Radical chemistry at night: comparisons between observed and modelled HO_x, NO_3 and N_2O_5 during the RONOCO project

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We thank the reviewers for their comments on the manuscript. We have improved the manuscript in a number of areas, as suggested by the reviewers, and provide detailed responses to comments below.

Review #1

The observations including HO2, NO3, and N2O5 from the RONOCO aircraft campaign were simulated with a box model. As in previous studies, heterogeneous losses of NO3 and N2O5 and unsaturated VOCs not measured are the largest uncertainties in model simulations. The main conclusion seems to be that the observations cannot be simulated well after model uncertainties are considered. The paper is informative and written well. It would have been a good read as a thesis chapter or a conference paper. For an ACP paper, it falls short. This paper addresses relevant scientific questions within the scope of ACP but did not present novel concepts, ideas, or tools. The observation data have already been published elsewhere. The conclusions reached are tentative. I cannot recommend the publication of this paper.

It is difficult to understand how the reviewer can acknowledge that the paper is informative, addresses relevant scientific questions and is within the scope of ACP, and yet is not suitable for publication. The observations have not been published elsewhere. The broadband cavity enhanced absorption spectrometer used to measure NO_3 and N_2O_5 has been described by Kennedy et al. (2011), and observations of NO_3 and N_2O_5 during test flights and case studies from the RONOCO campaign are discussed by Kennedy et al. The full data set for NO_3 and N_2O_5 has not been published or discussed in detail in previous work. The observations of OH and HO_2 have not been presented in any publication. To state that the observations have already been published elsewhere is incorrect and misleading.

The budget analysis in section 6 is presented quite well. However, the model performance presented in section 5 clearly shows that the model does not simulate well the observations. For example, the Rˆ2 value for model vs. observed HO2* is only 0.1 with a large bias. Simulated NO3 and N2O5 also have large biases with better Rˆ2 values. Since NO3 and N2O5 interconvert rapidly as stated in Line 11-13 on P. 9533, the Rˆ2 values for simulated NO3 and N2O5 should be similar or at least the two errors should be highly correlated. Instead, Figure 2 shows that the model errors of NO3 or N2O5 from the observations clearly have different patterns. Either the model has a problem or there are unknown issues in the measurement data.

Although NO_3 and N_2O_5 interconvert rapidly, losses for N_2O_5 are typically dominated by heterogeneous aerosol uptake, while those for NO_3 occur via a number of different processes (reaction with HO_2, RO_2, VOCs and RCHO for example). The more complex chemistry of NO_3 compared to N_2O_5 results in greater uncertainty in the modelled NO_3 concentrations, and reduces the correlation between model errors for NO_3 and N_2O_5 expected by the reviewer. The differences are a result of the more complex chemistry of NO_3 and do not necessarily indicate a problem with the model or with the measurements.

The budget analysis in section 6, which is the bulk of science content of this paper, provides little new science information. It would have been useful if the model performance were better. Section 7 is more interesting. But neither tweaking the sticking coefficient nor putting in specific unsaturated VOC species would improve the model simulations of HO2, NO3, and N2O5 at the same time. To be sure, it is not a new problem and it may be understandable that this paper cannot solve the problems also seen in previous studies. But for ACP publication, the level of new science in this paper is inadequate.

Modelling of simultaneous observations of HO_2, NO_3 and N_2O_5 at night in environments remote from sources of NO has not been reported previously. This work represents a comprehensive study of nighttime chemistry and a test of our understanding of oxidation processes at night which has not been possible previously owing to a lack of simultaneous measurements of short-lived species. The problems highlighted in this work have not been studies with such a comprehensive range of measurements in previous studies. The budget analysis indicates a much more active nighttime radical chemistry than previously expected, even with model underestimation of HO_2, and indicates the importance of NO_3 + HO_2 and NO_3 + RO_2 chemistry for modelling of nighttime oxidation. Such chemistry is often missing from regional and global models and will impact modelling of air quality and climate change. The model discrepancies for HO_2 and NO_{3x} highlight further problems with our understanding of nighttime chemistry. Without identification and publication of the model discrepancies at night reported in this work it is difficult to see how such problems will ultimately be resolved. We have also conducted further analysis regarding model sensitivity to the uptake coefficient for N_2O_5. Optimisation of the N_2O_5 uptake coefficient to give model agreement (i.e. modelled to observed ratio of unity) for NO_3 and N_2O_5 for each data point in the model has revealed relationships between the optimum uptake coefficient and the aerosol sulfate content, humidity and temperature. We believe this is an important result and should be communicated in the literature.

There is an error in model formulation. Equations (1) and (2) are appropriate only when Knudson number is >> 1 such as the stratospheric conditions. For RONOCO, the first order aerosol loss should be considerably lower than calculated using these equations.

The equations are typical of those used in tropospheric box modelling. We have added a diffusion term in the equation describing aerosol uptake, which makes little difference to the model results owing to the small diameter aerosols encountered during RONOCO.

The discussion of potential RO2 interferences also seems problematic. Line 16 on P. 9540 states that "An increase of approximately 4 times the total observed C=C reactivity results in significant improvements to model simulations for HO2* and simultaneously improves the modelled NO3x." If that much unsaturated VOCs are added, the RO2 interference could be quite significant.

Potential interferences resulting from RO_2 radicals are considered in all model simulations reported in this work, including those in which the VOC concentrations were increased. The method used to estimate the interference is based on experimental results obtained for the instrument as configured for the RONOCO campaign and is described in the appendix. While the absolute interference increases with increasing C=C in the model, the HO_2 concentration also increases and the relative interference is relatively unchanged by increasing the VOCs in the model. For the base model run, the interference is estimated at 16.99 %. For the model run using 4 times the total observed C=C reactivity, the interference is estimated at 16.84 %.

Review #2

The authors attempt to model interesting aircraft measurements of NO3, N2O5, HO2, and RO2 during the RONOCO campaign using the MCM. The model runs generally struggle to reproduce the measurements (r2 = 0.10 for HO2*, and 0.29 for NO3), in part because the VOC and aerosol data set was quite limited, and because the authors attempted to model the entire data set (which spans several seasons and a wide range of locations) with a single set of parameters.

The VOC and aerosol data are in fact rather comprehensive for aircraft studies of this nature and comparable to numerous measurement campaigns in the literature. While we conclude that observations of low levels of larger VOCs and monoterpenes are desirable, such measurements are extremely challenging owing to difficulties in preparing samples of known concentration for calibration purposes and are an area of ongoing research. This work highlights the importance of such research.

The entire data set has not been modelled with a single set of parameters as claimed by the reviewer. This is extremely misleading and perhaps indicative of a lack of understanding of the nature of this work by the reviewer. Measurements made on the aircraft are averaged on to a 60 s timescale, as described in Section 4 of the paper. For each 60 s period (i.e. for each data point), we simulate concentrations of the short-lived species by constraining to the observed concentrations of long-lived species for that data point. Each 60 s data point is treated individually and is independent of the rest of the data set. We do not attempt to simulate the entire data set with a single set of parameters.

Substantial conclusions or novel insights are not presented, and the manuscript generally is too weak to stand on its own. Because of the extent of the changes that I think would be required to convert this manuscript into a publishable form, I need to agree with reviewer #1 and recommend this paper be rejected.

Our conclusions have been obtained from a detailed modelling study using a comprehensive suite of observations. Such work has not been possible previously owing to a lack of simultaneous measurements of HO_2 and NO_{3x}. We do not necessarily expect the model to be able to reproduce the observations of HO_2 and NO_{3x} as seems to be expected by the reviewer. The aim of the work is to test our understanding of nighttime oxidation chemistry by comparing model results with observations, thereby highlighting areas of poor understanding. We are neither aiming nor expecting to show perfect agreement between modelled and observed concentrations but to display the level of our understanding of nighttime chemistry. Our work has indicated a much more active radical chemistry at night than previously expected, and highlights the importance of $NO_3 + HO_2$ and $NO_3 + RO_2$ chemistry for modelling of nighttime oxidation. As stated in response to reviewer #1, such chemistry is often missing from regional and global models and will impact modelling of air quality and climate change. Again, the model discrepancies for HO_2 and NO_{3x} highlight further problems with our understanding of nighttime chemistry, without identification and publication of which it is difficult to see how such problems will ultimately be resolved.

Major comments
-The paper promises "comparisons between observed and modelled HOx, NO3, and N2O5". Unfortunately, neither the observed nor the modelled data are presented in a meaningful way, e.g., by showing figures of time series of the measurements and model results. Instead, only scatter plots (e.g., Figure 2) of modelled vs. Observed data for the entire data set are presented, which are neither informative nor useful as there is a lot of scatter, and the slopes were likely affected by relatively few "outlier" points.

We can include figures of time series for observed and modelled data for HO_2, NO_3 and N_2O_5 if the reviewer feels this is necessary. However, we disagree that the data has not been presented in a meaningful way. The scatter plots show comparisons for all data points, and promote statistical analysis of the agreement between modelled and observed data through best fit lines and r^2 values. Such analysis is

not possible when simply displaying time series, and time series can often be misleading when viewed in isolation, particularly when comparing data obtained over several flights and over a range of altitudes and locations.

- The authors attempted to model all of their data using a single value for gamma(N2O5), which is a highly unrealistic assumption considering the temporal and spatial variability of N2O5 uptake that can occur on ambient aerosol [see, for example, Brown et al., Science 2006, 311, 67-70].

The model sensitivity to γ_{N2O5} is discussed in Section 7. We have expanded this discussion, and determine the optimum value for γ_{N2O5} for each data point in the model by optimising the model success for NO_3 and N_2O_5. Investigation of the relationships between the optimised values for γ_{N2O5} and aerosol composition has revealed that the optimum γ_{N2O5} increases with increasing sulfate content of the aerosol, and with increasing humidity and temperature. This work highlights the clear need for further experimental investigations of the dependence of γ_{N2O5} on temperature, humidity and aerosol composition for use in atmospheric models, and we believe should be communicated within the literature.

- Most of the campaign took place over the ocean water (Figure 1) at relatively low altitude (the color scale in Figure 1 is clearly mislabeled, and I am guessing below 800 m was the norm) so that it is possible that aircraft entered the marine boundary layer. The oceans are a source of sea salt aerosol and of dimethyl sulfide, which are strong sinks for N2O5 and NO3. Neither chemistry has been considered by the authors.

DMS was not observed above the 3 ppt limit of detection during the RONOCO campaign. We have added a comment on this in Section 7, and provide details of model results containing DMS set at 3 ppt to investigate the model sensitivity to concentrations up to the limit of detection. The aerosol measurements made during the campaign (to be discussed in detail by Morgan et al.) do not show any evidence for enhanced coarse mode aerosol at low altitudes, indicating that the aircraft did not enter the marine boundary layer.

- Vertical gradients are ignored by the authors, even though Fig 12 of Kennedy et al. suggests an anticorrelation of NO3 and N2O5 chemistry with altitude.

It is not clear why the reviewer states that vertical gradients are ignored. As stated previously, each data point is treated independently of all other data points, with the altitude explicitly set in the model for each point. Any vertical gradients are thus considered by the model, and thus form part of the correlations observed in the scatter plots. We include plots showing the modelled to observed ratios for HO_2, NO_3 and N_2O_5 as a function of altitude.

- The authors report having made measurements in July and in January but do not consider seasonal differences in the chemistry, which is unrealistic. In addition, isoprene and terpene emission rates are likely quite different between the summer and winter data set.

We do not need to explicitly consider differences in emission rates between summer and winter as this is achieved implicitly through constraint to observed concentrations. As stated, each data point is treated independently and any differences in emission rates and concentrations are thus accounted for. Isoprene aside, which was not observed during the winter campaign (as stated in the manuscript) the model agreement and budget analyses for summer and winter campaigns were very similar. We now include details of the model success and budget analyses for summer and winter separately as well as for the campaign average.

- The pie charts (Fig 3-7) are scientifically questionable as they are for campaign averages, and the properties plotted are in all likelihood highly variable in time and space (see, for example, Figure 12 in Sommariva et al., 2009). Hence, pie charts of campaign averages are generally are poor choice to present

the data. Some of the same info would have been better presented as time series (or maybe as weekly averages plotted against time of day).

The pie charts shown in Figures 3-7 are representative of the data. While the budgets are variable in time and space, plots of time series for the budgets analyses would prove difficult for a reader to interpret and to draw conclusions regarding the overall behaviour of short-lived species at night. We now include pie charts also showing the summer and winter results separately.

- A portion of the paper is spent discussing the model limitations, yet potential measurement errors or biases are by-and-large ignored in the model-measurement comparisons. These could have been substantial, in particular for nocturnal OH and HO2 measurements.

Measurement errors and uncertainties for OH, HO_2, NO_3 and N_2O_5 are in fact discussed in detail in Section 3 and in previous studies (Commane et al., 2010; Kennedy et al., 2011). By no means have we ignored such issues.

- In their modeling, the authors appear to put infinite trust in most measurements (e.g.,NO, NO2, and the VOCs) but zero trust in certain others (NO3, N2O5, HO2, or RO2), because why else would you calculate them. Yet I am sure that Kennedy et al. have a healthy level of trust in their measurements, and that Heard's group feel equally confident about their OH and HO2 measurements. What would have happened if the MCM had been constrained to some of the measured radical species, e.g., NO3, or OH? Does then the model runs agree with the observations? For example, does the MCM reproduce the observed HO2/OH ratio for fixed OH (or HO2)?

The statement that we show infinite trust in most measurements and zero trust in certain others is absolutely not the case. Measurement uncertainties for HO_x, NO_3 and N_2O_5 are discussed in Section 3 and are now also provided for the supporting measurements in Table 1. Our 'trust' in any measurement is not based on anything other than the reported uncertainties, and we would in no way suggest that the measurements by Kennedy et al. or by the Heard group are anything but robust and reliable. We have absolute 'trust' in the work of these groups and in their reported measurements and uncertainties.

The reason for calculating HO_2, NO_3 and N_2O_5 bears no relation to the level of our 'trust' in these measurements.

We simulate the short-lived species (i.e. OH, HO_2, NO_3 and N_2O_5) because these species have relatively short lifetimes and are thus unaffected by transport processes. By constraining to the longer-lived species (e.g. O_3, NO_2, VOCs) and simulating the concentrations of the short-lived species we are able to conduct a test of our understanding of the chemistry alone by comparing the modelled concentrations of the short-lived species to the observed concentrations. This is a well known method to test chemical mechanisms used in atmospheric models, and is well established in the literature.

It is unclear what our target species would be if we were to constrain to the short-lived species. Given that OH was not measured above the instrumental limit of detection it would not be possible to investigate observed HO_2 to OH ratios. Simulations of the longer-lived species would test both chemistry and transport processes, with separation of the two influences difficult. The selection of short-lived species as the model target provides a much simpler and more robust means to test the chemistry in the model.

- A general limitation of this work is that the list of VOCs used as model input (Table 2) is rather short and lacks entire classes of VOCs (e.g., terpenes, aldehydes). As a result, the MCM (6700 species, 17000 reactions) is underutilized (the authors state 2000 species, 8000 reactions are used). I wonder if a data set with such a limited VOC data is a good candidate to attempt a model-measurement comparison from a modeling perspective.

The VOC list is actually rather comprehensive, and certainly comparable to numerous other measurement campaigns of this nature. Aircraft measurements of terpenes and aldehydes are extremely challenging, and relatively rare on campaigns of this nature.

To assert that we have used a limited set of VOC data and under-utilised the MCM is extremely misleading. Environments in which all 142 non-methane primary VOCs described by the MCM are observable and play a role must be extremely rare. We are unaware of any measurement campaign in which all 142 non-methane primary VOCs have been measured that would enable full utilisation of the 6700 species and 17000 reactions in the MCM.

Minor comments
- Table 1 should include the measurements of NO3, N2O5, OH, and HO2 and state detection limits, time resolution, and uncertainties of all of the measurements, not just the auxiliary ones, and give citations to relevant papers. It appears that aerosols > 350 nm were not measured. A brief comment on the error this introduces is warranted.

Details regarding OH, HO_2, NO_3 and N_2O_5 measurements are given in Section 3 and have been added to those for the supporting measurements given in Table 1. Details regarding detection limits, time resolution and uncertainties can be included for all species. Aerosols below 350 nm in diameter were measured with the SMPS instrument and are included in the modelling work here. Larger aerosols were measured during the campaign with a PCASP instrument. The (SMPS+PCASP) data are within 10 % of the SMPS data alone. We therefore do not expect significant contributions from aerosols > 350 nm.

pg 9522, line 15. "Much less emphasis has been placed on the nighttime chemistry" It would be helpful to be more specific here. Nighttime chemistry of what (OH, O(1D), or NO3)?

We have changed this sentence to 'Much less emphasis has been placed on understanding nighttime oxidation chemistry and the role of radical species at night'.

pg 9523, line 17. "... indicating poor understanding ...." There is also the possibility of measurement errors in the earlier data sets, especially for OH and HO2 at night. These are very challenging measurements to make!

Indeed, they are challenging measurements to make. However, for a given instrument in a given campaign, with specified measurement uncertainties and limits of detection, measurements of OH and HO_2 at night are no more challenging than those in daytime (assuming the limit of detection is sufficiently low). In fact, the nighttime measurements may actually be subject to lower uncertainties for a given configuration owing to a lack of additional 'solar counts' which may influence measurements made during daylight hours. Poor model success at night, particularly when model success is improved during the daytime, does therefore indicate poorer understanding of the nighttime chemistry.

pg 9524, line 23, 25. I believe Sommariva et al., 2009, instead of Sommariva et al., 2006, should be cited here.

This will be amended.

pg 9530, line 12. Eq. 1 does not give an expression for the mean molecular speed, and should not be referred to here.

The mean molecular speed is given by Eq. 2. The text has been corrected.

line 18. The parameterization by Evans and Jacob is a questionable choice, as I have yet to see it agree with field observations, and better parameterizations are available in the literature.

The parameterisation by Evans and Jacob is used in a number of global models, use of this parameterisation in this work thus allows some assessment of its validity in other studies. We recognise that there are uncertainties associated with N_2O_5 uptake coefficients and thus report the sensitivity to the uptake coefficient in Section 7. We have expanded our discussion of model sensitivity to the N_2O_5 uptake coefficient in Section 7 (see above).

pg 9531 line 4. "Species which were not observed are set initially to zero in the model". Please indicate which species and state what magnitude error can be expected.

The concentration for any species which was not observed was initially set to zero. Thus, a primary VOC in the MCM which was not observed remained at zero concentration for the entire model run. The concentrations of degradation products of primary VOCs which were observed were calculated by the model. We have provided a list of species which were observed during the campaign and to which the model is constrained. Given the number of species in the MCM it is unreasonable to ask for a list of species which were initially set to zero concentration. The overall magnitude of error in the simulation is assessed through comparison of the observed and modelled concentrations of the relatively short-lived species such as HO_2, NO_3 and N_2O_5.

line 24-26. "potential interferences in HO2 measurements are expected to be small". Please justify this rather important assumption.

The potential interference is stated as $HO_2{}^* = [1.15 \times HO_2] + 2 \times 10^5$ cm^{-3}. On average, the interference is thus approximately 15 %. A detailed description of the method used to determine the interference is given in the appendix.

pg 9532. lines 1-11 "Model performance" and Figure 2, caption. Please state the numerical values with appropriate numbers of significant digits.

The text and the caption in Figure 2 states the equations for the lines of best fit, together with the r^2 values, with what are considered to be appropriate numbers of significant digits. It is not clear what the reviewer is asking for.

pg 9538, line 25-26. Laboratory and field studies actually span several orders of magnitude of gamma values, so being within range is not particularly difficult.

Agreed. But it is important that the value is not outside the range.

pg 9541, line 4. Monoterpene emission rates are quite different in summer and winter, which should have been considered here. Further, I would expect monoterpenes to be relatively short-lived and therefore to exhibit strong vertical gradients. Are there any vertical trends in the measurement-model comparisons? And what about dimethyl sulfide?

The majority of measurements were taken at relatively low altitudes, and thus there is relatively little opportunity to investigate vertical trends in measurement-model comparisons. We now include plots of observed to modelled ratios of HO_2 and NO_{3x} as a function of altitude. Given that inclusion of monoterpenes in the model simulations did not improve model success we did not pursue this to investigate different monoterpene concentrations in summer and winter. We now show the measurement-model comparisons for summer and winter separately. Please see earlier comments regarding DMS.

pg 9556. While the BAe146 is surely an impressive aircraft, I doubt that it flew at 6400 km altitude. Not even if Yeager had been at the controls.

The Figure caption has been corrected.

pg 9557. Most of the NO3* is likely present as N2O5 in winter, whereas the summertime data likely favors NO3. Thus, a model-measurement comparison of NO3 emphasizes the summer data, whereas one of N2O5 is more sensitive to the winter data. Is that perhaps the reason why the slope in Figure 2c is closer to unity than the data in Figure 2b?

We now also report the summer and winter model success separately. The differences in slopes between Figure 2b and Figure 2c reflects the greater complexity in NO_3 chemistry compared to that for N_2O_5.

pg 9564, Fig. 8. This figure should have been presented earlier in the manuscript. Further, several reaction pathways, e.g., the transformation of OH to HNO3, or of the Criegee to the HO2 or methylperoxy radical, are missing reactants and hence do not make sense as written.

Several reactants were omitted from the Figure for clarity, particularly those for well established loss processes for OH and HO_2. We have added reactants to the Figure. Transformation of excited Criegee intermediates to OH, HO_2 and CH_3O_2 are unimolecular decomposition processes and thus do not require additional reactants. The schematic represents a summary of the budget analyses in Section 6 and Figures 3-7 and thus would appear out of place if presented earlier in the manuscript.

Fig. 9. The fonts are too small to be readable.

The size of the font has been increased.