Radical chemistry at night: comparisons between observed and modelled HO\textsubscript{x}, NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} during the RONOCO project

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Abstract

The RONOCO aircraft campaign during July 2010 and January 2011 made observations of OH, HO$_2$, NO$_3$, N$_2$O$_5$ and a number of supporting measurements at night over the UK, and reflects the first simultaneous airborne measurement of these species. We compare the observed concentrations of these short-lived species with those calculated by a box model, constrained by the concentrations of the longer lived species, using a detailed chemical scheme. OH concentrations were below the limit of detection, consistent with the model predictions. The model systematically underpredicts HO$_2$ by a factor of $\sim$2 and overpredicts NO$_3$ and N$_2$O$_5$ by factors of around 75% and 50%, respectively. Cycling between NO$_3$ and N$_2$O$_5$ is fast and thus we define the NO$_{3x}$ (NO$_{3x}$ = NO$_3$ + N$_2$O$_5$) family. Production of NO$_{3x}$ is overwhelmingly dominated by the reaction of NO$_2$ with O$_3$, whereas its loss is dominated by aerosol uptake of N$_2$O$_5$, with NO$_3$ + VOCs and NO$_3$ + RO$_2$ playing smaller roles. The production of HO$_x$ and RO$_x$ radicals is mainly due to the reaction of NO$_3$ with VOCs. The loss of these radicals occurs through a combination of HO$_2$ + RO$_2$ reactions, heterogeneous processes and production of HNO$_3$ from OH + NO$_2$, with radical propagation primarily achieved through reactions of NO$_3$ with peroxy radicals. Thus NO$_3$ at night plays a similar role to both OH and NO during the day in that it both initiates RO$_x$ radical production and acts to propagate the oxidation chain. Model sensitivity to the N$_2$O$_5$ aerosol uptake coefficient ($\gamma_{N_2O_5}$) is discussed, and we find that a value of $\gamma_{N_2O_5} = 0.05$ improves model simulations for NO$_3$ and N$_2$O$_5$, but that these improvements are at the expense of model success for HO$_2$. Improvements to model simulations for HO$_2$, NO$_3$ and N$_2$O$_5$ can be realised simultaneously on inclusion of additional unsaturated volatile organic compounds, however the nature of these compounds is extremely uncertain.
1 Introduction

Fundamentally the troposphere acts to oxidise emitted compounds through multiple steps until their volatility or solubility drops sufficiently for them to condense to form aerosol, be removed through contact with the ground or by clouds, or be absorbed by the biosphere or oceans. This oxidation chemistry is of fundamental importance for air quality, climate, food security and ecosystem services. Primary pollutants, such as CH$_4$, volatile organic compounds (VOCs), oxides of nitrogen and SO$_2$, are removed by oxidation while secondary pollutants such as O$_3$ and secondary organic aerosol (SOA) are produced as part of the oxidation chain.

During the day, atmospheric oxidation is initiated by photochemical processes, notably the solar photolysis of O$_3$ to produce electronically excited oxygen atoms (O($^1$D)) that subsequently react with water vapour to produce OH. Over the last few decades there has been extensive research into the processes producing these oxidants and their subsequent chemistry (see for example Stone et al., 2012 and references therein). Much less emphasis has been placed on the nighttime chemistry.

When primary production of OH by solar photolysis cannot occur, other oxidants dominate, notably O$_3$ and NO$_3$ (Mihelcic et al., 1993; Carslaw et al., 1997; Salisbury et al., 2001; Fleming et al., 2006; Warneke et al., 2004; Brown et al., 2009, 2011).

Ozone-initiated oxidation of gas phase compounds is primarily limited to alkenes, where ozonolysis of the C=C double bond initiates the oxidation. Ozonolysis has been investigated in a range of laboratory, chamber and field studies (Salisbury et al., 2001; Fleming et al., 2006; Sommariva et al., 2007; Kanaya et al., 1999, 2002, 2007b; Geyer et al., 2003; Malkin et al., 2010; Johnson and Marston, 2008), and has been shown to be responsible for production of OH and HO$_2$ radicals at night (Salisbury et al., 2001; Fleming et al., 2006; Sommariva et al., 2007; Kanaya et al., 1999, 2002, 2007a; Emmerson and Carslaw, 2009; Ren et al. 2003, 2006; Volkamer et al., 2010).

The nitrate radical (NO$_3$) is produced by the reaction between O$_3$ and NO$_2$. During the day, NO$_3$ is rapidly photolysed, leading to low daytime concentrations (Wayne
et al., 1991; Brown and Stutz, 2012). However, during the night, NO₃ can accumulate, and a rapid equilibrium with N₂O₅ is established through the production of N₂O₅ via NO₃ + NO₂ followed by rapid thermal decomposition of N₂O₅ back to NO₃ and NO₂ (Wayne et al., 1991; Brown and Stutz, 2012). Losses of N₂O₅ are primarily due to reactions on aerosol surfaces, and there is thus much interest in determination of the aerosol uptake coefficient for N₂O₅ on atmospheric aerosols (Brown et al., 2006, 2009, 2011; Escoreia et al., 2010; Tang et al., 2010; Badger et al., 2006; Thornton and Abbatt, 2005; Hallquist et al., 2003; Thornton et al., 2003; Kane et al., 2001; Hu and Abbatt, 1997; Fried et al., 1994; Van Doren et al., 1991; Hanson and Ravishankara, 1991; Mozurkewich and Calvert, 1998). NO₃ radicals can react with a range of species, including alkenes, aldehydes and ROₓ radicals (Wayne et al., 1991; Brown and Stutz, 2012).

Although the initiation of nighttime chemistry by the reactions between NO₃ and O₃ with a range of VOCs is relatively well characterised, the subsequent chemistry has received relatively little attention. Measurements of NO₃ have been overestimated by model calculations in several studies (Mihelcic et al., 1993; Sommariva et al., 2006, 2007), with those of nighttime OH and HO₂ radicals typically underestimated, indicating poor understanding of nighttime tropospheric oxidation processes (Kanaya et al., 1999, 2002, 2007a,b; Emmerson and Carslaw, 2009; Geyer et al., 2003; Faloona et al., 2001; Martinez et al., 2003; Ren et al., 2006).

While a number of nighttime studies at ground-level close to local sources of NO have observed a limited role of NO₃ in nighttime radical production owing to surface losses of NO₃ and the rapid reaction between NO₃ and NO (Salisbury et al., 2001; Fleming et al., 2006; Sommariva et al., 2007; Kanaya et al., 1999, 2002, 2007a,b; Emmerson and Carslaw, 2009; Faloona et al., 2001; Martinez et al., 2003; Ren et al., 2003, 2005, 2006; Volkamer et al., 2010), several studies of NO₃ and N₂O₅ above ground-level and in more remote regions have indicated a more significant role for NO₃ in nighttime radical production and tropospheric oxidation (Platt et al., 1980; Povey et al., 1998; South et al., 1998; Aliwell et al., 1998; Allan et al., 2002; Stutz et al., 2004,
Measurements of NO$_3$ and N$_2$O$_5$ were made downwind of New York City during the New England Air Quality Study (NEAQS) by cavity ringdown spectroscopy (CRDS) onboard the National Oceanic and Atmospheric Administration (NOAA) research vessel (R/V) Ronald H. Brown in summer 2002 (Warneke et al., 2004; Brown et al., 2004; Aldener et al., 2006) and 2004 (Sommariva et al., 2009). While measurements of nighttime composition in New York City led to the conclusion that O$_3$-initiated oxidation processes were dominant at night (Ren et al., 2003, 2006), those made during NEAQS indicated little influence of O$_3$-initiated VOC oxidation at night, with oxidation of biogenic VOCs dominated by NO$_3$ (Warneke et al., 2004). Although OH was not measured during NEAQS, the total VOC loss rate owing to reaction with OH over a 24 h period was expected to be $1.7 \times 10^6$ cm$^{-3}$ s$^{-1}$, compared to the measured value of $1 \times 10^6$ cm$^{-3}$ s$^{-1}$ for NO$_3$ (Warneke et al., 2004). Conversion of NO$_x$ to HNO$_3$ at night through NO$_3$ and N$_2$O$_5$ was also found to occur at a comparable rate to that observed during daytime through the OH + NO$_2$ reaction, emphasising the importance of nighttime chemistry for determination of NO$_x$ budgets and O$_3$ production (Warneke et al., 2004; Brown et al., 2004; Aldener et al., 2006).

Modelling of NEAQS 2004 shipborne data using the Master Chemical Mechanism (MCM) (http://mcm.leeds.ac.uk/MCM/home.htm) (Jenkin et al., 2003; Saunders et al., 2003) demonstrated the importance of peroxy radicals for NO$_3$ loss, with NO$_3$ + RO$_2$ reactions representing a median of 15% of the total calculated NO$_3$ gas phase loss, and at times up to 60% of the total NO$_3$ loss (Sommariva et al., 2006). However, the total sinks for NO$_3$ and N$_2$O$_5$ were still underpredicted, leading to overpredictions of 30 to 50% of observed NO$_3$ and N$_2$O$_5$ concentrations (Sommariva et al., 2006).

Aircraft measurements of NO$_3$ and N$_2$O$_5$ at night during NEAQS were significantly higher than the few ppt typically reported at the surface, with the aircraft observations reaching 400 ppt NO$_3$ and 3.1 ppb N$_2$O$_5$ (Brown et al., 2006, 2007, 2009). The high NO$_3$ concentrations aloft during NEAQS 2004 resulted in significant nighttime oxidation.
of isoprene, with ~ 20% of isoprene emissions oxidised at night, and over 90% initiated by NO3 (Brown et al., 2009). It was suggested that NO3-initiated oxidation of isoprene could easily dominate isoprene loss on a regional scale, and it was found that isoprene secondary organic aerosol (SOA) mass derived from NO3-oxidation was 50% higher than that from OH-oxidation (Brown et al., 2009). These observations of NO3 and N2O5 loss processes over a wide range of conditions also demonstrated that the uptake coefficient for N2O5 (γN2O5) on aerosol particles displays a strong dependence on aerosol composition (Brown et al., 2006). A steady state analysis of NO3 and N2O5 sinks (Brown et al., 2003, 2006), indicated that γN2O5 can vary by over an order of magnitude, largely dependent on the sulfate mass or sulfate to organic ratio of the aerosol (Brown et al., 2006).

High mixing ratios of NO3 and N2O5 (up to 400 ppt and 2 ppb, respectively) were also reported in a subsequent aircraft study using the NOAA P-3 aircraft during the Texas Air Quality Study (TexAQS) in 2006 (Brown et al., 2011). Budget analyses for the campaign indicated that VOC oxidation at night was rapid, with the total rate of NO3-initiated oxidation typically 3 to 5 times that initiated by O3, and NO3 reactivity indicating the presence of unmeasured plumes of highly reactive VOCs (Brown et al., 2011). Loss of NO3 was dominated by its chemistry with unsaturated VOCs, with only 14 to 28% of NO3 loss occurring indirectly through heterogeneous chemistry of N2O5, although significant uncertainties in the N2O5 aerosol uptake coefficient were noted (Brown et al., 2011). Reactions of NO3 with peroxy radicals were estimated as contributing between 1 and 4% of the total NO3 loss, although no direct measurements of RO2 were available, with measurements of PAN used to estimate RO2 concentrations as being equal to the acetylperoxy (CH3C(O)O2) radical concentration produced by thermal decomposition of PAN (Brown et al., 2011).

Previous studies have shown that nighttime chemistry plays a significant role in defining the chemistry of the troposphere. However, there are significant uncertainties in the chemistry of the atmosphere at night. Many of these uncertainties are due to the lack of simultaneous observations of OH, HO2, NO3 and N2O5. Those observations
that do exist often occur within the centres of cities where NO emissions are high, with \( \text{NO}_3 \) concentrations thus kept low. These “inner city” conditions are not representative of most of the planet and thus do not offer suitable conditions for an evaluation of our understanding of nighttime chemistry.

In this paper we take advantage of simultaneous aircraft measurements of \( \text{OH}, \text{HO}_2, \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \), together with the concentrations of long lived components made away from recent emissions to analyse our understanding of nighttime chemistry as manifested by a constrained box model. We provide a brief overview of the campaign in Sect. 2 and measurement techniques in Sect. 3, followed by a description of the model approach in Sect. 4. In Sect. 5 we describe comparisons between modelled and observed concentrations and in Sect. 6 examine the processes controlling atmospheric composition at night. Potential sources of model uncertainty are discussed in Sect. 7, with suggestions for future work in Sect. 8 and conclusions drawn in Sect. 9.

2 The RONOCO campaign

The ROle of Nighttime chemistry in controlling the Oxidising Capacity of the Atmosphere (RONOCO) project took place in July 2010 and January 2011. Aircraft measurements were made at altitudes up to 6400 m over the UK and the North Sea onboard the UK FAAM BAe146 aircraft, based at East Midlands Airport (52.8°N, 1.3°W) during the campaign. The main objectives of the RONOCO campaign were to obtain comprehensive measurements of nighttime composition to further our understanding of nighttime chemistry thus enabling quantification of the key processes controlling atmospheric chemistry at night, and ultimately to facilitate assessment of the regional and global impacts of nighttime chemistry on air quality and climate change.

Measurements of \( \text{HO}_x \) were made on 16 flights throughout the campaign (7 flights in July 2010 and 9 flights in January 2011), while measurements of \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) were made on 17 flights (9 flights in July 2010 and 8 flights in January 2011). In our analysis we combine all of these flights into a single dataset. Figure 1 shows the locations of
HO\textsubscript{x}, NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} measurements made during RONOCO. We focus here on the analysis of measurements made at night, defined as periods when the solar zenith angle was greater than 99\(^\circ\), and thus do not include data from flights made in daylight hours or during dawn or dusk periods. Data from flight B537 (20 July 2010) has also been excluded from our analysis owing to a number of atypical observations during this flight which are discussed elsewhere (Kennedy et al., 2011; Walker et al., 2013).

3 Measurements during RONOCO

3.1 Detection of OH and HO\textsubscript{2}

OH and HO\textsubscript{2} radicals were measured by laser-induced fluorescence (LIF) spectroscopy at low pressure using the Fluorescence Assay by Gas Expansion (FAGE) technique (Heard and Pilling, 2003). The instrument has been described in detail elsewhere (Commane et al., 2010; Stone et al., 2011), and only a brief description is given here.

Ambient air from the aircraft exterior is drawn into a fluorescence cell maintained at pressures ranging from 1.9 Torr at sea level to 1.2 Torr at 6 km. The fluorescence cell has two excitation axes, with excess NO added at the second axis to titrate HO\textsubscript{2} to OH, enabling simultaneous detection of OH and HO\textsubscript{2}. OH radicals in both excitation axes are excited by laser light at \(\lambda \sim 308\) nm, generated by a solid state Nd:YAG pumped Ti:Sapphire laser system which is frequency tripled (Bloss et al., 2003). Channel photomultiplier tubes coupled to gated photon counters were used to detect the \(A^2 \Sigma^+ - X^2 \Pi_i\) OH fluorescence signal at \(\lambda \sim 308\) nm.

Calibration of the instrument is achieved by measurement of the fluorescence signal from known concentrations of OH and HO\textsubscript{2}, produced by the photolysis of water vapour, and was performed over a range of conditions before and after the RONOCO campaign. The instrument sensitivity to OH (\(C_{OH}\)) was determined to be \((2.50 \pm 0.1) \times 10^{-8} \text{ s}^{-1} \text{ cm}^3 \text{ mW}^{-1}\) and that to HO\textsubscript{2} (\(C_{HO_2}\)) was determined to be...
(1.33 \pm 0.5) \times 10^{-7} \text{s}^{-1} \text{cm}^3 \text{mW}^{-1}, \) with a 28\% 1\sigma calibration uncertainty for OH and HO$_2$. For OH, the 1\sigma limit of detection (LOD) was $1.8 \times 10^6 \text{cm}^{-3}$ for a 5 min averaging period during the summer campaign and $6.4 \times 10^5 \text{cm}^{-3}$ during the winter campaign. The HO$_2$ 1\sigma LOD was $6.9 \times 10^5 \text{cm}^{-3}$ for a 4 min averaging period during the summer and $6.0 \times 10^5 \text{cm}^{-3}$ during the winter, and is better than that for OH owing to lower losses on the walls of the sampling tube following the supersonic expansion. While instrument sensitivity does vary with the pressure in the detection cells, and thus with altitude, the cell pressures during RONOCO varied by less than 0.7 Torr (in the range 1.2 to 1.9 Torr). As discussed in detail by Commane et al. (2010), pressure dependent calibrations of the instrument are achieved by varying cell pressure using different sized pinholes through which ambient air is drawn in to the instrument to control the flow of gas in the cell. Over the range of cell pressures encountered during RONOCO, there is little variation $C_{\text{OH}}$ or $C_{\text{HO}_2}$ (Commane et al., 2010), and values reported here are thus the mean values determined during calibrations in this pressure range. Uncertainties associated with $C_{\text{OH}}$ and $C_{\text{HO}_2}$ are reflected in the 28\% 1\sigma calibration uncertainty for OH and HO$_2$. Further details regarding the FAGE instrument and calibration procedures will be provided by Walker et al. (2013).

3.2 Detection of NO$_3$ and N$_2$O$_5$

NO$_3$ and N$_2$O$_5$ were detected by broadband cavity enhanced absorption spectroscopy (BBCEAS), as described in detail by Kennedy et al. (2011). Briefly, air is drawn into three 94 cm long high finesse optical cavities, with each bound by two highly reflective mirrors, which are irradiated with collimated light from an incoherent broadband continuous wave light source. Each cavity is coupled to a spectrometer interfaced to a charge coupled device (CCD) detector by fibre optic bundles, where the wavelength dependent light intensity transmitted through the cavity is recorded.

NO$_3$ is identified and measured via its strong $B^2E' - X^2A'_2$ electronic transition centred around 662 nm, with light provided by a red light emitting diode (LED). N$_2$O$_5$ is
measured in a separate cavity maintained at 80°C following its thermal dissociation to NO₃ and NO₂ at 120°C in a heater situated prior to the cavity entrance, and thus measured as the sum of ambient NO₃ and thermally dissociated N₂O₅. The third cavity enables detection of NO₂ using light provided by a blue LED with output centred around 460 nm.

A crystalline source of N₂O₅, stabilised at temperatures between −80 and −77°C, was used to provide known amounts of NO₃ and N₂O₅ to facilitate calibration of the instrument in the laboratory. The in-flight 1σ LOD (determined at a pressure of 0.7 bar) for NO₃ was found to be 1.1 ppt for a 1 s integration time, with a corresponding LOD of 2.4 ppt for NO₃ + N₂O₅.

3.3 Supporting measurements

Measurements from several other instruments onboard the BAe146 during the RONOCO campaign have been used in the analysis presented here. Details of these supporting measurements are summarised in Table 1.

4 Model approach

Observations of OH, HO₂, NO₃ and N₂O₅ have been interpreted using the Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC), which is described in detail by Emmerson and Evans (2009) and Stone et al. (2010). DSMACC is a zero-dimensional model using the Kinetic Pre-Processor (KPP) (Sandu and Sander, 2006), and in this work uses a chemistry scheme described by the Master Chemical Mechanism version 3.2 (MCM v3.2 http://mcm.leeds.ac.uk/MCM/home.html) (Jenkin et al., 2003; Saunders et al., 2003). The MCM contains near explicit degradation schemes for 143 primary species, resulting in 6700 species in approximately 17 000 reactions and representing the most detailed and comprehensive chemistry scheme available for modelling tropospheric composition. Simulations reported here use degradation

Heterogeneous loss of several species (OH, HO\textsubscript{2}, CH\textsubscript{3}O\textsubscript{2}, NO\textsubscript{3}, N\textsubscript{2}O\textsubscript{5} and HNO\textsubscript{3}) to aerosol surfaces was represented in the model by parameterisation of a first-order loss process to the aerosol surface (Ravishankara, 1997):

\begin{equation}
k' = c_g A \gamma_x / 4
\end{equation}

\begin{equation}
c_g = (8RT/\pi M_w)^{1/2}
\end{equation}

where \(k'\) is the first-order rate coefficient for heterogeneous loss, \(c_g\) is the mean molecular speed of the gas (Eq. 1), \(A\) is the aerosol surface area per unit volume and \(\gamma_x\) is the uptake coefficient for species \(X\), \(R\) is the universal gas constant, \(T\) is the temperature and \(M_w\) is the molecular weight of the gas. For HO\textsubscript{2}, \(\gamma_{HO_2} = 0.028\) is used, based on the mean value reported by the parameterisation by Macintyre and Evans (2011). For N\textsubscript{2}O\textsubscript{5}, \(\gamma_{N_2O_5} = 0.020\) is used, based on the mean value reported from the parameterisation by Evans and Jacob (2005). Sensitivity to aerosol uptake coefficients is discussed in Sect. 7.2.

An additional first-order loss process for each species in the model is also included to represent deposition processes, with the first-order rate set to be equivalent to a lifetime of approximately 24 h. Model sensitivity to this parameter is discussed in Sect. 7.1.

All aircraft measurements are merged onto a 60 s timebase. Time points with observations of OH or HO\textsubscript{2} are modelled if observations of physical state (latitude, longitude, pressure, temperature and water vapour concentration), aerosol surface area and concentrations of CO, O\textsubscript{3}, NO\textsubscript{2}, NO\textsubscript{3} and VOCs are available. A summary of concentrations used to constrain the model is given in Table 2. Observed concentrations of CO, O\textsubscript{3}, H\textsubscript{2}O, VOCs and aerosol surface area for each 60 s time point are fixed and held constant throughout the corresponding model run, with concentrations
of CH$_4$ and H$_2$ kept constant at values of 1770 ppb (NOAA CMDL flask analysis, ftp://ftp.cmdl.noaa.gov/ccg/ch4/) and 550 ppb (Ehhalt and Rohrer, 2009; Novelli et al., 1999) respectively. Species which were not observed are set initially to zero in the model.

Constraints on nitrogen oxides (NO, NO$_2$, NO$_3$, N$_2$O$_5$, HONO and HO$_2$NO$_2$) were applied using the method described by Stone et al. (2010), with the primary constraint placed on NO$_2$. Thus, the initial concentration of NO$_2$ in the model is set to its observed value and the concentrations of each nitrogen oxide species, including NO$_2$, is permitted to vary according to its photochemistry as the model runs forwards. At the end of each 24 h period in the model, the calculated concentration of NO$_2$ is compared to its observed concentration, and the concentrations of all nitrogen oxide species are fractionally increased or decreased such that the modelled and observed concentrations of NO$_2$ are the same. The model is integrated forwards in time with diurnally varying photolysis rates until a diurnal steady state is reached, typically requiring between 5 and 10 days. Thus at the point of comparison between the model and observations we have a modelled NO$_2$ concentration equal to the observed concentration, together with concentrations of the other NO$_x$ species (NO, NO$_3$, N$_2$O$_5$, HONO, HO$_2$NO$_2$) consistent with that NO$_2$ concentration, the concentration of the other measured species, and the time since darkness fell.

Following the work of Fuchs et al. (2011), model calculations described in this work include representation of potential RO$_2$ interferences in LIF measurements of HO$_2$. We thus describe observed to modelled comparisons of HO$_2^*$, where HO$_2^* = \text{HO}_2 + f\text{RO}_2$, with the factor $f$ derived from a combination of experimental parameters and MCM chemistry, as described in the appendix. For the RONOCO campaign, potential interferences in HO$_2$ measurements are expected to be small on average, with HO$_2^* = [1.15 \times \text{HO}_2] + 2 \times 10^5 \text{ cm}^{-3}$.
5 Model performance

Figure 2 shows the model performance for HO$_2^*$, NO$_3$ and N$_2$O$_5$. Modelled concentrations of OH were on the order of 10$^4$ cm$^{-3}$ (mean (2.43 ± 2.32) $\times$ 10$^4$ cm$^{-3}$; median $= 1.69 \times 10^4$ cm$^{-3}$) and were consistently below the 1$\sigma$ instrumental limits of detection of 1.8 $\times$ 10$^6$ cm$^{-3}$ in summer and 6.4 $\times$ 10$^5$ cm$^{-3}$ in winter (for 5 min averaging periods). We do not consider the model performance for OH in any more detail.

The model displays a tendency to underpredict HO$_2^*$ and overpredict NO$_3$ and N$_2$O$_5$, as shown in Fig. 2. For HO$_2^*$, the line of best fit is given by $[\text{HO}_2^*]_{\text{mod}} = (0.45 \times [\text{HO}_2^*]_{\text{obs}}) + 2.95 \times 10^6$ cm$^{-3}$, with that for NO$_3$ given by $[\text{NO}_3]_{\text{mod}} = (1.75 \times [\text{NO}_3]_{\text{obs}}) - 2.33$ ppt and the best fit line for N$_2$O$_5$ described by $[\text{N}_2\text{O}_5]_{\text{mod}} = (1.46 \times [\text{N}_2\text{O}_5]_{\text{mod}}) - 42.43$ ppt.

Model underpredictions for nighttime HO$_2$ of a similar magnitude have been observed in a number of previous studies, and, where observations are available, model underpredictions of HO$_2$ tend to coincide with underpredictions of RO$_2$ and overpredictions of NO$_3$. Measurements of peroxy radicals in the Black Forest, Germany, were underestimated by a factor of 3 to 4, coinciding with an overprediction of NO$_3$ by a factor of $\sim 2$, with discrepancies for both NO$_3$ and peroxy radicals reconciled by consideration of the impact of unmeasured monoterpenes (Mihelcic et al., 1993). Observations of HO$_2$ at night on Rishiri Island, Japan, were strongly correlated with monoterpene emissions (Kanaya et al., 2002, 2007a) and were also generally underestimated by model calculations (Kanaya et al., 1999; 2002, 2007a). Model calculations for the Southern Oxidant Study (SOS) in Nashville, USA, underpredicted nighttime observations of HO$_2$ by a factor of 2 to 8, partly owing to the limited NO$_3$ + VOC and NO$_3$ + RO$_2$ chemistry in the model (Martinez et al., 2003). Model underpredictions for nighttime HO$_2$ have also been reported for campaigns near London (Emmerson and Carslaw, 2009), in New York (Ren et al., 2003, 2006) and Tokyo (Kanaya et al., 2007a), with investigation of the model discrepancy for the Tokyo campaign indicating the presence of unmeasured VOCs which, if included in the model, could reconcile the modelled HO$_2$
with the observations (Kanaya et al., 2007). The presence of unmeasured VOCs was also thought to be responsible for discrepancies between observed concentrations of NO$_3$ and calculations of NO$_3$ reactivity from measured sources and sinks during the TexAQS campaign (Brown et al., 2011).

In order to show the important processes occurring within the model and to thus provide insights into improving model fidelity we now diagnose the chemical processes occurring within the model. We start our analysis with the budgets of NO$_3$ and N$_2$O$_5$, we then turn our attention to the wider RO$_x$ family and finally to HO$_x$, HO$_2$ and OH.

6 Budget analyses

6.1 NO$_3$ and N$_2$O$_5$ budgets

NO$_3$ and N$_2$O$_5$ rapidly interconvert, with reaction of NO$_3$ with NO$_2$ and thermal decomposition of N$_2$O$_5$ occurring at a faster rate ($\sim 3 \times 10^7$ cm$^{-3}$ s$^{-1}$) than the conversion between OH and HO$_2$ ($\sim 3 \times 10^4$ cm$^{-3}$ s$^{-1}$ during RONOCO). This leads us to define the NO$_{3x}$ family, where NO$_{3x} = NO_3 + N_2O_5$. Production of NO$_{3x}$ occurs almost exclusively through the production of NO$_3$ by O$_3$ + NO$_2$, with minor production channels ($< 0.01 \%$) including OH + HNO$_3$ and reactions of Criegee biradicals with NO$_2$.

Figure 3 shows the loss pathways for NO$_{3x}$ at night, displayed as the probability distribution functions for the percentage contribution of each process to the total NO$_{3x}$ loss. The largest loss of NO$_{3x}$ is typically due to heterogeneous processes, through the uptake and hydrolysis of N$_2$O$_5$ on aerosol surfaces, representing 64 % of the total NO$_{3x}$ loss averaged over all simulated data points. However, there is high variability in the fraction of the total loss through heterogeneous processes, as displayed in Fig. 3. Reactions of NO$_3$ with VOCs comprises 10 % of the total NO$_{3x}$ loss on average, with a maximum value of 40 % when VOC concentrations are high and aerosol loadings low. Loss of NO$_{3x}$ through reactions of NO$_3$ with peroxy radicals represents 19 % of the total (11 % from organic RO$_2$ and 8 % from HO$_2$) on average, but there are data points
where the loss of NO$_{3x}$ through such reactions reaches 71%. Thus, although in a mean sense the loss of NO$_{3x}$ from the atmosphere is dominated by the heterogeneous uptake of N$_2$O$_5$ onto aerosol, there are significant other processes which can dominate under certain conditions.

These results are consistent with previous studies. Modelling of the NEAQS 2004 shipborne campaign using the MCM revealed similar losses of NO$_3$ to RO$_2$ in the marine boundary layer to those presented here, with a mean contribution of 19% to the total gas phase NO$_3$ loss and a maximum of up to 60% (Sommariva et al., 2009). In contrast, analysis of NO$_3$ budgets for the airborne TexAQS 2006 campaign suggested that only 1 to 4% of the total NO$_{3x}$ loss occurred as a result of reactions of NO$_3$ with peroxy radicals (Brown et al., 2011). However, no peroxy radical measurements were made during TexAQS, and RO$_2$ concentrations were estimated using observations of PAN and its thermal decomposition rate, and were thus almost certainly a significant underestimate, as noted in the analysis (Brown et al., 2011). Model calculations in this work indicate that the peroxy radical derived from thermal decomposition of PAN represents a maximum of 15% of the total organic peroxy radical concentration during RONO$_2$, with a median value of 0.3%.

6.2 RO$_x$ radical budgets

RO$_x$ radicals (RO$_2$ + RO + HO$_2$ + OH) play a central role in the chemistry of the troposphere. Figure 4 shows the production and loss processes for RO$_x$ radicals at night during RONO$_2$ (note that the discussion in this section concerns HO$_2$ and not HO$_2^*$). Initiation of radicals at night, and thus of nighttime oxidation chemistry, is dominated by reactions of NO$_3$ with unsaturated VOCs, with a mean campaign contribution of 80% compared to 18% for radical production by alkene ozonolysis reactions. Figure 5 shows that of the VOCs measured during the campaign (Table 2), the dominant species in terms of NO$_3$ reactivity are iso-butene (36%), trans-2-butene (27%) and, during the summer campaign, isoprene (10%), with O$_3$ reacting mainly with trans-2-butene (51%), propene (22%), ethene (13%) and iso-butene (5%). Reactions of NO$_3$ with
aldehydes also result in radical production at night, with NO$_3$ + HCHO contributing the greatest influence from aldehyde species.

Figure 4 shows that radical loss is controlled by a number of processes. Production of peroxides, through RO$_2$ + HO$_2$ and HO$_2$ + HO$_2$, represents 21% of the RO$_x$ radical loss, followed by production of HNO$_3$ by OH + NO$_2$ (16%), decomposition reactions of RO radicals to produce stable products (14%) and heterogeneous losses (2%). The large fraction of remaining loss processes (47% of the total) is comprised largely of a myriad of RONO$_2$ and RO$_2$NO$_2$ production routes.

Overall, reactions of NO$_3$ with VOCs typically control the production of radicals during the campaign, with the unsaturated C$_4$ compounds dominating. There are a significant number of radical loss processes which produce organic nitrogen compounds, peroxides and nitric acid.

### 6.3 HO$_x$ radical budgets

The processes controlling production and loss of nighttime HO$_x$ (HO$_x$ = OH + HO$_2$) radicals during RONOCO are shown in Fig. 6. Alkox radical (RO), produced primarily following production of RO$_2$ from NO$_3$ + alkene reactions and the subsequent reactions of RO$_2$ with NO$_3$, are a major source of HO$_x$, producing HO$_2$ through RO + O$_2$ reactions and on average representing 63% of the total HO$_x$ production. Specifically, the reaction of methoxy radicals (CH$_3$O) with O$_2$ dominates the HO$_x$ production from RO radicals (31% of the total HO$_x$ production), with CH$_3$O primarily produced at night by CH$_3$O$_2$ + NO$_3$, and nighttime CH$_3$O$_2$ production primarily occurring through OH-initiated oxidation of CH$_4$ (48%) and alkene ozonolysis reactions (37%). Alkene ozonolysis reactions also produce OH and HO$_2$ radicals directly through the decomposition of Criegee intermediates, and are responsible for 20% of the total HO$_x$ production. A further 17% of HO$_x$ radicals are generated as a result of direct HO$_2$ production by NO$_3$ + HCHO, using model calculated HCHO concentrations.

Reactions of HO$_2$ producing peroxides (HO$_2$ + RO$_2$ and HO$_2$ + HO$_2$) and formation of HNO$_3$ by the reaction of OH with NO$_2$ represent major sinks for HO$_x$ radicals,
comprising 23 % and 25 % of the total loss, respectively. Heterogeneous loss of OH and HO$_2$, primarily through aerosol uptake of HO$_2$, represents 11 % of the total HO$_x$ sink, with the remainder occurring primarily through reactions of OH with VOCs, and OH + CH$_4$ alone constituting 19 % of the total HO$_x$ sink.

Figure 7 shows the processes controlling modelled nighttime HO$_2$ concentrations during the campaign. Production of HO$_2$ is dominated by RO + O$_2$ reactions, comprising 42 % of the total on inclusion of CH$_3$O + O$_2$. Despite the low OH concentrations at night, there is also significant HO$_2$ production via OH + CO (31 %). Alkene ozonolysis reactions represent 5 % of the total HO$_2$ production, on average, with reactions of HCHO with NO$_3$ and OH contributing 8 % and 6 % to the total HO$_2$ production, respectively.

The dominant loss pathways for HO$_2$ are through reaction with NO$_3$ (45 % of the total) and O$_3$ (27 %), with both reactions representing radical propagation routes. Reactions of HO$_2$ with other peroxy radicals (both HO$_2$ and RO$_2$) constitute 17 % of the HO$_2$ loss, while uptake onto aerosols contributes only 7 % to the total HO$_2$ loss.

Production of OH at night occurred primarily through the reactions of HO$_2$ with NO$_3$ (53 %) and O$_3$ (33 %), with OH loss processes dominated by its reactions with CO (35 %), NO$_2$ (21 %) and CH$_4$ (12 %).

### 6.4 Summary of budget analyses

Figure 8 shows a summary of the processes controlling nighttime composition during RONOCO. In general we see a significant coupling between the NO$_3$x and RO$_x$ families. The NO$_3$x family is primarily controlled by the balance between its production from the reaction of NO$_2$ and O$_3$ and its loss predominantly to aerosols through N$_2$O$_5$. However, the component of the loss not through this path (36 %, on average) is responsible for a dynamic organic chemistry. The reactions of NO$_3$ with alkenes, and of NO$_3$ with C$_4$-alkenes in particular, represent the dominant radical source at night during RONOCO, with radical losses owing to a combination of heterogeneous processes, peroxide formation (through HO$_2$ + RO$_2$ and HO$_2$ + HO$_2$), decomposition of alkoxy radicals and
formation of HNO$_3$ through the reaction of OH with NO$_2$. The propagation of the radical oxidation chemistry, which during the day would be controlled by NO, is at night controlled by NO$_3$. Thus the NO$_3$ radical acts both as a chain initiator (like OH during the day) and the chain propagator (like NO during the day).

Production of HO$_x$ radicals is typically dominated by reactions of alkoxy (RO) radicals with O$_2$, with a minor contribution from alkene ozonolysis reactions. Loss of HO$_x$ is largely controlled by HO$_2$ + RO$_2$ reactions and OH + NO$_2$, while the loss of HO$_2$ is typically dominated by the radical propagations reactions HO$_2$ + NO$_3$ and HO$_2$ + O$_3$.

Now that the chemistry occurring in the model during the night has been described, the model sensitivity to various uncertainties can be evaluated so that the reasons for the model overprediction of NO$_3$x and underprediction of HO$_2$ can be investigated.

7 Sources of model uncertainties

Model calculations for RONOCO display a tendency to underpredict HO$_2^*$ whilst overpredicting NO$_3$ and N$_2$O$_5$. In this section we investigate the impact of potential sources of uncertainty on models of nighttime chemistry and composition. First we consider the impact of the timescale adopted in the model to describe physical losses of long-lived species in the model. Secondly, given the role of heterogenous uptake of N$_2$O$_5$ in determining NO$_3$x loss processes and the significant uncertainty in uptake coefficients in the literature (Brown et al., 2006, 2009, 2011; Escoreia et al., 2010; Tang et al., 2010; Badger et al., 2006; Thornton and Abbatt, 2005; Hallquist et al., 2003; Thornton et al., 2003; Kane et al., 2001; Hu and Abbatt, 1997; Fried et al., 1994; Van Doren et al., 1991; Hanson and Ravishankara, 1991; Mozurkewich and Calvert, 1998) we investigate the model sensitivity to $\gamma_{N_2O_5}$. We then focus on model uncertainties which have the potential to rectify both the model underprediction of HO$_2^*$ and overprediction of NO$_3$x, i.e. parameters which are simultaneously sinks of NO$_3$x and sources of HO$_x$ such as the reaction rate between NO$_3$ and RO$_2$ and the impact of missing VOCs.
7.1 Impact of timescale for physical loss

As described in Sect. 4, model calculations reported here include a first-order loss process to represent continuous physical loss processes to prevent the build-up of unmeasured species in the model. In our previous work as part of the African Monsoon Multidisciplinary Analyses (AMMA) campaign we investigated the impact of the rate of physical loss on HO\textsubscript{x} simulations (Stone et al., 2010). Results of model simulations for daytime chemistry during AMMA indicated little impact of the physical loss rate on modelled HO\textsubscript{2} concentrations, with the lifetimes with respect to physical loss varied between 1 h and 5 days (Stone et al., 2010). Figure 9a shows the impact of the modelled timescale for physical loss on the nighttime RONOCO simulations for HO\textsubscript{2} and NO\textsubscript{3x}. There is little impact on modelled HO\textsubscript{2} or NO\textsubscript{3x} on variation of the lifetime for physical loss from 12 to 48 h. Thus it does not seem likely that the simplistic treatment of deposition or mixing processes considered in the model is likely to explain the overall performance of the model.

7.2 Impact of \( \gamma \text{N}_2\text{O}_5 \)

Both laboratory and field studies of the value of \( \gamma \text{N}_2\text{O}_5 \) are highly variable (Brown et al., 2006, 2009, 2011; Escoreia et al., 2010; Tang et al., 2010; Macintyre and Evans, 2010; Badger et al., 2006; Thornton and Abbatt, 2005; Hallquist et al., 2003; Thornton et al., 2003; Kane et al., 2001; Hu and Abbatt, 1997; Fried et al., 1994; Van Doren et al., 1991; Hanson and Ravishankara, 1991; Mozurkewich and Calvert, 1998) with values varying over several orders of magnitude (10\textsuperscript{-4} to > 0.1). The base model uses a fixed value of \( \gamma \text{N}_2\text{O}_5 = 0.02 \), based on the global mean value (Evans and Jacob, 2005). Figure 9b shows the impact of varying \( \gamma \text{N}_2\text{O}_5 \) from 0 to 1 on the on the median modelled to observed ratios of HO\textsubscript{2} and NO\textsubscript{3x}. The best fit values for NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} (i.e. median modelled to observed ratio closest to unity) are achieved when \( \gamma \text{N}_2\text{O}_5 \sim 0.05 \) (which is within the range of laboratory studies). However, these higher values of \( \gamma \text{N}_2\text{O}_5 \) result in lower modelled HO\textsubscript{2} concentrations since the increased loss of NO\textsubscript{3x} to aerosol surfaces...
decreases the rate of radical production from NO₃-initiated oxidation processes and widens the gap between observed and modelled HO₂ concentrations.

Heterogeneous uptake of HO₂ was found to constitute a relatively minor loss process for HO₂ (7 % of the total) and ROₓ radicals (< 2 % of the total), as discussed in Sect. 6, and there is thus little model sensitivity to γ_HO₂.

### 7.3 Impact of \(k_{NO₃+RO₂}\)

The reaction between peroxy (RO₂) radicals and NO₃ are central to the production of HO₂ at night and play an important role in removing NO₃. There, have been however, very few studies of this important class of compounds (see for example Vaughan et al., 2006) compared to equivalent studies of daytime radical reactions. The MCM considers three different reactions rates for this class, one for CH₃O₂, one for RC(O)O₂ and one for all other RO₂, with no temperature dependence considered and all reaction products assumed to be analogous to the corresponding reaction of the RO₂ radical with NO.

Figure 9c shows the sensitivity of the mean modelled to observed ratios of HO₂ and NO₃x on \(k_{NO₃+RO₂}\), where all \(k_{NO₃+RO₂}\) have been increased by the same factor. We find that increases in \(k_{NO₃+RO₂}\) lead to increases in modelled HO₂∗ and decreases in modelled NO₃x, but large (> 10) changes in \(k_{NO₃+RO₂}\) are required to significantly improve the model success. However, there have been no measurements of the kinetics of peroxy radicals derived from NO₃-initiated oxidation, which are significant at night, and there may be significant differences in the behaviour of peroxy radicals derived from OH- and O₃-initiated oxidation, which are used to estimate \(k_{NO₃+RO₂}\) in the model, and those derived from NO₃-initiated oxidation. The presence of unknown VOCs, and thus of unknown RO₂ radicals, leads to further uncertainties in \(k_{NO₃+RO₂}\). The available database of laboratory data concerning radical processing in nighttime atmospheres is extremely limited.
7.4 Impact of VOC concentrations

Reactions of NO$_3$ with VOCs are important for both NO$_3$ loss and RO$_x$ radical production. Previous studies have invoked unmeasured VOCs to explain both model overpredictions of NO$_3$ and underpredictions of HO$_2$.

Figure 10 displays the comparison between modelled and observed concentrations of HO$_2$, NO$_3$ and N$_2$O$_5$ for a model run in which the concentrations of all species containing C=C were set to zero. Compared to the base model run (Fig. 2), the run with no unsaturated hydrocarbons shows a marked increase in modelled concentrations of NO$_3x$ and very little HO$_2$ production, demonstrating the significance of unsaturated VOCs as both a sink of NO$_3x$ and a source of HO$_2$. The presence of unquantified or unmeasured VOCs thus has the potential to improve model simulations for both HO$_2$ and NO$_3x$.

Figure 9d shows the impact of increasing the concentration of unsaturated VOCs on the mean modelled to measured ratios of HO$_2$, NO$_3$ and N$_2$O$_5$, represented as the increase in reactivity towards NO$_3$, where the reactivity is given by $\sum k_{\text{NO}_3,\text{VOC}}[\text{VOC}]$. An increase of approximately 4 times the total observed C=C reactivity results in significant improvements to model simulations for HO$_2^*$ and simultaneously improves the modelled NO$_3x$.

Thus significant concentrations of unmeasured VOCs during RONOCO may explain the model measurement discrepancy. Previous work using two-dimensional gas chromatography (2D-GC) in urban environments isolated and classified over 500 different VOCs not routinely measured, with significant impacts on atmospheric chemistry (Lewis et al., 2000). 2D-GC analyses of the whole air samples (WAS) collected during the RONOCO campaign have also revealed the presence of a large number of VOCs which are not routinely measured (Lidster et al., 2013). Although the 2D-GC analyses identify the presence of additional species, and, based on expected relationships between polarity and boiling point, can identify the presence of additional unsaturated VOCs, the current absence of readily available calibration standards for long-chain
alkenes and other unsaturated VOCs makes full identification and quantification of such species impractical.

One class of compounds which could have a significant impact on the nighttime chemistry is monoterpenes. A model run in which \( \alpha \)-pinene was included at a concentration equivalent to the limit of detection (131 to 280 ppt) for the proton transfer mass spectrometer (PTR-MS) onboard the BAe146 during RONOCO decreased the median modelled to observed ratios for NO\(_3\) and N\(_2\)O\(_5\) from 1.68 and 1.64, respectively, for the base model run to 0.76 and 0.82, respectively. Thus total monoterpenes in the 100 ppt range would significantly improve the fidelity of the NO\(_3\) and N\(_2\)O\(_5\) simulation. However, the median modelled to observed ratio for HO\(_2^*\) was reduced from 0.56 for the base model run to 0.34 on inclusion of \( \alpha \)-pinene. This reduction is predominantly due to \( \alpha \)-pinene derived RO radicals undergoing internal rearrangements to produce carbonyl compounds and NO\(_2\), in preference to reaction with O\(_2\) to produce carbonyl compounds and HO\(_2\) as exhibited by other unsaturated VOCs. Similarly, inclusion of styrene in the model at concentrations equivalent to those observed for ethylbenzene (median \( \sim \) 8 ppt) reduced the median modelled to observed ratios for NO\(_3\) and N\(_2\)O\(_5\) to 1.31 and 1.11, respectively, but also reduced the median modelled to observed ratio for HO\(_2^*\) to 0.29 owing to similar behaviour of styrene-derived RO\(_2\) and RO radicals to those derived from monoterpenes. Low concentrations of species such as monoterpenes and styrene which display high reactivity towards NO\(_3\) can thus have a significant impact on NO\(_3x\) concentrations, and the presence of such compounds may reduce the N\(_2\)O\(_5\) aerosol uptake coefficient required to achieve model success for NO\(_3x\), but the larger hydrocarbons appear to be less efficient at generating HO\(_2\) and cannot fully explain the model discrepancies observed for this work.

We thus conclude that unquantified species containing C=C could reconcile model and measured NO\(_3\), N\(_2\)O\(_5\) and HO\(_2\). However, their exact nature remains unknown. Any compound would have to be heavy enough to not be measured using the GC-FID system yet small enough not to exhibit the tendency for radical internal rearrangement which limits the ability to produce HO\(_2\).
8 Future studies

The RONOCO dataset is one of the few datasets that has made extensive nighttime observations of both HO\textsubscript{x} and NO\textsubscript{3x}, particularly in regions with significant NO\textsubscript{x} concentrations but remote from primary sources. There is a paucity of previous studies of these chemical regimes leading to uncertainty about the chemistry occurring in such chemical systems. The uncertainties found in this study could be reduced by providing direct observations of higher alkenes and terpenes at low levels. Given the high modelled RO\textsubscript{2} to HO\textsubscript{2} ratios, a measurement of RO\textsubscript{2} concentrations would provide a significant constraint on the chemistry. From a laboratory perspective, measurements of RO\textsubscript{2} + NO\textsubscript{3} rate coefficients for a variety of RO\textsubscript{2} radicals and under a range of temperatures and pressures would also improve our understanding of this system.

9 Conclusions

Nighttime measurements of HO\textsubscript{2}\textsuperscript{*}, NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} over the UK during the RONOCO project have been compared to box model calculations simulations using the MCM. The model tends to underestimate HO\textsubscript{2}\textsuperscript{*}, whilst overestimating NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5}. We find that NO\textsubscript{3} + VOC chemistry is the most significant source of RO\textsubscript{x} radicals in the model, and that reactions of NO\textsubscript{3} with peroxy radicals dominate radical propagation. We observe a strong coupling between HO\textsubscript{2} and NO\textsubscript{3} at night, in both the measurements and the model calculations, although there are significant uncertainties associated with modelling of nighttime oxidation chemistry. Model simulations for NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} can be improved through the use of increased aerosol uptake coefficients for N\textsubscript{2}O\textsubscript{5}, but the improvements for NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} are at the expense of model success for HO\textsubscript{2}. Improvements to model simulations for HO\textsubscript{2}, NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} can be achieved through the inclusion of additional unsaturated VOCs in the model. However, these missing VOCs would have to be in significant concentrations and have a significant HO\textsubscript{2} yield.
We conclude that the inclusion of appropriate NO\textsubscript{3} + VOC and NO\textsubscript{3} + RO\textsubscript{2} chemistry is essential to successful model simulations of tropospheric oxidation at night.

**Model treatment of potential RO\textsubscript{2} interferences in HO\textsubscript{2} measurements**

Following the work of Fuchs et al. (2011), the Leeds aircraft FAGE instrument was investigated for potential interferences in measurements of HO\textsubscript{2} from alkene-derived RO\textsubscript{2} radicals. Experimental conditions will be discussed in detail by Whalley et al. (2013), and will be provided only briefly here. Interference testing was conducted using the FAGE calibration setup described by Commane et al. (2010), in which equal amounts of OH and HO\textsubscript{2} are produced by passing a known flow (\(\sim 50\text{ dm}^3\text{ min}^{-1}\)) of humidified ultra-high purity air (BTCA 178, BOC Special Gases) across a low pressure mercury lamp of known actinic flux:

\[
\begin{align*}
\text{H}_2\text{O} + h\nu (\lambda = 184.9\text{ nm}) & \rightarrow \text{H} + \text{OH} \\
\text{H} + \text{O}_2 + M & \rightarrow \text{HO}_2 + M 
\end{align*}
\]

In order to generate RO\textsubscript{2} radicals in the flow an excess of the parent hydrocarbon was added to the flow, such that the OH radicals produced were converted stoichiometrically to RO\textsubscript{2}, resulting in equal amounts of HO\textsubscript{2} and RO\textsubscript{2} in the flow:

\[
\begin{align*}
\text{OH} + \text{RH} & \rightarrow \text{R} + \text{H}_2\text{O} \\
\text{R} + \text{O}_2 + M & \rightarrow \text{RO}_2 + M 
\end{align*}
\]

Comparison of observed signals in the HO\textsubscript{2} detection cell with and without addition of the parent hydrocarbon thus enables determination of the RO\textsubscript{2} interference. For this work, interferences were investigated for RO\textsubscript{2} radicals derived from ethene giving an interference of \((39.7 \pm 4.8)\%\) for 1 : 1 HO\textsubscript{2} : RO\textsubscript{2} mixtures.

The chemistry responsible for producing RO\textsubscript{2} interferences in HO\textsubscript{2} measurements by FAGE appears to be well described by the MCM (Fuchs et al., 2011; Whalley et al., 9543)
2013), and the total potential interference in the measurements made during RONOCO were thus estimated with an MCM based box model. The box model, constrained to the characteristics of the FAGE instrument (cell pressure of 1.8 Torr; cell temperature of 260 K; NO concentration \( \sim 10^{14} \text{ cm}^{-3} \)) and initialised with equal amounts of HO\(_2\) and all organic RO\(_2\) radicals described in the MCM was run forwards in time until the modelled interferences from RO\(_2\) radicals derived from ethene reached the experimentally derived values of 40 \%. An interference factor, \( f \), was then determined from the model output for each RO\(_2\) radical, where \( f \) is the fractional change in the modelled HO\(_2\) signal (i.e. the amount of OH produced) for a 1 : 1 mixture of HO\(_2\) and RO\(_2\). The modelled \( \text{HO}_2^\ast \) (the combination of HO\(_2\) and potential interferences from RO\(_2\)) was subsequently determined for each time point using \( \text{HO}_2^\ast = \text{HO}_2 + f\text{RO}_2 \) for direct comparison with the FAGE measurements. Figure A1 shows the comparison between modelled \( \text{HO}_2^\ast \) and HO\(_2\) for RONOCO, indicating that interferences during the campaign were generally small.

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References


Whalley, L. K., Lewis, A. C., McQuaid, J. B., Purvis, R. M., Lee, J. D., Stemmiller, K., Zellweger, C., and Ridgeon, P.: Two high-speed, portable GC systems designed for the mea-

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Table 1. Supporting measurements made onboard the BAe146 aircraft during the RONOCO project and used in the model analysis presented here.

<table>
<thead>
<tr>
<th>Species measured</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>Aero Laser AL5002 Fast Carbon Monoxide Monitor (Gerbig et al., 1999).</td>
</tr>
<tr>
<td>O₃, NO, NO₂</td>
<td>TECO 49C UV absorption.</td>
</tr>
<tr>
<td>NO, NO₂</td>
<td>FAAM fast NOₓ instrument; TECO 42C analyser using heated Molybdenum filament to convert NO₂ to NO with detection of NO by chemiluminescence (Brough et al., 2003).</td>
</tr>
<tr>
<td>NO₂, ΣANs, ΣPNs</td>
<td>Thermal decomposition of ΣANs and ΣPNs to NO₂; detection of NO₂ by laser-induced fluorescence (LIF) (Dari-Salisburgo et al., 2009; Di Carlo et al., 2012).</td>
</tr>
<tr>
<td>PAN</td>
<td>Gas chromatography with electron capture detection (Whalley et al., 2004).</td>
</tr>
<tr>
<td>VOCs</td>
<td>Gas chromatography with flame ionisation detection (GC-FID) (Hopkins et al., 2006).</td>
</tr>
<tr>
<td>Aerosol surface area</td>
<td>Scanning mobility particle sizer (SMPS) for particles of diameter 20–350 nm.</td>
</tr>
</tbody>
</table>

The NO₂ measurements used to constrain the model were made by the LIF instrument (Dari-Salisburgo et al., 2009; Di Carlo et al., 2012). ΣANs = sum of alkyl nitrates; ΣPNs = sum of peroxy nitrates; PAN = peroxy acetyl nitrate; VOCs = volatile organic compounds.

Aerosol surface area is estimated for ambient relative humidity based on the measured dry size distribution and composition.
Table 2. Summary of inputs to the model. Zero values indicate measurements below the instrumental limits of detection.

<table>
<thead>
<tr>
<th>Species</th>
<th>Mean ±1σ</th>
<th>Median</th>
<th>Range</th>
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</thead>
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<tr>
<td>O₃/ppb</td>
<td>37.0 ± 8.1</td>
<td>35.5</td>
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</tr>
<tr>
<td>CO/ppb</td>
<td>110.4 ± 27.1</td>
<td>99.9</td>
<td>71–250</td>
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<tr>
<td>H₂O/ppm</td>
<td>10418 ± 2425</td>
<td>10.491</td>
<td>178–15 509</td>
</tr>
<tr>
<td>NO₂/ppt</td>
<td>1614.4 ± 1749.2</td>
<td>946.7</td>
<td>66–14 570</td>
</tr>
<tr>
<td>NO/ppt</td>
<td>24.6 ± 278.9</td>
<td>0</td>
<td>0–4501</td>
</tr>
<tr>
<td>ethane/ppt</td>
<td>1109.5 ± 882.0</td>
<td>940.8</td>
<td>0–3208</td>
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<tr>
<td>propane/ppt</td>
<td>414.0 ± 416.5</td>
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<td>iso-butane/ppt</td>
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<td>50.4 ± 57.1</td>
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<td>0–455</td>
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<td>methypentanes/ppt</td>
<td>28.3 ± 31.2</td>
<td>21.3</td>
<td>0–224</td>
</tr>
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<td>n-hexane/ppt</td>
<td>17.0 ± 18.3</td>
<td>11.9</td>
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</tr>
<tr>
<td>n-heptane/ppt</td>
<td>6.9 ± 10.1</td>
<td>5.7</td>
<td>0–146</td>
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<td>n-octane/ppt</td>
<td>2.6 ± 4.5</td>
<td>0</td>
<td>0–45</td>
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<td>ethene/ppt</td>
<td>130.5 ± 121.2</td>
<td>117.6</td>
<td>0–590</td>
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<tr>
<td>propene/ppt</td>
<td>30.9 ± 45.4</td>
<td>12.0</td>
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<tr>
<td>acetylene/ppt</td>
<td>158.9 ± 161.0</td>
<td>96.8</td>
<td>0–516</td>
</tr>
<tr>
<td>trans-2-butene/ppt</td>
<td>3.2 ± 2.1</td>
<td>3.8</td>
<td>0–10</td>
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<td>1-butene/ppt</td>
<td>6.7 ± 7.7</td>
<td>5.5</td>
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<tr>
<td>iso-butene/ppt</td>
<td>5.4 ± 8.4</td>
<td>4.9</td>
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<tr>
<td>cis-2-butene/ppt</td>
<td>0.1 ± 0.6</td>
<td>0</td>
<td>0–7</td>
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<tr>
<td>1,3-butadiene/ppt</td>
<td>2.8 ± 17.1</td>
<td>0</td>
<td>0–230</td>
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<tr>
<td>trans-2-pentene/ppt</td>
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<td>0–11</td>
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<td>1-pentene/ppt</td>
<td>0.9 ± 2.5</td>
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<td>0–24</td>
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<tr>
<td>isoprene/ppt</td>
<td>0.9 ± 3.2</td>
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<td>benzene/ppt</td>
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<td>toluene/ppt</td>
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<td>ethylbenzene/ppt</td>
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<td>m-xylene/ppt</td>
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<td>o-xylene/ppt</td>
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<td>methacrolein/ppt</td>
<td>7.3 ± 27.9</td>
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<td>acetone/ppt</td>
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<td>257.9</td>
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<td>PAN/ppt</td>
<td>31.2 ± 44.2</td>
<td>19.0</td>
<td>0–234</td>
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Fig. 1. Locations of the BAe146 aircraft during the RONOCO campaign for which measurements of HO$_2^*$ and NO$_3$ or N$_2$O$_5$ are available, coloured by altitude.
Fig. 2. Comparison of modelled and observed concentrations of (a) \( \text{HO}_2^* \), (b) \( \text{NO}_3 \) and (c) \( \text{N}_2\text{O}_5 \) for the base MCM model run. In each plot, the solid red line indicates the 1 : 1 line, with 50 % limits given by the broken red lines. The best fit lines are shown in blue, and are described by 

\[
\text{[HO}_2^*\text{]}_{\text{mod}} = \left(0.45 \pm 0.07\right) \times \text{[HO}_2^*\text{]}_{\text{obs}} + \left(2.95 \pm 2.23\right) \times 10^6 \text{ cm}^{-3} \ (r^2 = 0.10),
\]

\[
\text{[NO}_3\text{]}_{\text{mod}} = \left(1.75 \pm 0.17\right) \times \text{[NO}_3\text{]}_{\text{obs}} - \left(2.33 \pm 3.61\right) \text{ ppt} \ (r^2 = 0.29)
\]

and 

\[
\text{[N}_2\text{O}_5\text{]}_{\text{mod}} = \left(1.46 \pm 0.12\right) \times \text{[N}_2\text{O}_5\text{]}_{\text{mod}} - \left(42.43 \pm 19.65\right) \text{ ppt} \ (r^2 = 0.64).
\]
Fig. 3. Processes controlling losses of $\text{NO}_{3x}$ (= $\text{NO}_3 + \text{N}_2\text{O}_5$) in the model, displayed as (a) the campaign mean and (b) the probability distribution functions for the percentage contributions to the total loss for heterogeneous uptake of $\text{NO}_{3x}$ to aerosol surfaces (purple), $\text{NO}_3 + \text{VOCs}$ (blue), $\text{NO}_3 + \text{HO}_2$ (green) and $\text{NO}_3 + \text{RO}_2$ (all organic peroxy radicals) (red).
Fig. 4. Processes controlling the instantaneous production (a) and loss (b) of RO$_x$ (= RO + RO$_2$ + OH + HO$_2$) radicals at night.
**Fig. 5.** Reactivity of (a) NO$_3$ and (b) O$_3$ towards observed volatile organic compounds (VOCs) at night during the RONOCO project.
Fig. 6. Processes controlling the instantaneous production (a) and loss (b) of \( \text{HO}_x \) (= \( \text{OH} + \text{HO}_2 \)) radicals at night.
Fig. 7. Processes controlling the instantaneous production (a) and loss (b) of HO$_2$ radicals at night.
Fig. 8. Schematic summarising the dominant chemical pathways occurring during tropospheric oxidation at night during RONOCO.
Fig. 9. Sensitivity of median modelled to observed ratios of HO$_2^*$ (blue), NO$_3$ (red) and N$_2$O$_5$ (green) towards (a) the deposition lifetime adopted in the model; (b) $\gamma$N$_2$O$_5$; (c) rate coefficients for NO$_3$ + RO$_2$ ($k_{\text{NO}_3\text{+RO}_2}$) adopted in the model; (d) concentrations of unsaturated VOCs in the model. Changes to $k_{\text{NO}_3\text{+RO}_2}$ and unsaturated VOC concentrations are represented as the factor by which $k_{\text{NO}_3\text{+RO}_2}$ and total unsaturated VOC concentration have been increased compared to the base run.
Fig. 10. Comparison between modelled and observed concentrations of (a) HO$_2^*$, (b) NO$_3$ and (c) N$_2$O$_5$ for a model run in which alkene concentrations are set to zero. In each plot, the solid red line indicates the 1:1 line, with 50% limits given by the broken red lines. The best fit lines are shown in blue, and are described by $[\text{HO}_2^*]_{\text{mod}}=\{(0.15 \pm 0.08) \times [\text{HO}_2^*]_{\text{obs}}\}-(1.75 \pm 2.55) \times 10^6 \text{cm}^{-3}$ ($r^2 < 0.01$), $[\text{NO}_3]_{\text{mod}}=\{(1.83 \pm 0.18) \times [\text{NO}_3]_{\text{obs}}\}+(2.06 \pm 3.76) \text{ppt}$ ($r^2 = 0.29$) and $[\text{N}_2\text{O}_5]_{\text{mod}}=\{(1.63 \pm 0.14) \times [\text{N}_2\text{O}_5]_{\text{mod}}\}-(39.20 \pm 22.19) \text{ppt}$ ($r^2 = 0.61$).
Fig. A1. Comparison between modelled HO$_2^*$ (the sum of HO$_2$ and potential RO$_2$ interferences) and modelled HO$_2$ for RONOCO. The solid red line indicates the 1 : 1 line, with 50 % limits given by the broken red lines. The best fit line is shown in blue and is described by HO$_2^*$ = [1.15 × HO$_2$] + 2 × 10$^5$ cm$^{-3}$. 