from the parent hydrocarbon) were used to initialise  
300 the model. The model ~~run time was varied until the model was predicted interference from~~  
301 ~~ethene-derived RO<sub>2</sub> radicals was equal to the experimentally determined interference, thereby~~  
302 ~~tuning the model to the conversion efficiency of HO<sub>2</sub> to OH, run until the modelled~~  
303 ~~interference (i.e. concentration of OH produced) from ethene derived RO<sub>2</sub> radicals matched~~  
304 ~~the interference measured in the interference experiments described above (~40%).~~ An  
305 interference factor, *f*, was calculated for each RO<sub>2</sub> in the MCM as follows:

$$306 \quad f = \frac{[\text{OH}]_{\text{HO}_2+\text{RO}_2} - [\text{OH}]_{\text{HO}_2}}{[\text{OH}]_{\text{HO}_2}} \quad (1)$$

307 where [OH]<sub>HO<sub>2</sub>+RO<sub>2</sub></sub> and [OH]<sub>HO<sub>2</sub></sub> are the modelled concentrations of OH produced from the  
308 reactions of RO<sub>2</sub> and HO<sub>2</sub>, and the concentration from HO<sub>2</sub> alone, respectively. The greatest  
309 interference was calculated to come from isoprene-derived peroxy radicals, followed by  
310 aromatic compounds and C<sub>2</sub> to C<sub>5</sub> alkenes. The smallest modelled interference is from the C<sub>1</sub>  
311 to C<sub>3</sub> alkanes. ~~The interference factors were applied to model-predicted RO<sub>2</sub> speciation and~~

Comment [HW3]: See Reviewers'  
Comments Sect. 1.2

Comment [HW4]: See Reviewers'  
Comments Sect 1.2, Sect. 2.2, and Sect 2.3

Comment [HW5]: See Reviewers'  
Comments Sect 1.2

312 concentrations for the RONOCO flights. Model-predicted RO<sub>2</sub> species were dominated by  
313 CH<sub>3</sub>O<sub>2</sub> (33 %; *f* = 1.1 %) and HO<sub>2</sub> (24 %; *f* = 0.0 %), with smaller contributions from RO<sub>2</sub>  
314 derived from *iso*-butene (12 %; *f* = 0.5 %), *cis*-2-butene and *trans*-2-butene (10 %; *f* = 0.05  
315 %), and isoprene (2 %; *f* = 7.6 %). RO<sub>2</sub> species with high interference factors were a minor  
316 component of the total RO<sub>2</sub>. A modelled value of HO<sub>2</sub> including the total potential  
317 interference, [HO<sub>2</sub>]\*, was calculated using:

318 
$$[\text{HO}_2^*] = [\text{HO}_2]_{\text{mod}} + f[\text{RO}_2]_{\text{mod}} \quad (2)$$

**Comment [HW6]:** Changed equation: “\*” inside square brackets and not superscript

319 Direct comparison between modelled values of [HO<sub>2</sub>]\* and the FAGE-measured values of  
320 [HO<sub>2</sub>] was therefore made possible. The model-predicted interference during the RONOCO  
321 campaign ~~is can be~~ described by [HO<sub>2</sub>]\* = 1.15[HO<sub>2</sub>] + 2 × 10<sup>5</sup> molecule cm<sup>-3</sup>. The average  
322 model-predicted interference in the HO<sub>2</sub> measurements is 14 %. The HO<sub>2</sub> measurements  
323 made during RONOCO and SeptEx were not adjusted since speciated RO<sub>2</sub> measurements  
324 were not available. The measurements are hereafter referred to as HO<sub>2</sub>\*.

**Comment [HW7]:** See Reviewers' Comments Sect. 2.4

**Comment [HW8]:** See Reviewers' Comments Sect. 1.1

325 The magnitude of the RO<sub>2</sub> interference can be reduced by reducing the concentration of NO  
326 in the detection cell. This also reduces the instrument sensitivity to HO<sub>2</sub>. Since conversion of  
327 RO<sub>2</sub> to OH requires at least two NO molecules, while conversion of HO<sub>2</sub> requires only one  
328 molecule, the ratio of HO<sub>2</sub> signal to RO<sub>2</sub> signal can be made favourable by reducing [NO]  
329 (Whalley et al., 2013). This effect has been investigated for the ground-based instrument, and  
330 will be investigated for the aircraft instrument prior to future HO<sub>x</sub> measurement campaigns.  
331 An overview of the laboratory and computational studies of the interference in different  
332 FAGE instruments is given in a recent review by Stone et al. (2012).

### 333 **3.3 BBCEAS measurements of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>**

334 NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> were measured by the University of Cambridge broadband cavity enhanced  
335 absorption spectroscopy (BBCEAS) instrument. The instrument was designed and built  
336 specifically for the RONOCO project and is described in detail in Kennedy et al. (2011). A  
337 brief description is given here.

338 The instrument consists of three 94 cm long high finesse optical cavities formed by pairs of  
339 highly reflecting mirrors. The cavities are irradiated by incoherent broadband continuous  
340 wave light sources. Two of the cavities, for the detection of N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub>, are irradiated by  
341 red light emitting diodes (LEDs) centred at 660 nm. The third cavity, for the detection of  
342 NO<sub>2</sub>, is irradiated by a blue LED centred at 460 nm. The light from the LEDs is collimated

343 using optical fibres and a focussing lens at the input of each cavity. A spectrometer,  
344 consisting of a spectrograph and charge couple device (CCD), is positioned at the end of each  
345 cavity to measure the wavelength-dependent intensity of transmitted light.

346 Ambient air is sampled through a rear-facing inlet on the aircraft fuselage, positioned  
347 approximately 4 m from the aircraft nose and 10 cm from the aircraft body. The air from the  
348 inlet is divided into two flows. The flow directed to the  $N_2O_5$  cavity is heated to 120 °C to  
349 ensure near complete (> 99.6 %) thermal dissociation of  $N_2O_5$  to  $NO_2$  and  $NO_3$ . The cavity  
350 itself is heated to 80 °C and is used to measure the sum of the concentrations of ambient  $NO_3$   
351 plus  $NO_3$  from thermal decomposition of  $N_2O_5$ . The second flow is unheated and is directed  
352 first through the  $NO_3$  cavity and then through the  $NO_2$  cavity. Background spectra are  
353 recorded at half hour intervals during flights by halting the flow of ambient air and purging  
354 the cavities with nitrogen.

355  $NO_3$  is detected by its strong  $B^2E' - X^2A_2'$  electronic transition centred at 662 nm. The  
356 concentration of  $NO_3$  is determined by separating the finely structured  $NO_3$  absorption  
357 features from the broad features caused by Rayleigh and Mie scattering using a fitting  
358 technique analogous to that employed in differential optical absorption spectroscopy  
359 (DOAS). A strong water vapour absorption feature that spectrally overlaps with  $NO_3$   
360 absorption around 662 nm is simulated for the pressure and temperature measured in the  
361 cavity and is removed from the measured absorption spectrum. The concentration of  $N_2O_5$  is  
362 determined by subtracting the concentration of ambient  $NO_3$  measured in the unheated cavity  
363 from the sum of the concentrations of ambient and dissociated  $NO_3$  measured in the heated  
364 cavity.

365 Contributions to uncertainties in ambient measurements of  $NO_3$  and  $N_2O_5$ , including wall  
366 losses of  $NO_3$  and  $N_2O_5$ , temperature- and pressure-dependent absorption cross sections of  
367  $NO_3$  and  $H_2O$ , and the length of the cavity occupied by the sample, have been thoroughly  
368 investigated in laboratory experiments or addressed in the data analysis routine. In addition,  
369 wall losses of  $NO_3$  and  $N_2O_5$  were determined before and after each flight to account for  
370 changes in the surface properties of the inlet and detection cell walls, which were found to be  
371 negligible. The total uncertainty in the measured concentration of ambient  $NO_3$  was 11 %.  
372 The uncertainty in the measured concentration of ambient  $N_2O_5$  is determined for each  
373 individual ambient measurement, being dependent on the  $NO_3/N_2O_5$  ratio, and was on the

Comment [HW9]: See Reviewers'  
Comments Sect 2.5

374 order of 15 %. During RONOCO flights the  $1\sigma$  limits of detection for  $\text{NO}_3$  and the sum of  
375  $\text{NO}_3 + \text{N}_2\text{O}_5$  were 1.1 pptv and 2.4 pptv, respectively, for a 1 second integration time.

376

#### 377 **4 Overview of OH and HO<sub>2</sub>\* measurements**

378 FAGE measurements were made on 16 flights during RONOCO and 9 flights during SeptEx.

379 There was insufficient laser power during flights B534 to B536 in the summer campaign to  
380 measure both OH and HO<sub>2</sub>\* by dividing the laser light between the two cells. OH was  
381 therefore not measured during these flights. Low laser power throughout the summer  
382 fieldwork caused relatively high fluctuations in laser power and therefore higher background  
383 variability. This resulted in higher limits of detection for OH ( $1.8 \times 10^6$  molecule  $\text{cm}^{-3}$ ) and  
384 HO<sub>2</sub>\* ( $6.9 \times 10^5$  molecule  $\text{cm}^{-3}$ ).

385 Table 4 summarises the OH and HO<sub>2</sub>\* measurements during RONOCO and SeptEx and gives  
386 the instrument's average  $1\sigma$  limit of detection for ~~a 5one~~ minute ~~averaging period of data~~. OH  
387 was not detected above the limit of detection during the summer or winter RONOCO flights,  
388 resulting in upper limits of  $1.8 \times 10^6$  molecule  $\text{cm}^{-3}$  and  $6.4 \times 10^5$  molecule  $\text{cm}^{-3}$  for mean  
389 summer and winter concentrations, respectively. These upper limit values are similar to  
390 previously reported nighttime OH measurements (Geyer et al., 2003; Holland et al., 2003;  
391 Ren et al., 2003b; Emmerson and Carslaw, 2009). The mean daytime OH concentration  
392 during SeptEx was  $1.8 \times 10^6$  molecule  $\text{cm}^{-3}$ , which was above the limit of detection. The  
393 mean HO<sub>2</sub>\* mixing ratio was highest during SeptEx (2.9 pptv), and was higher during  
394 summer (1.6 pptv) than during winter (0.7 pptv). The OH and HO<sub>2</sub>\* datasets for RONOCO  
395 and SeptEx are shown as altitude profiles in Fig. 43 and Fig. 54, respectively.

396 Table 5 gives the mean and maximum HO<sub>2</sub>\* mixing ratios at different times of day during  
397 summer, SeptEx and winter. Dawn, day, dusk and night are defined by the solar zenith angle  
398 as follows: dawn and dusk are between  $90$  and  $102^\circ$  and are distinguished by the time of day;  
399 day is between  $0^\circ$  and  $90^\circ$ ; night is between  $102^\circ$  and  $180^\circ$ .

400 The mean dusk HO<sub>2</sub>\* mixing ratio in summer was higher than the mean nighttime mixing  
401 ratio, suggesting that photochemical production was still active at dusk in summer. The  
402 reverse was true for the winter data, with the highest mean HO<sub>2</sub>\* mixing ratio being at night.  
403 This suggests that when photochemical production was suppressed in the winter daytime due  
404 to low photolysis rates, production via reactions of  $\text{NO}_3$  and  $\text{O}_3$  with alkenes was an  
405 important route to radical initiation. The RONOCO HO<sub>2</sub>\* measurements are similar to

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Comments Sect 1.3

406 nighttime, ground-based, urban measurements. For example, during the TORCH campaign,  
407 [HO<sub>2</sub>] peaked at  $1 \times 10^8$  molecule cm<sup>-3</sup> at night (Emmerson et al., 2007), and during the  
408 PMTACS-NY 2001 field campaign, nighttime HO<sub>2</sub> concentrations of  $8 \times 10^6$  molecule cm<sup>-3</sup>  
409 were measured (Ren et al., 2003b).

#### 410 **4.1 Case study flight B537: high nighttime HO<sub>2</sub>\* concentrations**

411 The highest HO<sub>2</sub>\* concentration ( $3.2 \times 10^7$  molecule cm<sup>-3</sup>; 13.7 pptv) was measured during  
412 nighttime flight B537 on 20<sup>th</sup> July 2010. Take-off from East Midlands Airport was at 22:00  
413 local time (21:00 UTC, sunset at 20:18 UTC). The flight track, coloured by altitude, is shown  
414 in Fig. 65. The flight involved a profile descent from 3350 m to 460 m down the Norfolk  
415 coast and a missed approach at Southend Airport (51.6° N, 0.70° E). Plumes from European  
416 continental outflow (see Fig. 76) were intersected by a series of runs at altitudes between 460  
417 m and the upper boundary of the polluted layer.

418 Flight B537 is an unusual flight within the RONOCO dataset, with high concentrations of  
419 CO, O<sub>3</sub>, NO<sub>3</sub>, and high temperatures compared to the values measured during other nighttime  
420 flights (see Table 3). The ambient aerosol surface area was significantly higher during B537  
421 (nearly 800 μm<sup>2</sup> cm<sup>-3</sup>) than during other flights (between 100 and 400 μm<sup>2</sup> cm<sup>-3</sup>), and the  
422 organic aerosol concentration was significantly enhanced (Morgan et al., 2014). Footprint  
423 maps for flight B537, indicating regions where the sampled air was in contact with the  
424 surface prior to the flight, are shown in Fig. 67. The air sampled during the flight originated  
425 primarily over northern France, Belgium and Germany.

426 A region of high surface pressure was positioned over the UK on the 20<sup>th</sup> July, with a mean  
427 air pressure of 1012.6 hPa over the 24 hours prior to the flight. The mean air temperature 24  
428 hours prior to the flight (22:00 19/07/2010 to 22:00 20/07/2010), measured at a number of  
429 Met Office weather stations in Greater London, was 22.6 °C, and reached a maximum value  
430 of 28.6 °C. Wind speeds prior to the flight were low, with an average value of 4.7 knots  
431 (2.4 m s<sup>-1</sup>). No rainfall was recorded at any of the Greater London weather stations during the  
432 24 hours prior to the flight. 12.4 hours of sunshine were recorded on the 20<sup>th</sup> July at  
433 Heathrow Airport (51.5 °N, 0.45 °W). High temperatures, combined with low wind speed,  
434 exposure to solar radiation, and little precipitation promote the formation of ozone as a result  
435 of photochemical processing of VOCs emitted at the surface (e.g. Lee et al., 2006), and offer  
436 an explanation for the high ozone mixing ratios measured during flight B537. Peak surface  
437 daytime ozone concentrations measured in Teddington, London, on 20<sup>th</sup> July were on the

438 order of  $2.0 \times 10^{12}$  molecule  $\text{cm}^{-3}$  (~78 ppbv) (data available at [www.airquality.co.uk](http://www.airquality.co.uk)).  
439 Similar levels were recorded at a number of locations within Greater London.

440 ~~Figure 8~~Figure 7 shows a time series of altitude,  $\text{HO}_2^*$ ,  $\text{O}_3$ , and  $\text{NO}_3$  mixing ratios during the  
441 flight, demonstrating very similar behaviour between the two radical species. During the  
442 missed approach at Southend Airport the mixing ratios of  $\text{HO}_2^*$  and  $\text{NO}_3$  increased with  
443 decreasing altitude, to reach values of 4.5 pptv and 35 pptv, respectively, at 50 m above the  
444 ground. The maximum  $\text{HO}_2^*$  and  $\text{NO}_3$  mixing ratios were measured over the North Sea east  
445 of Ipswich ( $52.16^\circ \text{N}$ ,  $2.34^\circ \text{E}$ ) at an altitude of 509 m, in the outflow of the London plume.

446 ~~Figure 9~~Figure 8 shows scatter plots of  $\text{HO}_2^*$  against  $\text{NO}_3$  and  $\text{O}_3$  during flight B537 and  
447 during the other nighttime flights during RONOCO. Strong positive correlation is evident  
448 between  $\text{HO}_2^*$  and  $\text{NO}_3$  during B537 ( $r = 0.97$ ), while during the remaining night flights  
449 there is still a significant, though weaker, correlation ( $r = 0.58$ ). Moderate negative  
450 correlation is evident between  $\text{HO}_2^*$  and  $\text{O}_3$  during B537 ( $r = -0.46$ ), with weak positive  
451 correlation existing for the other nighttime flights ( $r = 0.19$ ). The data suggest that  $\text{NO}_3$  was  
452 an important initiator of  $\text{HO}_x$  radicals during flight B537, and that  $\text{O}_3$  played a limited role  
453 overall during the nighttime flights. Further investigation of the roles of  $\text{NO}_3$  and  $\text{O}_3$  in alkene  
454 oxidation and radical initiation at night is described in Sect. 5.

455

## 456 5 Oxidation of alkenes and production of $\text{HO}_2$ : method of analysis

457 Following the work of Salisbury et al. (2001), the total rates of reaction,  $\Phi$ , of  $\text{O}_3$  and  $\text{NO}_3$   
458 with the alkenes measured during RONOCO and SeptEx have been calculated:

$$459 \quad \Phi_{\text{O}_3} = \sum_i^{\text{alkene}} k_{\text{O}_3+\text{alk}_i} [\text{O}_3][\text{alkene}_i] \quad (3)$$

$$460 \quad \Phi_{\text{NO}_3} = \sum_i^{\text{alkene}} k_{\text{NO}_3+\text{alk}_i} [\text{NO}_3][\text{alkene}_i] \quad (4)$$

461 The reactions of  $\text{O}_3$  and  $\text{NO}_3$  with alkenes yield OH,  $\text{HO}_2$ , and  $\text{RO}_2$  radicals. Consideration of  
462 the reaction mechanisms of  $\text{NO}_3$  and  $\text{O}_3$  enables calculation of the rate of instantaneous  
463 production of  $\text{HO}_2$  ( $P_{\text{HO}_2}$ ) from the reactions of  $\text{NO}_3$  and  $\text{O}_3$  with the alkenes measured  
464 during RONOCO, using the chemistry scheme, rate constants and branching ratios in the  
465 MCM (Jenkin et al., 1997; Saunders et al., 2003).

466 ~~Figure 10~~Figure 9 shows a generalized reaction scheme for the reaction of NO<sub>3</sub> with an  
 467 alkene. The reaction between NO<sub>3</sub> and an alkene proceeds via addition of NO<sub>3</sub> to the double  
 468 bond to form a nitrooxyalkyl radical, followed by rapid reaction with oxygen to yield a  
 469 nitrooxyalkyl peroxy radical, RO<sub>2</sub> (shown as a single step in Fig. 109). The RO<sub>2</sub> radical can  
 470 react with a number of species, of which NO, NO<sub>3</sub> and RO<sub>2</sub> lead to production of an alkoxy  
 471 radical (RO). Radical termination occurs via reaction of RO<sub>2</sub> with HO<sub>2</sub> to yield a peroxide  
 472 (ROOH) or with RO<sub>2</sub> to yield carbonyl (RC(O)CH<sub>3</sub>) and alcohol (RCH<sub>2</sub>OH) products.  
 473 Reaction of RO with oxygen proceeds via abstraction of a hydrogen atom to yield HO<sub>2</sub> or an  
 474 aldehyde (RCHO). This generalised scheme can be applied to the reactions of NO<sub>3</sub> with all  
 475 the alkenes measured. The rate of instantaneous production of HO<sub>2</sub> is found by first  
 476 calculating the fraction of RO<sub>2</sub> that reacts to produce RO ( $F_{RO}$ ), and the fraction of RO that  
 477 reacts to produce HO<sub>2</sub> ( $F_{HO_2}$ ):

$$478 \quad F_{RO} = \frac{k_3[NO] + k_4[NO_3] + 0.6k_5[RO_2]}{k_2[HO_2] + k_3[NO] + k_4[NO_3] + k_5[RO_2]} \quad (5)$$

$$479 \quad F_{HO_2} = \frac{k_6[O_2]}{k_7 + k_6[O_2]} \quad (6)$$

480 where RO<sub>2</sub> represents all peroxy radicals. Average values of  $F_{RO}$  for the NO<sub>3</sub> + alkene  
 481 reactions range between 0.50 for *trans*-2-pentene- and 1-pentene-derived RO<sub>2</sub> species and  
 482 0.61 for ethene-derived RO<sub>2</sub> species.  $F_{HO_2}$  varies between 0 and 1 for the alkenes studied.

483 Overall, the rate of production of HO<sub>2</sub> ( $P_{HO_2}$ ) from reactions of NO<sub>3</sub> with alkenes is then  
 484 given by:

$$485 \quad P_{HO_2} = k_i[NO_3][\text{alkene}_i] \times F_{RO} \times F_{HO_2} \quad (7)$$

486 The reaction scheme for the reaction of O<sub>3</sub> with alkenes is more complicated because the  
 487 number and type of radicals produced in the O<sub>3</sub> + alkene reaction depends on the structure of  
 488 the alkene. The simplest case is the reaction of ozone with ethene. Ozone adds to the double  
 489 bond to form a five-membered ring called a primary ozonide. Decomposition of the ozonide  
 490 yields an excited Criegee intermediate (CH<sub>2</sub>OO\*) and a carbonyl compound (in this case  
 491 formaldehyde, HCHO). The energy-rich Criegee intermediate can be stabilised by collision  
 492 with a third body or undergo decomposition to yield products including OH, CO, and HO<sub>2</sub>.  
 493 The primary ozonide produced in the O<sub>3</sub> + propene reaction (see Fig. 110) can decompose via  
 494 two channels, yielding carbonyls and Criegee intermediates with different structures and

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Comments Sect 2.6

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495 different products, including RO<sub>2</sub>. Reaction of RO<sub>2</sub> with NO, NO<sub>3</sub> and RO<sub>2</sub> (all peroxy  
496 radicals) yields RO, which in turn yields HO<sub>2</sub>.

497 The rates of production of HO<sub>2</sub> from reactions of O<sub>3</sub> with alkenes ( $P_{\text{HO}_2}$ ) have been  
498 calculated as follows:

$$499 \quad P_{\text{HO}_2, \text{Direct}} = k_i [\text{O}_3] [\text{alkene}_i] \times \alpha_{\text{HO}_2} \quad (8)$$

$$500 \quad P_{\text{HO}_2, \text{RO}_2} = k_i [\text{O}_3] [\text{alkene}_i] \times \alpha_{\text{RO}_2} \times F_{\text{RO}} \times F_{\text{HO}_2} \quad (9)$$

$$501 \quad P_{\text{HO}_2} = P_{\text{HO}_2, \text{Direct}} + P_{\text{HO}_2, \text{RO}_2} \quad (10)$$

502 where  $P_{\text{HO}_2, \text{Direct}}$  is the rate of direct HO<sub>2</sub> production from Criegee intermediate  
503 decomposition,  $\alpha_{\text{HO}_2}$  is the branching ratio to HO<sub>2</sub>-producing channels from the Criegee  
504 intermediate,  $P_{\text{HO}_2, \text{RO}_2}$  is the rate of HO<sub>2</sub> production from RO<sub>2</sub> radicals produced in the O<sub>3</sub> +  
505 alkene reaction,  $\alpha_{\text{RO}_2}$  is the branching ratio to RO<sub>2</sub>-producing channels from the Criegee  
506 intermediate,  $F_{\text{RO}}$  is the fraction of RO<sub>2</sub> radicals that react to produce RO radicals, and  $F_{\text{HO}_2}$   
507 is the fraction of RO radicals that react to produce HO<sub>2</sub> radicals, which is equal to 1 for all the  
508 alkenes studied. Average values of  $F_{\text{RO}}$  for the O<sub>3</sub> + alkene reactions range between 0.54 for  
509 1-pentene-derived RO<sub>2</sub> species and 0.64 for 1-butene- and *trans*-2-pentene-derived RO<sub>2</sub>  
510 species.

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Comments Sect. 2.6

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511 The reactions of RO<sub>2</sub> with NO to form RONO<sub>2</sub> have been omitted from the calculations  
512 because the branching ratio is small (0.001 to 0.02) for the radicals studied (Carter and  
513 Atkinson, 1989; Lightfoot et al., 1992). The reaction of CH<sub>3</sub>O<sub>2</sub> with NO<sub>2</sub> to form CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub>  
514 has been omitted from the calculations, since the reverse reaction is much faster than the  
515 forward direction ( $k_f = 6.4 \times 10^{-12} \text{ s}^{-1}$ ;  $k_{\text{rev}} = 1.08 \text{ s}^{-1}$  at a mean temperature of 286.5 K during  
516 RONOCO).

517 The primary aims of the analysis presented here are threefold: 1. To calculate the total rate of  
518 initiation through reactions of NO<sub>3</sub> and O<sub>3</sub> with alkenes; 2. To determine the relative  
519 importance of NO<sub>3</sub> and O<sub>3</sub> in nighttime HO<sub>2</sub> production; 3. To investigate differences in  
520 radical production between different seasons and different times of day. The correlation  
521 between [HO<sub>2</sub>\*] and [NO<sub>3</sub>], especially during flight B537, will be investigated.

522  $P_{\text{HO}_2}$  has been calculated for each alkene measured for every 60-second data point where all  
523 the requisite data were available and where HO<sub>2</sub>\* was above the limit of detection of the

524 FAGE instrument. Concentrations of RO<sub>2</sub> were calculated by scaling the observed HO<sub>2</sub>\*  
525 concentrations with the RO<sub>2</sub>/HO<sub>2</sub>\* ratio calculated using a box model constrained to the  
526 concentrations of long-lived species measured during the flights (Stone et al., 2014b), i.e.  
527  $RO_{2,obs} = HO_{2,*obs} \times RO_{2,mod}/HO_{2,*mod}$ . The rates of reaction and rates of production of HO<sub>2</sub>  
528 presented hereafter are average values for individual flights, seasons, or times of day.

Comment [HW13]: See Reviewers'  
Comments Sect. 1.4

## 530 6 Results

### 531 6.1 Nighttime oxidation of alkenes

532 ~~Figure 12~~Figure 11 shows histograms of the rate of reaction between O<sub>3</sub> and NO<sub>3</sub> with  
533 individual alkenes during summer and winter, for the nighttime data only. The reactivity of  
534 measured alkenes ( $\Phi_{O_3} + \Phi_{NO_3}$ ) was greater during summer flights than during winter flights  
535 by a factor of 2.2. The reactions of NO<sub>3</sub> are largely responsible for this seasonal difference,  
536 since the contribution from O<sub>3</sub> + alkene reactions varies little between summer  
537 ( $4.1 \times 10^4$  molecule cm<sup>-3</sup> s<sup>-1</sup>) and winter ( $3.9 \times 10^4$  molecule cm<sup>-3</sup> s<sup>-1</sup>). The factor of 4.1  
538 difference between the rate of NO<sub>3</sub> reactions in summer ( $9.8 \times 10^4$  molecule cm<sup>-3</sup> s<sup>-1</sup>) and  
539 winter ( $2.4 \times 10^4$  molecule cm<sup>-3</sup> s<sup>-1</sup>) can be attributed to the higher mean concentration of  
540 NO<sub>3</sub> in summer ( $5.8 \times 10^8$  molecule cm<sup>-3</sup>) compared to winter ( $2.0 \times 10^8$  molecule cm<sup>-3</sup>).

541 This seasonal difference in NO<sub>3</sub> concentrations ~~is attributable to~~ ~~may have been the result of~~  
542 ~~the lower mean nighttime temperature in winter (277.7 K) compared to summer (286.7 K)~~  
543 ~~which disfavors NO<sub>3</sub> in~~ ~~the its~~ thermal equilibrium ~~with~~  $N_2O_5 \rightleftharpoons NO_3 + NO_2$ .  $K_{eq}[NO_2]$ ,  
544 ~~which determines  $[N_2O_5]/[NO_3]$ , is calculated to be 4.8 in summer and 29.6 in winter.~~ At

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Comments Sect. 2.7

545 night in summer,  $\Phi_{NO_3}$  was greater than  $\Phi_{O_3}$  by a factor of 2.4, but in winter  $\Phi_{O_3}$  was a factor  
546 of 1.6 greater than  $\Phi_{NO_3}$ . ~~Figure 12~~Figure 11 illustrates the importance of the butene isomers  
547 (within the VOCs measured) in the reactions of O<sub>3</sub> and NO<sub>3</sub>, and therefore radical initiation  
548 and propagation. Reactions with *iso*-butene dominated NO<sub>3</sub> reactivity in summer (42 %) and  
549 winter (53 %), with *trans*-2-butene also contributing significantly (28 % in summer and 32 %  
550 in winter). Reactions of O<sub>3</sub> were dominated by *trans*-2-butene (42 % in summer and 34 % in  
551 winter) and propene (26 % in summer and 38 % in winter). The importance of these alkenes  
552 is attributed to their relatively high abundances compared to the other alkenes measured,  
553 during both summer and winter, combined with their fast rates of reaction with O<sub>3</sub> and NO<sub>3</sub>.

Comment [HW15]: See Reviewers'  
Comments Sect. 2.7

554 For comparison with the reactions of O<sub>3</sub> and NO<sub>3</sub>, the total rate of reaction of measured  
555 alkenes with OH has been calculated using upper limits on OH concentrations of  $1.8 \times 10^6$

556 molecule  $\text{cm}^{-3}$  and  $6.4 \times 10^5$  molecule  $\text{cm}^{-3}$  for the summer and winter flights, respectively,  
557 based on the FAGE instrument's limit of detection. The high upper limits make the total rate  
558 of reaction of OH with alkenes,  $\Phi_{\text{OH}}$ , unrealistically high for both summer ( $1.6 \times 10^5$   
559 molecule  $\text{cm}^{-3} \text{ s}^{-1}$ ) and winter ( $7.8 \times 10^4$  molecule  $\text{cm}^{-3} \text{ s}^{-1}$ ). However, the OH reactivity will  
560 likely be considerably lower than the values calculated using the OH upper limits. A box  
561 model constrained to concentrations of long-lived species measured during the flights (Stone  
562 et al., 2014b) predicts a mean OH concentration of  $2.4 \times 10^4$  molecule  $\text{cm}^{-3}$ , significantly  
563 lower than the upper limits given by the instrument's limit of detection. Using the mean  
564 modelled value for OH gives  $\Phi_{\text{OH}} = 2.1 \times 10^3$  molecule  $\text{cm}^{-3} \text{ s}^{-1}$  for summer, and  $\Phi_{\text{OH}} =$   
565  $2.9 \times 10^3$  molecule  $\text{cm}^{-3} \text{ s}^{-1}$  for winter, indicating a diminished role for OH in alkene  
566 oxidation at night in agreement with previous studies (e.g. Geyer et al., 2003; Emmerson et  
567 al., 2005).

## 568 6.2 Daytime oxidation of alkenes

569 [Figure 13](#) ~~Figure 12~~ shows histograms of rates of reaction of  $\text{O}_3$  and OH with alkenes during  
570 SeptEx, and  $\text{O}_3$  and  $\text{NO}_3$  with alkenes during winter RONOCO flights, for daytime data only.  
571 OH was detected above the limit of detection ( $1.2 \times 10^6$  molecule  $\text{cm}^{-3}$ ) during the SeptEx  
572 flights, so the FAGE OH data were included in the calculations, using a reaction scheme  
573 analogous to the one shown in Fig. [109](#).  $\text{NO}_3$  was not detected during the day in SeptEx.  $\text{NO}_3$   
574 is not expected to be present at measurable concentrations during daylight hours due to  
575 photolysis, but a mean concentration of  $8.3 \times 10^7$  molecule  $\text{cm}^{-3}$  (3.3 pptv) was measured  
576 during the day in the winter RONOCO flights. These measurements of low mixing ratios of  
577  $\text{NO}_3$  may be partly caused by interference from other daytime species as observed by Brown  
578 et al. (2005), or by the variability of the instrument baseline, which can be on the order of 1–2  
579 pptv during vertical profiles on the aircraft (Kennedy et al., 2011). This variability is small  
580 compared to the range of  $\text{NO}_3$  values typically observed during RONOCO flights (0–50 pptv  
581 during summer; 0–10 pptv during winter). During SeptEx,  $\Phi_{\text{OH}}$  exceeded  $\Phi_{\text{O}_3}$  by a factor of  
582 8. Ethene and propene were the two most abundant alkenes measured during SeptEx and  
583 contributed significantly to OH reactivity.  $\text{O}_3$  reactivity with alkenes was dominated by  
584 propene and *trans*-2-butene (6<sup>th</sup> most abundant alkene measured during SeptEx).  $\text{NO}_3$   
585 reactivity with alkenes was dominated by *trans*-2-butene and isobutene (3<sup>rd</sup> most abundant  
586 alkene measured during winter daytime flights). The total rate of reaction of  $\text{O}_3$  and OH with  
587 alkenes during daytime SeptEx flights ( $3.7 \times 10^5$  molecule  $\text{cm}^{-3} \text{ s}^{-1}$ ) exceeded the total rate of

588 reaction of O<sub>3</sub> and NO<sub>3</sub> during daytime winter RONOCO flights ( $6.6 \times 10^4$  molecule cm<sup>-3</sup>  
589 s<sup>-1</sup>) by a factor of 6, and was more than double the total rate of reaction of O<sub>3</sub> and NO<sub>3</sub> with  
590 alkenes during nighttime summer flights ( $1.4 \times 10^5$  molecule cm<sup>-3</sup> s<sup>-1</sup>). In winter daytime  
591 flights,  $\Phi_{O_3}$  was greater than  $\Phi_{NO_3}$  by a factor of 2.4.

592 ~~Figure 11b~~ and Fig. 132b reveal that reactions of O<sub>3</sub> dominated alkene reactivity  
593 during both daytime and nighttime winter RONOCO flights. The concentrations of alkenes  
594 were generally higher at night, with the total alkene concentration (sum of concentrations of  
595 alkenes measured) being  $2.1 \times 10^9$  molecule cm<sup>-3</sup> in the day, and  $3.4 \times 10^9$  molecule cm<sup>-3</sup> at  
596 night. The total measured alkene reactivity ( $\Phi_{O_3} + \Phi_{NO_3}$ ) was marginally higher during the  
597 day, by a factor of 1.04. This difference is attributable mainly to the change in  $\Phi_{O_3}$ .

598 Comparison of Fig. 124a and Fig. 132b reveals that the total measured alkene reactivity  
599 ( $\Phi_{O_3} + \Phi_{NO_3}$ ) was higher during the summer nighttime flights ( $1.4 \times 10^5$  molecule cm<sup>-3</sup> s<sup>-1</sup>)  
600 than during the winter daytime flights ( $6.6 \times 10^4$  molecule cm<sup>-3</sup> s<sup>-1</sup>), indicating a low  
601 oxidising environment during winter daytime. The additional contribution to measured alkene  
602 reactivity from reactions with OH has been calculated using the OH upper limits as described  
603 in Sect. 6.1. Even with this additional, upper limit OH reactivity ( $1.6 \times 10^5$  molecule cm<sup>-3</sup> s<sup>-1</sup>  
604 and  $1.1 \times 10^5$  molecule cm<sup>-3</sup> s<sup>-1</sup> for summer nighttime and winter daytime, respectively) the  
605 total summer nighttime alkene reactivity remains higher than that during winter daytime,  
606 confirming the importance of the summer nocturnal troposphere for the oxidation of the  
607 measured alkenes.

### 608 **6.3 Nighttime production of HO<sub>2</sub> from reactions of O<sub>3</sub> and NO<sub>3</sub> with alkenes**

609 Table 6 gives total rates ( $\Sigma P_{HO_2}$ ) of instantaneous production of HO<sub>2</sub> from the reactions of O<sub>3</sub>  
610 and NO<sub>3</sub> with alkenes. NO<sub>3</sub> was not detected during the dawn summer RONOCO flights and  
611 there were no daytime RONOCO flights during summer. NO<sub>3</sub> dominated HO<sub>2</sub> production  
612 during dusk and night (68 %), in agreement with Geyer et al. (2003) who found that NO<sub>3</sub> was  
613 responsible for 53 % of HO<sub>2</sub> production at night in the BERLIOZ campaign. During winter,  
614 O<sub>3</sub> dominated HO<sub>2</sub> production at all times, with a nighttime contribution of 70 %. This is in  
615 agreement with the results from the winter PMTACS-NY 2004 field campaign (Ren et al.,  
616 2006).

617 The total rate of instantaneous production of HO<sub>2</sub> at night was 3.3 times greater in summer  
618 than in winter, with production from O<sub>3</sub> decreasing by a factor of 1.5, and production from  
619 NO<sub>3</sub> decreasing by a factor of 7.8, between summer and winter. The mean temperature

620 difference between summer and winter of 9 K is thought to be responsible for the lower NO<sub>3</sub>  
621 concentrations in winter ( $2.0 \times 10^8$  molecule cm<sup>-3</sup>, 8.2 pptv, compared to  $5.8 \times 10^8$  molecule  
622 cm<sup>-3</sup>, 24.5 pptv in summer), owing to the increased thermal stability of N<sub>2</sub>O<sub>5</sub>, and for the  
623 reduced rate of temperature-dependent reactions between NO<sub>3</sub> and alkenes, and subsequent  
624 reactions. There was very little difference between summer and winter mean O<sub>3</sub> mixing  
625 concentrations ( $9.6 \times 10^{11}$  molecule cm<sup>-3</sup>, 39.6 ppbv, and  $9.4 \times 10^{11}$  molecule cm<sup>-3</sup>, 38.6  
626 ppbv, respectively).

627 Production of HO<sub>2</sub> via reactions of NO<sub>3</sub> and O<sub>3</sub> with alkenes is now examined in more detail.  
628 The rate of production from individual alkenes was calculated, and plotted in a histogram, as  
629 shown in Fig. 143 for the summer and winter nighttime data. During both summer and  
630 winter, reactions of O<sub>3</sub> and NO<sub>3</sub> with *trans*-2-butene were important sources of HO<sub>2</sub>,  
631 contributing on average 62 % to O<sub>3</sub>-initiated HO<sub>2</sub> production and 36 % to NO<sub>3</sub>-initiated  
632 production during the summer and winter flights. Reactions of NO<sub>3</sub> with isoprene were  
633 important during summer, contributing 28 % to NO<sub>3</sub>-initiated production. The importance of  
634 *trans*-2-butene, despite its relatively low abundance during summer and winter nighttime  
635 RONOCO flights (1.8 pptv and 1.7 pptv, respectively, compared to ethene mixing ratios of  
636 55.0 and 104.5 pptv), is attributed to its fast rates of reaction with both O<sub>3</sub> and NO<sub>3</sub> compared  
637 to the other alkenes measured. The importance of the isoprene + NO<sub>3</sub> reactions during the  
638 summer RONOCO flights is similarly attributed to its fast rate of reaction with NO<sub>3</sub>  
639 compared to the other alkenes measured. In addition there is no aldehyde-forming channel  
640 from the isoprene-derived RO radical ( $k_7$  in Fig. 109), so that the yield of HO<sub>2</sub> from RO is  
641 equal to 1. The reaction of isobutene with NO<sub>3</sub> can proceed via one of two channels to  
642 produce two different RO<sub>2</sub> radicals but only one channel, with a branching ratio of 0.2,  
643 produces HO<sub>2</sub>. Isobutene is therefore not a dominant contributor to HO<sub>2</sub> production, despite  
644 being the single largest contributor to NO<sub>3</sub> reactivity during daytime and nighttime RONOCO  
645 flights (Fig. 124 and Fig. 132). ~~Figure 14~~Figure-13 highlights the small change in total  
646 production from O<sub>3</sub> between summer and winter, and the dramatic change in total production  
647 from NO<sub>3</sub> between summer and winter.

648 Reactions of formaldehyde with NO<sub>3</sub> were included in the analysis where formaldehyde data  
649 were available (mean HCHO = 955 pptv). The NO<sub>3</sub> + HCHO reaction contributed a further  
650  $5.5 \times 10^3$  molecule cm<sup>-3</sup> s<sup>-1</sup> (15 %) to HO<sub>2</sub> production from NO<sub>3</sub> reactions, so that production  
651 from NO<sub>3</sub> contributed 79 % of the total production.

## 652 6.4 Production of HO<sub>2</sub> during flight B537

653 Flight B537, on 20<sup>th</sup> July 2010, has been identified as an interesting flight, with high  
654 concentrations of HO<sub>2</sub>\* (3.2 × 10<sup>8</sup> molecule cm<sup>-3</sup>; 13.6 pptv), ozone (peaking at  
655 1.8 × 10<sup>12</sup> molecule cm<sup>-3</sup>, 89.9 ppbv) and NO<sub>3</sub> (peaking at 4.1 × 10<sup>9</sup> molecule cm<sup>-3</sup>;  
656 176.9 pptv), and a strong positive correlation between HO<sub>2</sub>\* and NO<sub>3</sub> ( $r = 0.97$ , see Fig. 98).  
657 NO, NO<sub>2</sub>, and aerosol surface area were also elevated during the flight during flight B537  
658 compared to their mean summer values. The highest concentration of ethene (1.43 × 10<sup>10</sup>  
659 molecule cm<sup>-3</sup>; 0.61 ppbv) during the summer RONOCO flights was measured during B537.  
660  $\Sigma P_{\text{HO}_2}$  from O<sub>3</sub> + alkene reactions (2.6 × 10<sup>4</sup> molecule cm<sup>-3</sup> s<sup>-1</sup>) was higher in flight B537  
661 than in all the other summer flights, contributing 42 % of HO<sub>2</sub> production, with NO<sub>3</sub> + alkene  
662 reactions contributing 3.6 × 10<sup>4</sup> molecule cm<sup>-3</sup> (58 %). The total rate of HO<sub>2</sub> production from  
663 O<sub>3</sub> and NO<sub>3</sub> reactions during flight B537 was 6.2 × 10<sup>4</sup> molecule cm<sup>-3</sup> s<sup>-1</sup>. While this is  
664 higher than the average value of  $\Sigma P_{\text{HO}_2}$  for the summer flights (5.4 × 10<sup>4</sup> molecule cm<sup>-3</sup> s<sup>-1</sup>) it  
665 is not the highest rate of production during the summer flights. During B534 unusually high  
666 concentrations of isoprene, *cis*-2-butene, and 1,3-butadiene contributed to a total rate of HO<sub>2</sub>  
667 production of 7.9 × 10<sup>4</sup> molecule cm<sup>-3</sup>, which is the highest calculated value.

668 [Figure 15](#)~~Figure 14~~ shows that the reactions of O<sub>3</sub> and NO<sub>3</sub> with *trans*-2-butene are once  
669 again important, contributing 74 % of  $\Sigma P_{\text{HO}_2, \text{O}_3}$ , and 45 % of  $\Sigma P_{\text{HO}_2, \text{NO}_3}$ . The correlation  
670 between HO<sub>2</sub>\* and NO<sub>3</sub> is attributed to production of HO<sub>2</sub> by reactions of NO<sub>3</sub> with alkenes,  
671 especially *trans*-2-butene. Figure 165 shows HO<sub>2</sub>\* versus the total instantaneous rate of  
672 production from the reactions of O<sub>3</sub> and NO<sub>3</sub> with alkenes during flight B537, at each 60-  
673 second data point during the flight for which the requisite data were available. Note that the  
674 rates plotted in Fig. 165 are higher than those shown in Fig. 154, where the rates of  
675 production of HO<sub>2</sub> from each alkene have been averaged across the whole flight. A strong  
676 positive correlation exists between HO<sub>2</sub>\* and both  $\Sigma P_{\text{HO}_2, \text{O}_3}$  ( $r = 0.6$ ) and  $\Sigma P_{\text{HO}_2, \text{NO}_3}$  ( $r = 0.8$ ),  
677 indicating the importance of these reactions for production of HO<sub>2</sub> during this flight.

678

## 679 7 Comparison with model results

680 The observations of OH, HO<sub>2</sub>\*, NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> have been interpreted in the context of  
681 nighttime oxidation chemistry using a box model constrained to observations of VOCs, NO<sub>x</sub>,  
682 O<sub>3</sub>, CO and other long-lived species measured during the RONOCO flights (Stone et al.,  
683 2014b). The Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC)

684 (Emmerson and Evans, 2009; Stone et al., 2010; Stone et al., 2014b) was initiated with  
685 concentrations of measured species, using a chemistry scheme based on the Master Chemical  
686 Mechanism (MCM, version 3.2: Jenkin et al., 1997; Jenkin et al., 2003; Saunders et al., 2003;  
687 Bloss et al., 2005, via <http://mcm.leeds.ac.uk/MCM>) and was allowed to run to diurnal steady  
688 state. The model output includes concentrations of OH, HO<sub>2</sub>, NO<sub>3</sub>, RO<sub>2</sub>, and other species.  
689 Data from daytime flights, or during dawn or dusk periods, were not included in the model  
690 analysis. Data from flight B537 were also excluded, owing to the atypical observations of  
691 HO<sub>2</sub><sup>\*</sup>, NO<sub>3</sub>, O<sub>3</sub> and other chemical species made during this flight. The modelling study and  
692 results are described in more detail by Stone et al. (2014b).

693 The model predicts a mean OH concentration of  $2.4 \times 10^4$  molecule cm<sup>-3</sup> for the summer  
694 flights, which is consistent with the measured OH concentrations for which the instrument's  
695 limit of detection is an upper limit only. The base model underpredicts HO<sub>2</sub><sup>\*</sup> by around  
696 200 %, and overpredicts NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> by 80 and 50 %, respectively. These discrepancies  
697 were investigated by determining the processes controlling radical production and loss in the  
698 model, and using those results to improve model performance. Model production of HO<sub>2</sub> is  
699 dominated by reactions of RO + O<sub>2</sub> (42 %), with a significant contribution from OH + CO  
700 (31 %) despite low OH concentrations at night. RO<sub>x</sub> (= RO + RO<sub>2</sub> + OH + HO<sub>2</sub>) radical  
701 initiation in the model is dominated by reactions of NO<sub>3</sub> with unsaturated VOCs (80 %), with  
702 a much smaller contribution (18 %) from alkene ozonolysis. Modelled HO<sub>2</sub> loss is dominated  
703 by its reactions with NO<sub>3</sub> (45 %) and O<sub>3</sub> (27 %), both of which are radical propagating routes,  
704 and which are the dominant routes to OH production in the model. In fact NO<sub>3</sub> was found to  
705 control both radical initiation and propagation in the model.

706 These results are in general agreement with the results of the analysis presented in Sect. 6.1,  
707 though the model predicts a more important role for NO<sub>3</sub> (80 % of RO<sub>x</sub> radical production,  
708 which is 7.2 times the contribution from O<sub>3</sub> + alkenes) than is predicted by the analysis based  
709 on the observations alone (69 % of HO<sub>2</sub> radical production during summer, which is 2.1  
710 times the contribution from O<sub>3</sub> + alkenes). ~~The model, and~~ predicts a relatively small role for  
711 O<sub>3</sub> ~~in in both summer and winter radical initiation (18 % of RO<sub>x</sub> radical production compared~~  
712 ~~to a minimum value of 31 % calculated using the observations)~~. The model is constrained to  
713 measured values of O<sub>3</sub>, but overpredicts NO<sub>3</sub>. The mean measured NO<sub>3</sub> nighttime mixing  
714 ratio was 24.5 pptv in the summer and 8.2 pptv in the winter. The mean modelled summer  
715 and winter values are 37.4 pptv and 20.7 pptv, respectively. This discrepancy between  
716 modelled and measured NO<sub>3</sub> helps to explain the model overprediction of the role of NO<sub>3</sub> in

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717 HO<sub>x</sub> radical initiation during the RONOCO flights. Modelled NO<sub>3</sub> reactivity was dominated  
718 by *iso*-butene (36 %) and *trans*-2-butene (27 %), and modelled O<sub>3</sub> reactivity was dominated  
719 by *trans*-2-butene (51 %), in agreement with the nighttime alkene reactivities presented in  
720 Sect. 6.1.

721 Improvement to the model predictions of NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> and HO<sub>2</sub>\* was made by increasing the  
722 concentration of unsaturated VOCs in the model. Increasing the total observed alkene  
723 concentration by 4 times resulted in a modelled to observed ratio of 1.0 for HO<sub>2</sub>\* and of ~1.2  
724 for NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. Two-dimensional gas chromatography (GC × GC) analysis of the whole  
725 air samples taken during RONOCO has revealed a large number of VOCs extra to those  
726 routinely measured (Lidster et al., 2014). Calibration standards for the majority of these  
727 species are not yet available, and so quantification of their concentrations is not possible, but  
728 their detection confirms that the model overprediction of NO<sub>3</sub> and underprediction of HO<sub>2</sub>\*  
729 are attributable to reactions of NO<sub>3</sub> with unquantified unsaturated hydrocarbons.

730 The presence of unquantified unsaturated VOCs during the RONOCO campaign, suggested  
731 by the model and confirmed by the two-dimensional GC analysis, has implications for the  
732 conclusions drawn from the analysis based on the observations. The relative contributions of  
733 NO<sub>3</sub> and O<sub>3</sub> to nighttime radical initiation will change with the composition of unsaturated  
734 VOCs in the sampled air, due to the different rates of reaction of NO<sub>3</sub> and O<sub>3</sub> with different  
735 VOC species, and the rates of production of HO<sub>2</sub> following these reactions. The model results  
736 indicate that reaction of NO<sub>3</sub> with the unquantified VOCs leads to increased production of  
737 HO<sub>2</sub>. The role of NO<sub>3</sub> in nighttime radical production would therefore be enhanced by the  
738 inclusion of the unquantified VOCs in the observational analysis.

739

## 740 **8 Conclusions and future work**

741 Nighttime radical chemistry has been studied as part of the RONOCO and SeptEx campaigns  
742 onboard the BAe-146 research aircraft during summer 2010 and winter 2011. NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, OH  
743 and HO<sub>2</sub>\* were measured simultaneously for the first time from an aircraft, with OH and  
744 HO<sub>2</sub>\* being measured by the University of Leeds aircraft FAGE instrument. OH was detected  
745 above the limit of detection during the daytime SeptEx flights only, with a mean  
746 concentration of  $1.8 \times 10^6$  molecule cm<sup>-3</sup>. Upper limits of  $1.8 \times 10^6$  molecule cm<sup>-3</sup> and  
747  $6.4 \times 10^5$  molecule cm<sup>-3</sup> are placed on mean OH concentrations for the summer and winter  
748 RONOCO (night, dawn, and dusk) measurement campaigns, respectively. HO<sub>2</sub>\* was detected

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749 above the limit of detection during the summer and winter RONOCO flights and during  
750 SeptEx, with a maximum mixing ratio of 13.6 pptv measured during nighttime flight B537 on  
751 20<sup>th</sup> July 2010. Mean nighttime HO<sub>2</sub>\* mixing ratios were significantly higher in summer than  
752 in winter. Significant concentrations (up to 176.9 pptv) of NO<sub>3</sub> were measured during  
753 nighttime flights, since the air masses sampled were sufficiently removed from the surface  
754 that the loss of NO<sub>3</sub> by reaction with NO was minimised. The RONOCO flights were  
755 therefore an excellent opportunity to study the role of NO<sub>3</sub> in nocturnal oxidation and radical  
756 initiation.

757 The rates of reaction of O<sub>3</sub> and NO<sub>3</sub> with the alkenes measured have been calculated. At night  
758 during summer, NO<sub>3</sub> dominated alkene reactivity. Several previous nighttime studies have  
759 also found NO<sub>3</sub> to be the dominant nocturnal oxidant (e.g. Geyer et al., 2003; Brown et al.,  
760 2011). During nighttime winter RONOCO flights the total rate of reaction of NO<sub>3</sub> with  
761 alkenes was much reduced, but the rate of reaction of O<sub>3</sub> with alkenes was similar to that in  
762 summer. During day and night in winter, O<sub>3</sub> + alkene reactions were faster than NO<sub>3</sub> + alkene  
763 reactions. Overall, during RONOCO, the combined rate of alkene oxidation by O<sub>3</sub> and NO<sub>3</sub>  
764 was highest at night during summer.

765 Calculation of rates of instantaneous production of HO<sub>2</sub> from reactions of O<sub>3</sub> and NO<sub>3</sub> with  
766 alkenes, using measurements made during the flights, has revealed that nighttime production  
767 was dominated by NO<sub>3</sub> in summer and by O<sub>3</sub> in winter. The rate of instantaneous production  
768 of HO<sub>2</sub> from reactions of NO<sub>3</sub> with alkenes decreased significantly from summer to winter  
769 (87 %), whereas production from O<sub>3</sub> + alkene reactions was similar in summer and winter,  
770 decreasing by just 31 %. Strong positive correlation between HO<sub>2</sub>\* and NO<sub>3</sub>, especially  
771 during flight B537, is attributed to the production of HO<sub>2</sub> from reactions of NO<sub>3</sub> with alkenes,  
772 particularly *trans*-2-butene and other isomers of butene.

773 Significant concentrations of HO<sub>2</sub>\* were detected at night, with the highest HO<sub>2</sub>\*  
774 concentration (13.6 pptv) being measured during a summer nighttime flight, indicating that  
775 HO<sub>x</sub> radical chemistry remains active at night under the right conditions. The role of HO<sub>x</sub> is  
776 diminished in the low photolysis winter daytime atmosphere, with alkene ozonolysis being  
777 primarily responsible for oxidation and radical initiation, in agreement with previous studies  
778 (e.g. Heard et al., 2004; Emmerson et al., 2005). Both the analysis presented here and the  
779 results of the box modelling study by Stone et al. (2014b) indicate that in air masses removed  
780 from sources of NO, NO<sub>3</sub> plays an important role in the oxidation of alkenes and radical  
781 initiation at night, in agreement with previous studies (e.g. Brown et al., 2011). Alkene

782 ozonolysis also plays a significant role in nocturnal oxidation in agreement with Salisbury et  
783 al. (2001), Geyer et al. (2003), [Ren et al. \(2003a\)](#), [Emmerson et al. \(2005\)](#), [Ren et al. \(2006\)](#),  
784 [and Volkamer et al. \(2010\)](#) and others. The balance between the roles of NO<sub>3</sub> and O<sub>3</sub> was  
785 controlled in part by [NO<sub>3</sub>], with colder winter temperatures forcing the NO<sub>3</sub>-N<sub>2</sub>O<sub>5</sub>  
786 equilibrium towards N<sub>2</sub>O<sub>5</sub>.

787 The total rate of reaction of O<sub>3</sub> and NO<sub>3</sub> with alkenes during nighttime summer flights ( $1.4 \times$   
788  $10^5$  molecule cm<sup>-3</sup> s<sup>-1</sup>) was higher than during daytime winter flights ( $6.6 \times 10^4$  molecule  
789 cm<sup>-3</sup> s<sup>-1</sup>) by a factor of 2.1. Whilst it should be remembered that measurements at different  
790 times of day and in different seasons reflect composition changes in air masses (such as the  
791 abundance of reactive alkenes) this result supports the hypothesis that oxidation of certain  
792 VOCs, in particular the reactive alkenes, in the nocturnal summer atmosphere can be as rapid  
793 as in the winter daytime atmosphere.

794 A box model of nighttime chemistry constrained to measurements of long lived species has  
795 been used to investigate the nighttime chemistry sampled during RONOCO (Stone et al.,  
796 2014b). The base model underpredicts HO<sub>2</sub>\* and overpredicts NO<sub>3</sub>. These discrepancies were  
797 minimised by increasing the concentration of alkenes in the model, thereby increasing  
798 reaction of NO<sub>3</sub> with alkenes, and production of HO<sub>2</sub>. The presence of unquantified  
799 unsaturated VOCs has been confirmed by 2D-GC analysis, though the exact nature and  
800 concentrations of the 'missing' species is unclear. The inclusion of these species in the  
801 analysis presented in this paper would likely increase the role of NO<sub>3</sub> for oxidation of alkenes  
802 and production of HO<sub>2</sub> at night.

803

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811

**Comment [HW17]:** See Reviewers'  
Comments Sect. 2.10

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347 Wong, K. W., and Stutz, J.: Influence of nocturnal vertical stability on daytime chemistry: A  
348 one-dimensional model study, *Atmospheric Environment*, 44, 3753-3760, 2010.

1 Table 1. Examples of modelling studies and observations of HO<sub>x</sub> radicals and VOC oxidation at night. PERCA = Peroxy Radical Chemical  
 2 Amplification; LIF = Laser Induced Fluorescence; DOAS = Differential Optical Absorption Spectroscopy; MCM = Master Chemical Mechanism;  
 3 MIESR = Matrix Isolation Electron Spin Resonance; RACM = Regional Atmospheric Chemistry Mechanism; CRDS = Cavity Ring Down  
 4 Spectroscopy; CIMS = Chemical Ionisation Mass Spectrometry; GC = Gas Chromatography; PTRMS = Proton Transfer Reaction Mass Spectrometry;  
 5 FTIR = Fourier Transform Infrared Spectroscopy; DUALER (DUAL channel peroxy radical chemical amplifier); OA-CRD = Off Axis Cavity Ring  
 6 Down Spectroscopy; CRM-PTR-MS = Comparative Reactivity Method Proton Transfer Mass Spectrometry.

Location, Campaign, Date	Methods	Results	Reference
Mace Head, Ireland, EASE97, 1997	Measurements: [HO <sub>2</sub> +RO <sub>2</sub> ] measured by PERCA; HO <sub>x</sub> measured by LIF; NO <sub>3</sub> measured by DOAS). Modelling: Campaign-tailored box model constrained to measurements, based on MCM.	2 nights of HO <sub>x</sub> measurements: HO <sub>2</sub> = 1–2 and 0.5–0.7 pptv; OH not detected above limit of detection ( $\sim 2.5 \times 10^5 \text{ cm}^{-3}$ ). NO <sub>3</sub> dominated radical production in westerly (clean) air masses; O <sub>3</sub> dominated in NE, SE, and SW air masses and dominated radical production overall during the campaign.	Salisbury et al. (2001); Creasey et al. (2002)
Pabstthum, Germany, BERLIOZ 1998,	Measurements: HO <sub>x</sub> measured by LIF; NO <sub>3</sub> measured by DOAS and MIESR. Modelling: Zero-dimensional model using lumped VOC reactivity, constrained to measured species.	Nighttime OH = $1.85 \times 10^5 \text{ cm}^{-3}$ , compared to modelled value of $4.1 \times 10^5 \text{ cm}^{-3}$ . Nighttime HO <sub>2</sub> = $3 \times 10^7 \text{ cm}^{-3}$ , model results in agreement. NO <sub>3</sub> chemistry responsible for 53 % of HO <sub>2</sub> and 36 % of OH during the night. O <sub>3</sub> + alkene responsible for 47 % of HO <sub>2</sub> and 64 % of OH during the night.	Geyer et al. (2003); Holland et al. (2003)
Birmingham, PUMA, 1999 and 2000	Measurements: HO <sub>x</sub> measured by LIF. Modelling: Photochemical box model constrained to measurements, based on MCM.	Daytime OH initiation dominated by O <sub>3</sub> + alkenes, HONO photolysis, and O( <sup>1</sup> D) + H <sub>2</sub> O during summer. O <sub>3</sub> + alkenes dominated in winter. O <sub>3</sub> + alkenes main radical source at night.	Emmerson et al. (2005); Harrison et al. (2006)
New York, PMTACS-NY, 2001	Measurements: HO <sub>x</sub> measured by LIF.	Nighttime OH $\sim 7 \times 10^5 \text{ cm}^{-3}$ and nighttime HO <sub>2</sub> $\sim 8 \times 10^6 \text{ cm}^{-3}$ . Increase in HO <sub>x</sub> after midnight attributed to increase in O <sub>3</sub> due to transport. O <sub>3</sub> + alkenes main source of nighttime HO <sub>x</sub> .	Ren et al. (2003a); Ren et al. (2003b)

Mace Head, NAMBLEX, 2002	Measurements: HO <sub>x</sub> measured by LIF; NO <sub>3</sub> measured by DOAS. Modelling: Zero-dimensional box models constrained to measured species, based on MCM.	Nighttime HO <sub>2</sub> = 2–3 × 10 <sup>7</sup> cm <sup>-3</sup> ; OH below detection limit (6 × 10 <sup>4</sup> cm <sup>-3</sup> ). Model overestimated HO <sub>2</sub> . On average, O <sub>3</sub> + alkene reactions contributed 59 % and NO <sub>3</sub> + alkene reactions contributed 41 % to RO <sub>2</sub> production at night, but NO <sub>3</sub> and RO <sub>2</sub> concentrations were always higher in semi-polluted air masses than in clean marine air masses and NO <sub>3</sub> reactions dominated in these conditions.	Fleming et al. (2006); Smith et al. (2006); Sommariva et al. (2007)
Writtle, London, TORCH, 2003	Measurements: HO <sub>x</sub> measured by LIF, RO <sub>2</sub> measured by PERCA, during a heatwave/pollution episode. Modelling: zero-dimensional box model constrained to measured species.	OH and HO <sub>2</sub> observed above the limit of detection on several nights. OH peaked at 8.5 × 10 <sup>5</sup> cm <sup>-3</sup> ; HO <sub>2</sub> peaked at 1 × 10 <sup>8</sup> cm <sup>-3</sup> . Model overpredicted nighttime OH and HO <sub>2</sub> on average by 24 % and 7 %; underpredicted [HO <sub>2</sub> +ΣRO <sub>2</sub> ] by 22 %.	Lee et al. (2006); Emmerson et al. (2007); Emmerson and Carslaw (2009)
Mexico City, MCMA 2003	Measurements: HO <sub>x</sub> measured by LIF, NO <sub>3</sub> measured by DOAS. Modelling: Zero-dimensional model based on MCM v3.1, constrained to measured species.	Polluted city location characterized by high levels of NO, NO <sub>2</sub> and O <sub>3</sub> . Maximum nighttime OH ~ 1 × 10 <sup>6</sup> cm <sup>-3</sup> ; maximum nighttime HO <sub>2</sub> ~ 6 pptv. Nighttime production of radicals dominated by O <sub>3</sub> + alkene reactions (76–92 %); NO <sub>3</sub> + alkene plays a minor role. Daytime radical production ~ 25 times higher than night.	Shirley et al. (2006); Sheehy et al. (2010); Volkamer et al. (2010)
New York City, PMTACS-NY winter 2004	Measurements: HO <sub>x</sub> measured by LIF. Modelling: Zero-dimensional model based on RACM and constrained by measurements.	Mean maximum OH = 0.05 pptv; mean maximum HO <sub>2</sub> = 0.7 pptv. Model under-prediction of HO <sub>2</sub> was pronounced when NO was high. O <sub>3</sub> + alkene reactions were dominant nighttime source.	Ren et al. (2006)
Gulf of Maine, Northeast United States, NEAQS, 2004	Measurements: NO <sub>3</sub> and N <sub>2</sub> O <sub>5</sub> measured by CRDS. Modelling: Zero-dimensional model based on MCM v3.1, constrained to measured species. No measurements of OH, HO <sub>2</sub> , or RO <sub>2</sub> .	Ship-based measurements onboard <i>RV Ronald H. Brown</i> in the Gulf of Maine, influenced by unpolluted marine air masses and polluted air masses from USA and Canada. Maximum modelled nighttime HO <sub>2</sub> = 7.0 × 10 <sup>8</sup> cm <sup>-3</sup> . Base model overestimated NO <sub>3</sub> and NO <sub>2</sub> observations by 30–50 %. In anthropogenic air masses reaction with VOCs and RO <sub>2</sub> each accounted for 40 % of modelled NO <sub>3</sub> loss.	Sommariva et al. (2009)
Houston, Texas, TexAQS, 2006	Measurements: NO <sub>3</sub> and N <sub>2</sub> O <sub>5</sub> measured by CRDS, VOCs measured by CIMS, GC, and PTRMS. No direct measurements of OH, HO <sub>2</sub> ,	Loss rates and budgets of NO <sub>3</sub> and highly reactive VOCs calculated. NO <sub>3</sub> primarily lost through reaction with VOCs. VOC oxidation dominated by NO <sub>3</sub> , which was 3–5 times more important than O <sub>3</sub> .	Brown et al. (2011)

or RO<sub>2</sub>.

Pearl River Delta, China, PRIDE-PRD, 2006	Measurements: HO <sub>x</sub> measured by LIF; OH reactivity measured by laser-flash photolysis and LIF; VOCs measured by FTIR and GC. Modelling: Box model based on RACM and the Mainz Isoprene Mechanism, and constrained by measurements.	Rural site 60 km downwind of large urban region (Guangzhou), with low local wind speeds favouring accumulation of air pollutants. Maximum nighttime OH (hourly average) = $5 \times 10^6 \text{ cm}^{-3}$ ; maximum nighttime HO <sub>2</sub> (hourly average) = $1 \times 10^9 \text{ cm}^{-3}$ . Unknown recycling mechanism required for the model to reproduce measured nighttime values. OH reactivity peaked at night. Missing nighttime reactivity attributed to unmeasured secondary organic compounds.	Lou et al. (2010); Lu et al. (2012); Lu et al. (2013)
Beijing, CAREBEIJIN G2006, 2006	Measurements: HO <sub>x</sub> measured by LIF; OH lifetime measured by laser flash photolysis and LIF; VOCs measured by GC. Modelling: Box model based on RACM and the Mainz Isoprene Mechanism, and constrained by measurements.	Suburban rural site south of Beijing, under the influence of slowly moving, aged polluted air from the south. OH reactivity peaked at night. Model generally underestimated observed nighttime OH concentrations.	Lu et al. (2013); Lu et al. (2014)
Cape Verde, RHaMBLE, 2007	Measurements: HO <sub>x</sub> measured by LIF. Modelling: Box model based on MCM with added halogen chemistry scheme, constrained to measurements of long-lived species.	Clean tropical Atlantic measurement site with occasional continental influence. OH was not measured at night. HO <sub>2</sub> was detected on two nights, up to $2.5 \times 10^7 \text{ cm}^{-3}$ . Model underprediction of HO <sub>2</sub> was significantly reduced by constraining the model to 100 pptv of peroxy acetyl nitrate (PAN) at night.	Whalley et al. (2010)
Huelva, Spain, DOMINO, 2008	Measurements: [HO <sub>2</sub> +RO <sub>2</sub> ] measured by DUALER; HO <sub>x</sub> measured by LIF; NO <sub>3</sub> and N <sub>2</sub> O <sub>5</sub> measured by OA-CRD; OH reactivity measured by CRM-PTR-MS. No measurements of anthropogenic VOCs.	Coastal forested site with strong urban-industrial and weak biogenic influences. Maxima in [HO <sub>2</sub> +RO <sub>2</sub> ] and [HO <sub>2</sub> ] were observed around noon and midnight. Enhanced nighttime [HO <sub>2</sub> +RO <sub>2</sub> ] (up to 80 pptv) was observed in air masses from the urban-industrial region. Maximum nighttime HO <sub>2</sub> = 8 pptv. Measured NO <sub>3</sub> was generally below LOD; calculated NO <sub>3</sub> up to 20 pptv. Calculated production of RO <sub>2</sub> from NO <sub>3</sub> +alkenes accounts for 47–54 % of observed [HO <sub>2</sub> +RO <sub>2</sub> ]. Ozonolysis of unmeasured alkenes could account for remaining [HO <sub>2</sub> +RO <sub>2</sub> ].	Andrés-Hernández et al. (2009)

7 Table 2. Details of supporting measurements.

Species	Instrument, Technique	Time resolution; Limit of detection (LOD)	References
CO	Aero Laser AL5002 Fast Carbon Monoxide Monitor. Excitation and fast response fluorescence at $\lambda = 150$ nm.	1 s; 3.5 ppbv	Gerbig et al. (1999)
O <sub>3</sub>	Thermo Scientific TEi49C Ozone analyser. Absorption spectroscopy at $\lambda = 254$ nm.	1 s; 0.6 ppbv	Hewitt et al. (2010)
NO, NO <sub>2</sub> , NO <sub>x</sub> (NO + NO <sub>2</sub> )	Air Quality Design dual channel fast-response NO <sub>x</sub> instrument. Chemiluminescence from NO + O <sub>3</sub> reaction. Conversion of NO <sub>2</sub> to NO by photolysis.	10 s; 3 pptv for NO, 15 pptv for NO <sub>2</sub>	Stewart et al. (2008)
NO <sub>2</sub> , $\Sigma$ ANs, $\Sigma$ PNs	TD-LIF (thermal dissociation laser induced fluorescence). Detection of NO <sub>2</sub> by laser-induced fluorescence. Thermal decomposition of $\Sigma$ ANs (total alkyl nitrate) and $\Sigma$ PNs (total peroxy nitrate) to NO <sub>2</sub> .	1 s; 9.8 pptv for NO <sub>2</sub> , 28.1 pptv for $\Sigma$ ANs, 18.4 pptv for $\Sigma$ PNs	Dari-Salisburgo et al. (2009); Di Carlo et al. (2013)
Alkenes	Whole air samples (WAS) analysed by laboratory-based gas chromatography with flame ionization detection (GC-FID).	Typically 30 s; variable limits of detection	Hopkins et al. (2003)
NO <sub>3</sub> , N <sub>2</sub> O <sub>5</sub>	BBCEAS (broadband cavity-enhanced absorption spectroscopy) of NO <sub>3</sub> at $\lambda = 642$ – $672$ nm. N <sub>2</sub> O <sub>5</sub> measured following thermal dissociation to NO <sub>3</sub> + NO <sub>2</sub> .	1 s; 1.1 pptv for NO <sub>3</sub> , 2.4 pptv for NO <sub>3</sub> + N <sub>2</sub> O <sub>5</sub>	Kennedy et al. (2011)
HCHO	Hantzsch technique: Liquid-phase reaction of formaldehyde followed by excitation, and fluorescence of resulting adduct at $\lambda = 510$ nm.	60 s; 81 pptv	Still et al. (2006)

8 Table 3. Mean mixing ratios of selected gas phase species, and air temperature, measured during  
 9 RONOCO and SeptEx. The flight and season during which the maximum values were measured  
 10 are given in parentheses. NO<sub>2</sub> data are from the TD-LIF instrument. Zero values indicate  
 11 measurements below the limit of detection.

Species	Summer RONOCO	SeptEx	Winter RONOCO	Maximum
CO / ppbv	102.3	117.1	139.3	256.0 (B537, summer)
O <sub>3</sub> / ppbv	39.6	40.4	38.6	89.8 (B537, summer)
NO <sub>3</sub> / pptv	21.1	0	6.2	176.9 (B537, summer)
NO / ppbv	0.05	0	0	18.9 (B539, summer)
NO <sub>2</sub> / ppbv	1.6	1.7	2.3	18.6 (B568, winter)
Temperature / K	286.5	286.2	276.4	297.5 (B537, summer)

12 Table 4. Combined daytime and nighttime mean concentrations of OH and mean mixing ratios of  
 13 HO<sub>2</sub>\* with the FAGE instrument's average 1σ limits of detection for a 5 minute averaging period  
 14 during the RONOCO and SeptEx fieldwork.

**Comment [HW18]:** See Reviewers' Comments Sect 1.3

	OH / molecule cm <sup>-3</sup>		HO <sub>2</sub> * / pptv	
	Mean concentration	Limit of detection	Mean mixing ratio	Limit of detection
Summer		1.8 × 10 <sup>6</sup>	1.6	0.03
SeptEx	1.8 × 10 <sup>6</sup>	1.2 × 10 <sup>6</sup>	2.9	0.02
Winter		6.4 × 10 <sup>5</sup>	0.7	0.02

15 | Table 5. Mean and, in parentheses, maximum HO<sub>2</sub>\* mixing ratios measured during RONOCO  
16 | and SeptEx.

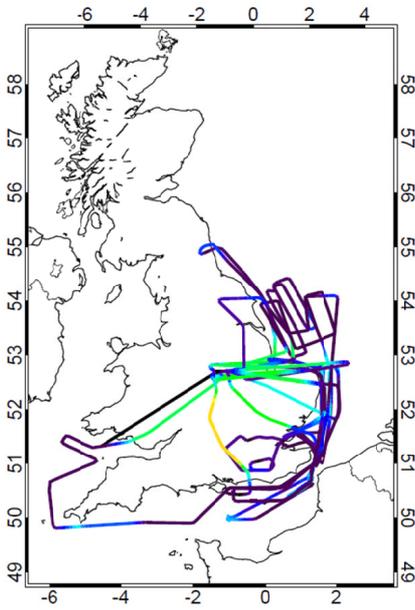
	Mean (maximum) HO <sub>2</sub> * mixing ratio / pptv		
	Summer	SeptEx	Winter
Dawn	0.74 (1.19)		0.54 (1.81)
Day		3.78 (11.79)	0.49 (1.68)
Dusk	2.73 (9.97)		0.32 (0.97)
Night	1.86 (13.58)		0.98 (2.02)

17 | Table 6. Average Rates of instantaneous production of HO<sub>2</sub> from reactions of O<sub>3</sub> and NO<sub>3</sub> with  
 18 | alkenes.

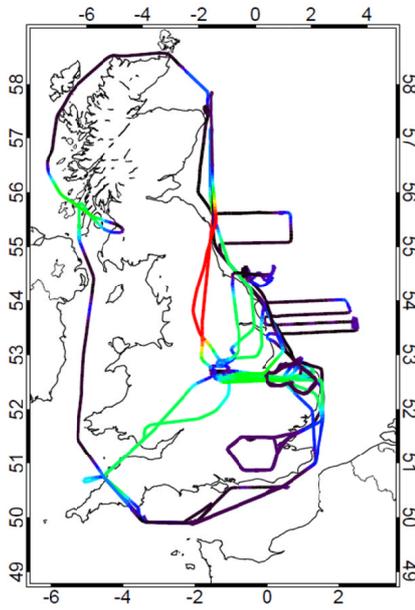
**Comment [HW19]:** See Reviewers' Comments Sect 1.4

Measurements	HO <sub>2</sub> production rate ( $\Sigma P_{\text{HO}_2}$ ) / 10 <sup>4</sup> molecule cm <sup>-3</sup> s <sup>-1</sup>			
	Dawn	Day	Dusk	Night
<b>Summer</b>				
NO <sub>3</sub>	0		2.8	3.8
O <sub>3</sub>	0.5		2.2	1.7
Total	0.5		5.0	5.5
<b>Winter</b>				
NO <sub>3</sub>	0.4	0.4	0.4	0.5
O <sub>3</sub>	1.4	1.5	1.2	1.2
Total	1.8	1.9	1.6	1.7

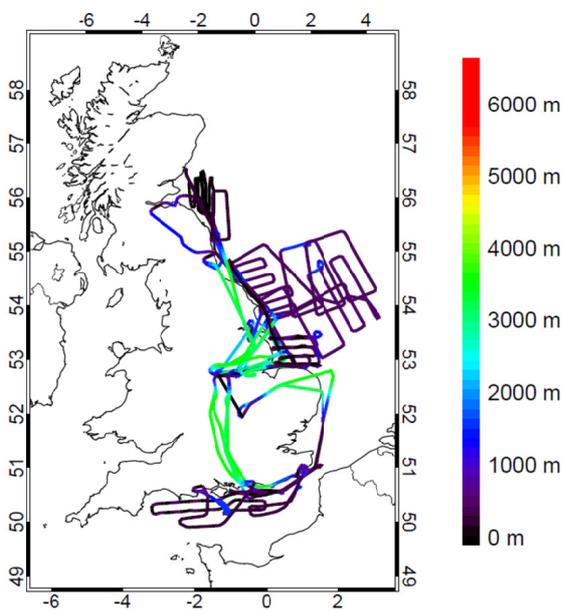
(a) Summer RONOCO



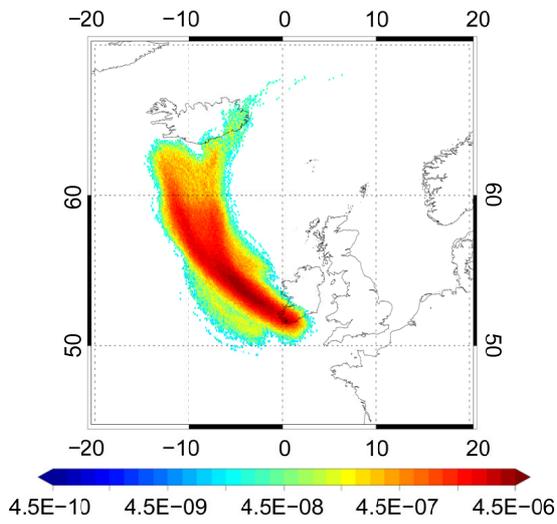
(b) SeptEx



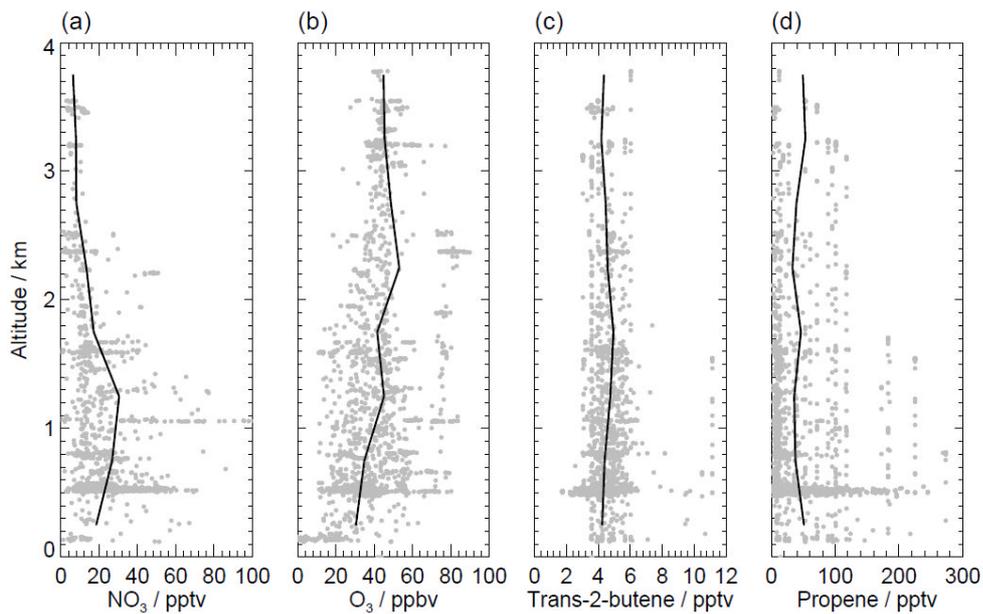
(c) Winter RONOCO



5  
0 Figure 1. Flight paths for: (a) Summer RONOCO, (b) SeptEx, and (c) winter RONOCO  
9 measurement campaigns, coloured by altitude.

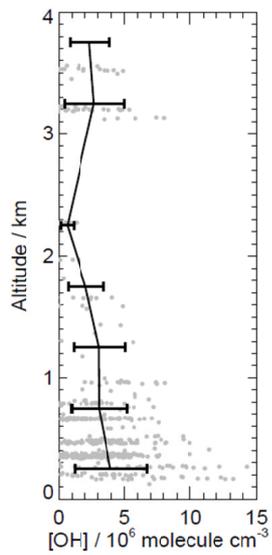


5  
 14 Figure 2. Footprint map for flight B535 on 17<sup>th</sup> July 2010, showing model particle densities ( $\text{g s m}^{-3}$ ) in a 300 m deep layer from the surface, integrated over a 24 hour period beginning 48  
 15 hours prior to the flight.



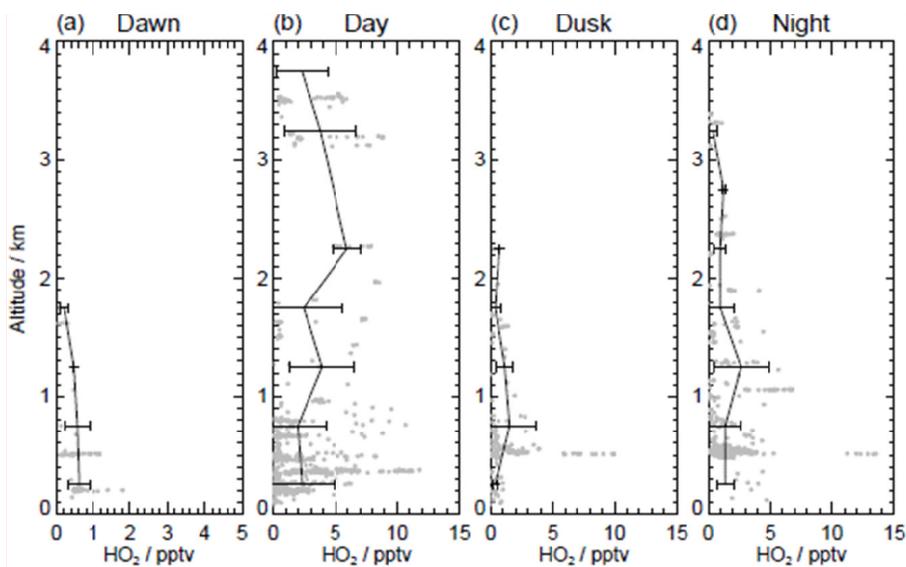
9  
 14 Figure 3. Nighttime altitude profiles of a)  $\text{NO}_3$ ; b)  $\text{O}_3$ ; c) *trans*-2-butene; d) propene, showing  
 15 60 second data (grey points) and mean values in 500 m altitude bins (solid black lines).

Comment [HW20]: See Reviewers' Comments Sect 1.4

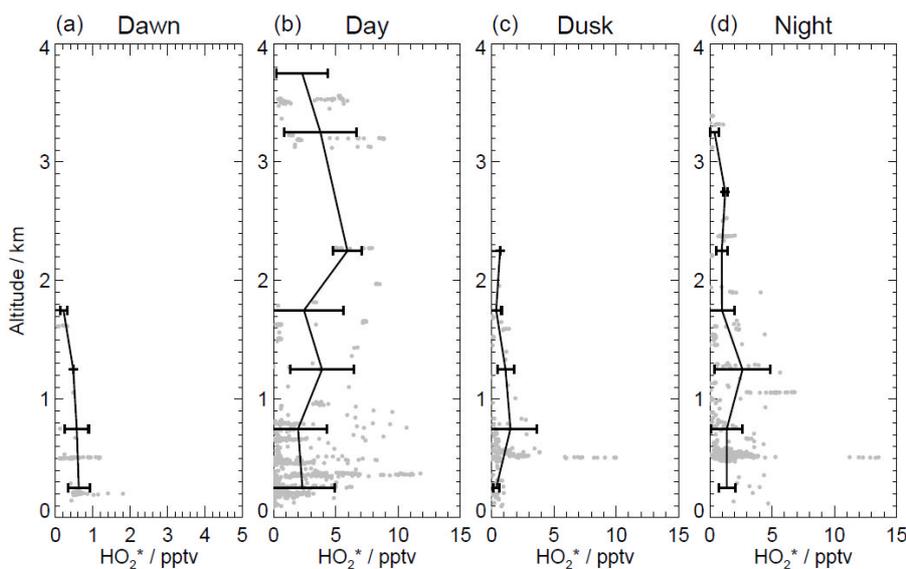


5  
 0 | Figure 43. Altitude profile of OH measured during SeptEx showing 60 second data (grey  
 1 | points) and mean values in 500 m altitude bins (solid black lines). Error bars are  $1\sigma$ .

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**Comment [HW21]:** Figure updated with HO<sub>2</sub>\*. See Reviewers' Comments Sect. 1.1.



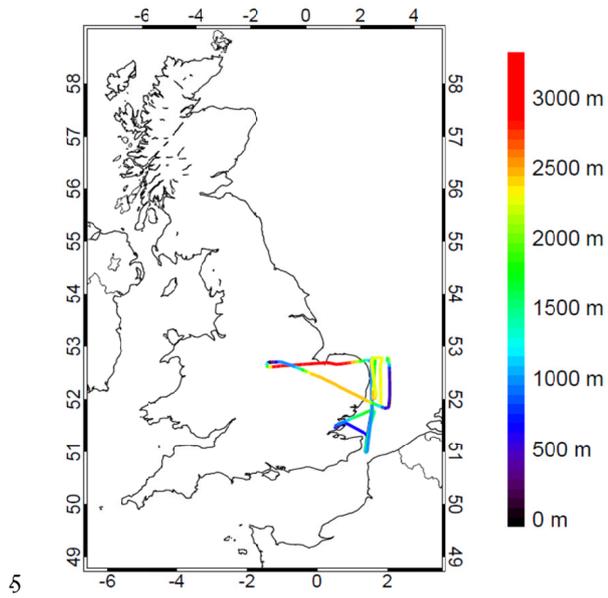
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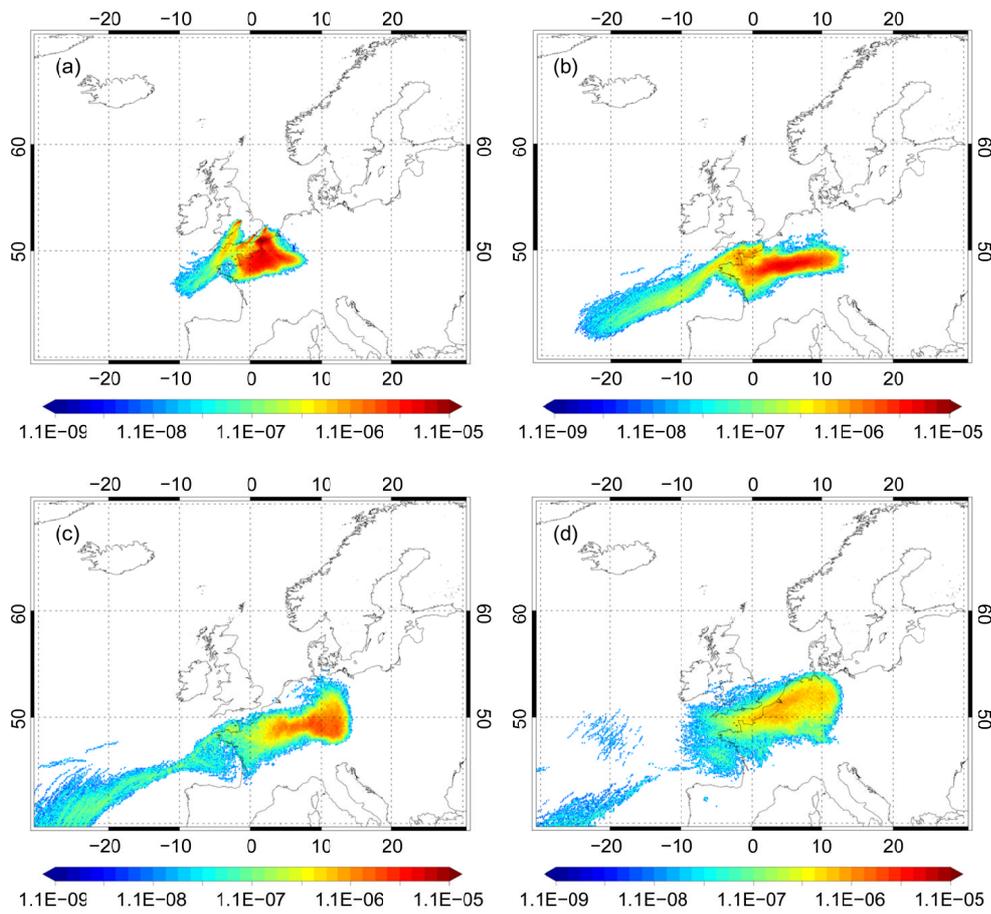
15 **Figure 54.** Altitude profiles of HO<sub>2</sub>\* measured in RONOCO and SeptEx during: a) dawn; b)  
 15 day; c) dusk; d) night, showing 60 second data (grey points) and mean values in 500 m  
 17 altitude bins (solid black lines). Error bars are 1σ.

**Comment [HW22]:** See Reviewers' Comments Sect. 1.1

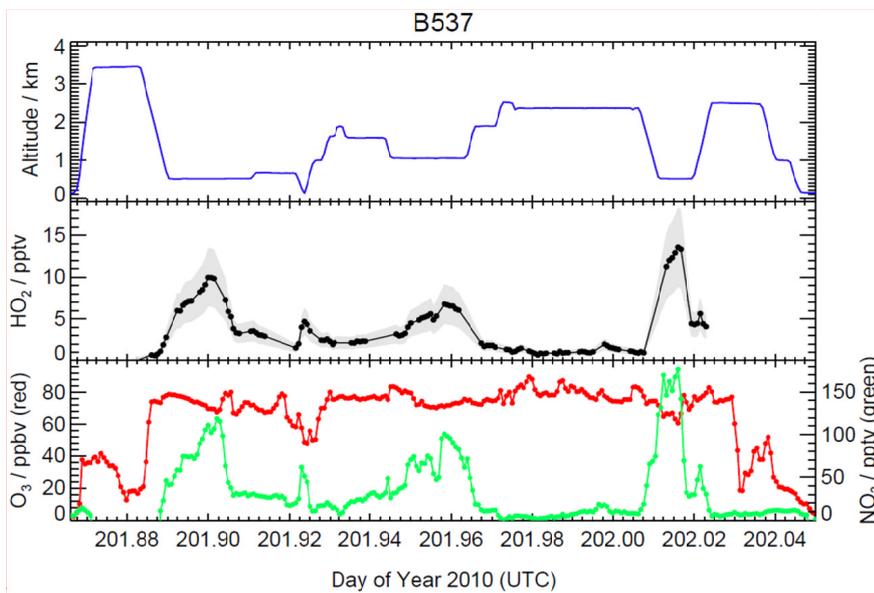
**Formatted:** Font: Not Italic



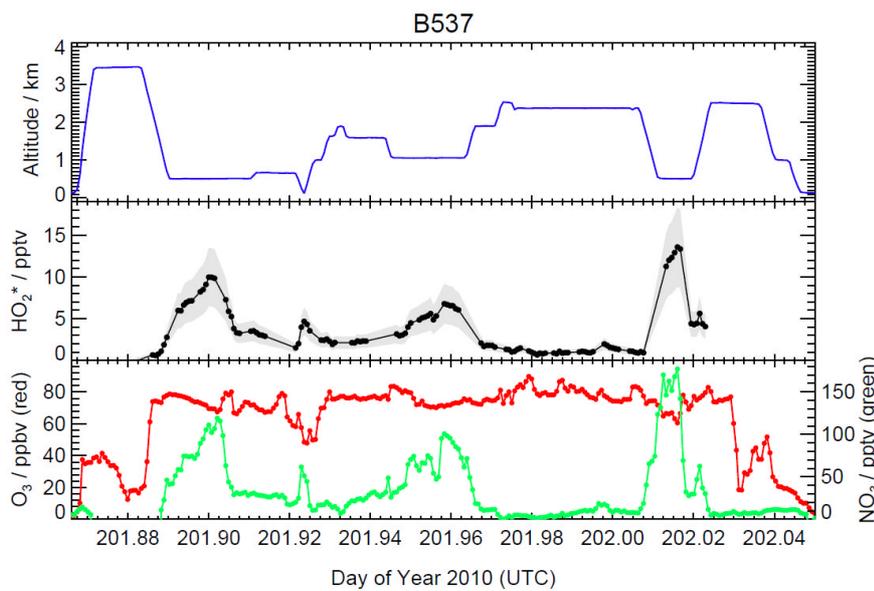
5 | Figure 65. Flight track of flight B537 on 20<sup>th</sup> July 2010, coloured by altitude.



5  
 14 | Figure 76. Footprint maps for flight B537 on 20<sup>th</sup> July 2010, showing model particle densities  
 15 (g s<sup>-3</sup>) in a 300 m deep layer from the surface, integrated over 24 hour periods beginning  
 15 (a) 24 hours, (b) 48 hours, (c) 72 hours, and (d) 96 hours prior to the flight.

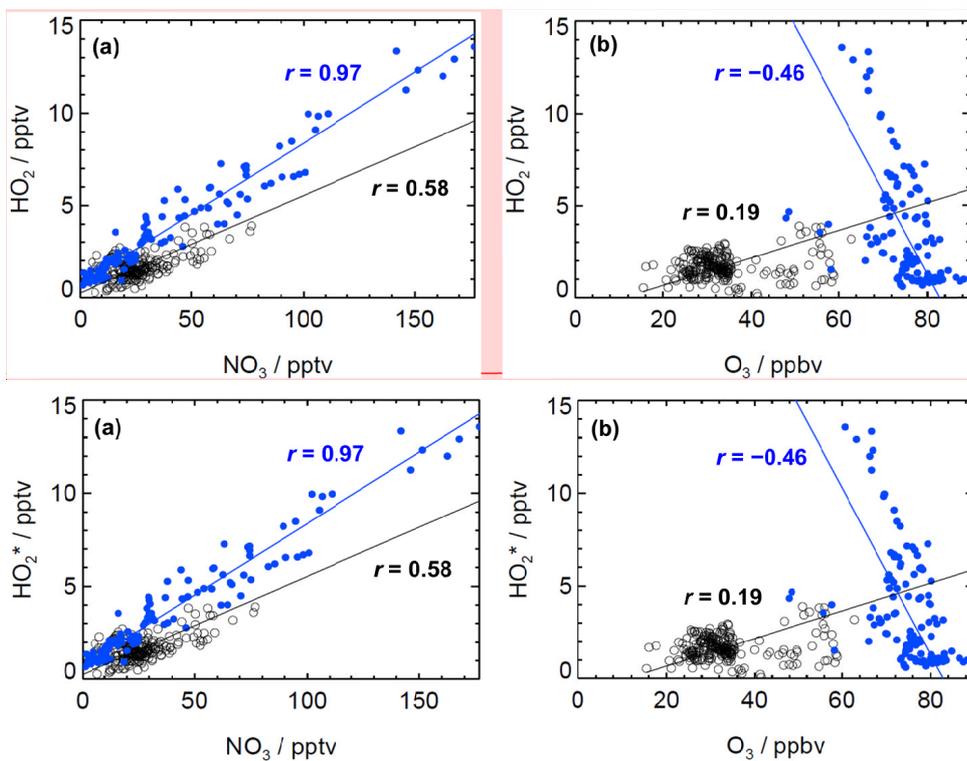


**Comment [HW23]:** Figure updated with HO<sub>2</sub>\*. See Reviewers' Comments Sect. 1.1.



**Comment [HW24]:** See Reviewers' Comments Sect. 1.1

**Figure 87.** Time series of altitude (top panel, blue), HO<sub>2</sub>\* (middle panel, black, with grey shading representing the uncertainty in the measurements), O<sub>3</sub> (bottom panel, red) and NO<sub>3</sub> (bottom panel, green) during nighttime flight B537 on 20<sup>th</sup> July 2010.



**Comment [HW25]:** Figure updated with HO<sub>2</sub>\*. See Reviewers' Comments Sect. 1.1

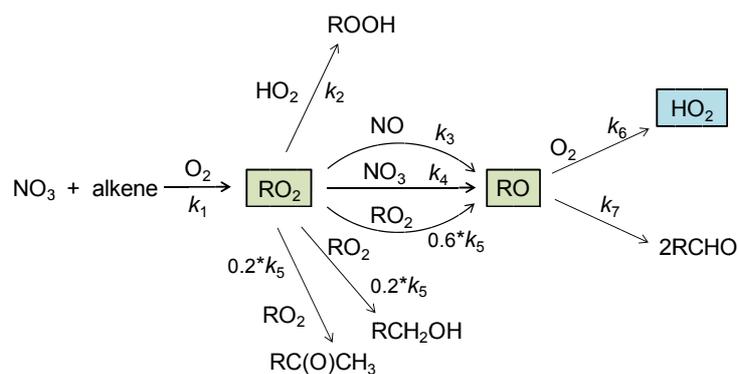
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7

10 **Figure 98.** HO<sub>2</sub>\* versus (a) NO<sub>3</sub> and (b) O<sub>3</sub> during flight B537 (blue, filled circles) and during  
 13 all other nighttime flights (black, open circles). The solid lines are lines of best fit to the data.

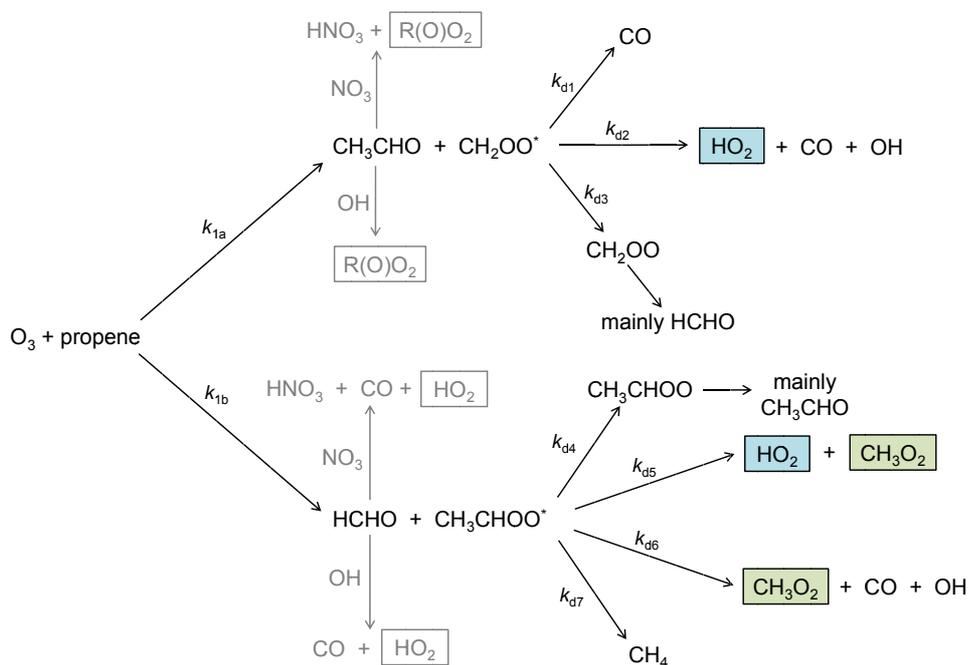
**Comment [HW26]:** See Reviewers' Comments Sect. 1.1



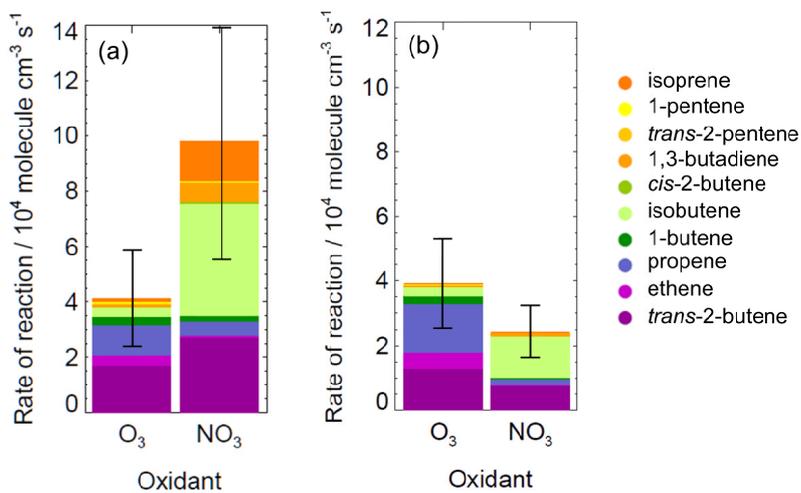
9

15 **Figure 109.** Generalised reaction scheme for production of RO<sub>2</sub> and HO<sub>2</sub> following reaction  
 16 of NO<sub>3</sub> with an alkene.

13

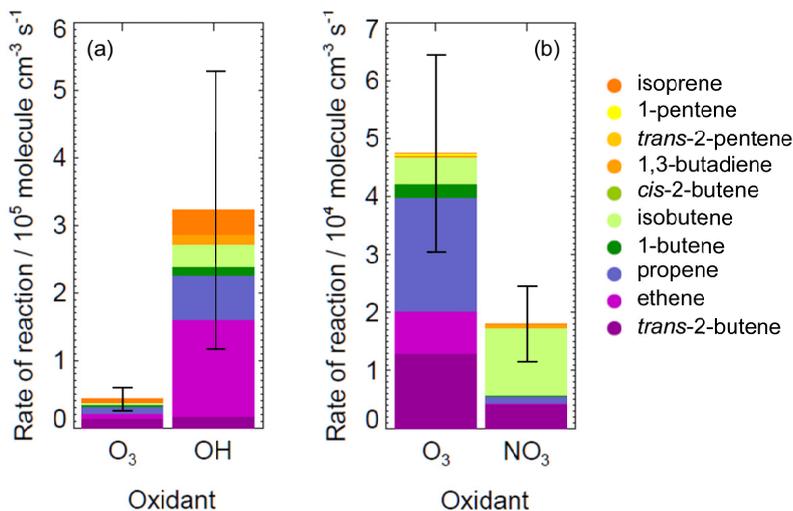


5  
 0 Figure 11+0. Reaction scheme for  $O_3 + \text{propene}$ , showing production of  $\text{HO}_2$  and the methyl  
 9 peroxy radical,  $\text{CH}_3\text{O}_2$ .



3  
 17 Figure 12+1. Average nighttime rates of reaction between  $O_3$  and  $NO_3$  with alkenes during:  
 18 a) summer; and b) winter RONOCO flights. Error bars represent the combined uncertainty in  
 10 the measurements.

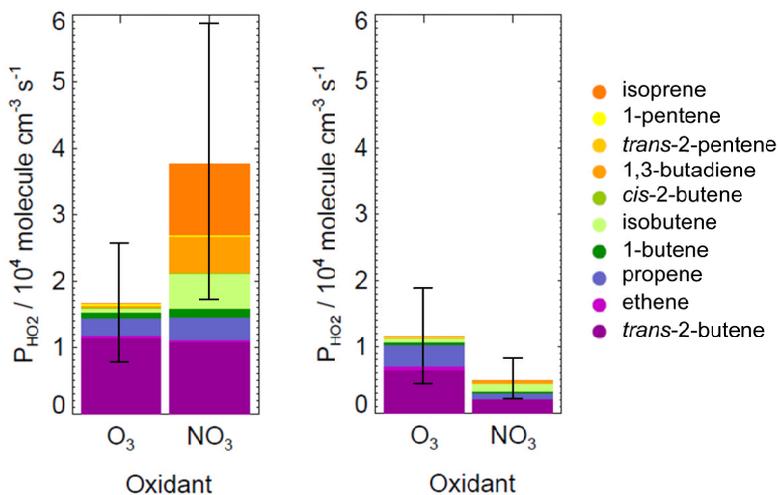
Comment [HW27]: See Reviewers' Comments Sect 1.4



5

12 Figure 1342. Average daytime rates of reaction of (a)  $O_3$  and OH with alkenes during  
 18 SeptEx; and (b)  $O_3$  and  $NO_3$  with alkenes during winter. Note the different scales.  $NO_3$  was  
 14 not detected during daytime SeptEx flights (LOD = 1.1pptv); OH was not detected during  
 26 daytime winter flights (LOD =  $6.4 \times 10^5$  molecule  $cm^{-3}$ ). Error bars represent the combined  
 25 uncertainties in the measurements.

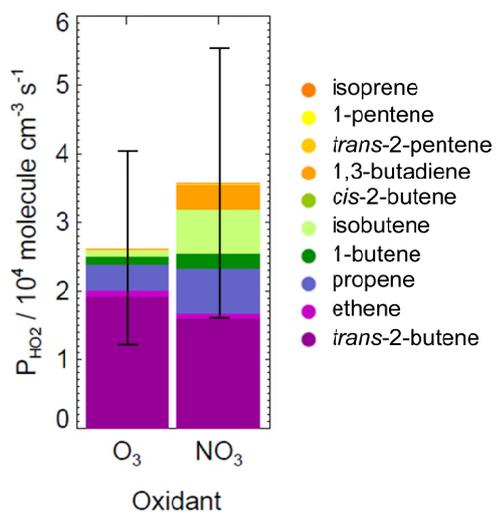
Comment [HW28]: See Reviewers' Comments Sect 1.4



10

10 Figure 1413. Averaged rates of instantaneous production of  $HO_2$  from reactions of  $O_3$  and  
 11  $NO_3$  with alkenes during: a) summer; and b) winter RONOCO flights. Error bars represent the  
 12 combined uncertainty in the measurements.

Comment [HW29]: See Reviewers' Comments Sect 1.4

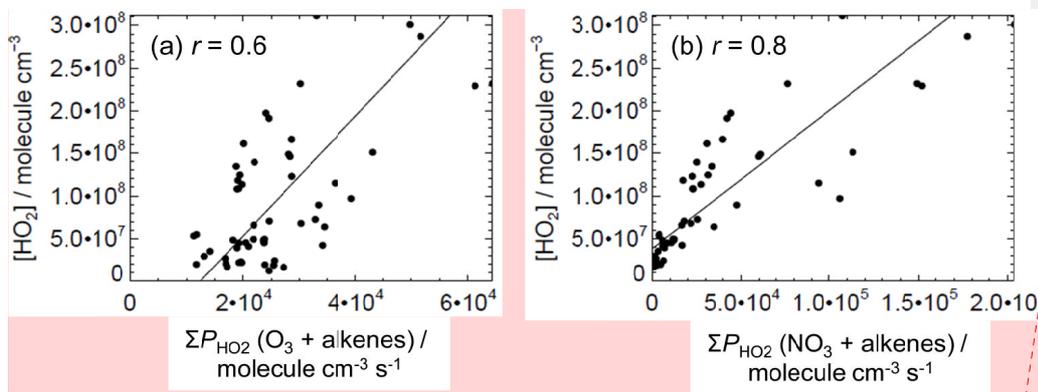


5

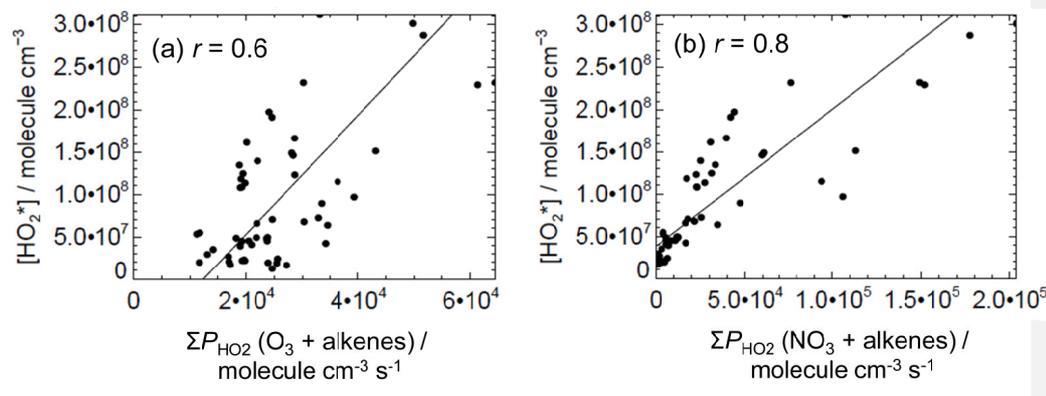
14 Figure 15-14. Average Rates of instantaneous production of HO<sub>2</sub> ( $P_{HO_2}$ ) from reactions of O<sub>3</sub>  
 15 and NO<sub>3</sub> with alkenes during flight B537. Error bars represent the combined uncertainty in  
 15 the measurements.

9

Comment [HW30]: See Reviewers' Comments Sect 1.4



**Comment [HW31]:** Figure updated with 'HO2\*'. See Reviewers' Comments Sect. 1.1



5

5

15 **Figure 1615.**  $[\text{HO}_2^*]$  versus total rate of instantaneous production of  $\text{HO}_2$  from reactions of:  
 15 a)  $\text{O}_3$ ; and b)  $\text{NO}_3$  during flight B537. Correlation coefficients ( $r$ ) are given in each plot. Solid  
 17 lines are lines of best fit to the data.

**Comment [HW32]:** See Reviewers' Comments Sect. 1.1