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# Night-time radical chemistry during the NAMBLEX campaign

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## Abstract

Night-time chemistry in the Marine Boundary Layer has been modelled using a number of observationally constrained zero-dimensional box-models. The models were based upon the Master Chemical Mechanism (MCM) and the measurements were taken during the North Atlantic Marine Boundary Layer Experiment (NAMBLEX) campaign at Mace Head, Ireland in July–September 2002.

The model could reproduce, within the combined uncertainties, the measured concentration of HO<sub>2</sub> (within 30–40%) during the night 31 August–1 September and of HO<sub>2</sub>+RO<sub>2</sub> (within 15–30%) during several nights of the campaign. The model always overestimated the NO<sub>3</sub> measurements made by Differential Optical Absorption Spectroscopy (DOAS) by up to an order of magnitude or more, but agreed with the NO<sub>3</sub> Cavity Ring-Down Spectroscopy (CRDS) measurements to within 30–50%. The most likely explanation of the discrepancy between the two instruments and the model is reaction of the nitrate radical with inhomogeneously distributed NO, which was measured at concentrations of up to 10 ppt, even though this is not enough to fully explain the difference between the DOAS measurements and the model.

A rate of production and destruction analysis showed that radicals were generated during the night mainly by the reaction of ozone with light alkenes. The cycling between HO<sub>2</sub>/RO<sub>2</sub> and OH was maintained during the night by the low concentrations of NO and the overall radical concentration was limited by slow loss of peroxy radicals to form peroxides. A strong peak in [NO<sub>2</sub>] during the night 31 August–1 September allowed an insight into the radical fluxes and the connections between the HO<sub>x</sub> and the NO<sub>3</sub> cycles.

## 1 Introduction

Radical chemistry during the night is controlled by the reactivity of ozone and of the nitrate radical. NO<sub>3</sub> is formed by the reaction of ozone and nitrogen dioxide (R1), but is

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present in significant concentrations only during the night, since it is quickly photolyzed by sunlight yielding either NO<sub>2</sub> or NO.



NO<sub>3</sub> reacts with NO<sub>2</sub> to form N<sub>2</sub>O<sub>5</sub>, which thermally decomposes giving back NO<sub>2</sub> and NO<sub>3</sub> (R2). In the night-time boundary layer NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> quickly reach an equilibrium, unless the concentration of NO<sub>2</sub> is very low (Allan et al., 2000). N<sub>2</sub>O<sub>5</sub> therefore acts as an important reservoir of oxidized nitrogen, directly or through the production of HNO<sub>3</sub> via the reaction with water (R3–R4) (Atkinson et al., 2003). N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub> are also uptaken on aerosol.



NO<sub>3</sub> reacts with alkenes and some aromatics (Atkinson and Arey, 2003). The reaction proceeds either by H-abstraction or by addition to the double-bond producing peroxy and nitro-peroxy radicals which then react with NO, HO<sub>2</sub> or other peroxy radicals. Reaction with NO leads to the formation of HO<sub>2</sub> and, via the reaction of HO<sub>2</sub> with NO and/or O<sub>3</sub>, to the formation of OH. In this way the nitrate radical acts as a source of HO<sub>x</sub> during the night, when ozone and formaldehyde photolysis, the main sources of HO<sub>x</sub> radicals during the day, are absent.

Another significant source of HO<sub>x</sub> during the night is the decomposition of Criegee intermediates from the reaction of ozone with alkenes (Atkinson and Arey, 2003). The relative importance of NO<sub>3</sub> and O<sub>3</sub> as HO<sub>x</sub> sources during the night depends on NO<sub>x</sub> and hydrocarbon concentrations.

Many studies on NO<sub>3</sub> chemistry have been reported, e.g. Allan et al. (1999, 2000); Brown et al. (2003, 2004); Vrekoussis et al. (2004), but comparatively few have been published on HO<sub>x</sub> night-time chemistry, especially in the marine boundary layer. HO<sub>2</sub>

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was measured at night at concentrations of up to  $7.6 \times 10^7$  molecule  $\text{cm}^{-3}$  at Oki Island (Kanaya et al., 1999),  $1.4 \times 10^8$  molecule  $\text{cm}^{-3}$  at Okinawa (Kanaya et al., 2001) and  $1.1 \times 10^8$  molecule  $\text{cm}^{-3}$  at Rishiri Island (Kanaya et al., 2002). In all three campaigns the radical source was attributed to the reactions of alkenes and monoterpenes with  $\text{O}_3$  with little or no contribution by  $\text{NO}_3$  chemistry. Carslaw et al. (1997) found a positive correlation between  $\text{NO}_3$  and  $\text{HO}_2 + \text{RO}_2$  during spring and autumn at Weybourne on the North Sea, evidence of production of peroxy radicals from reactions of the nitrate radical. No OH and  $\text{HO}_2$  measurements were made during that campaign. Salisbury et al. (2001) reported a study of nocturnal peroxy radicals at Mace Head under comparatively clean conditions during the EASE97 campaign.  $\text{HO}_2$  was measured on two nights at concentrations of up to  $5.1 \times 10^7$  molecule  $\text{cm}^{-3}$ . Their study showed that ozone-initiated oxidation routes of alkenes outweighed those of  $\text{NO}_3$ , except when the air was coming from the west and south-west sector. An analysis of peroxy radicals during the night at Cape Grim was also reported by Monks et al. (1996).

This paper discusses modelling and measurements of radicals (OH,  $\text{HO}_2$ , organic peroxy radicals and  $\text{NO}_3$ ) at Mace Head, Ireland, during the North Atlantic Marine Boundary Layer Experiment (NAMBLEX) (Heard et al., 2005). The campaign took place during the summer of 2002 (July–September) and involved ten British universities (Aberystwyth, Bristol, Birmingham, Cambridge, East Anglia, Edinburgh, Leeds, Leicester, UMIST, York) and the National University of Ireland, Galway. A complete overview of the campaign is in Heard et al. (2005). Description and analysis of the radical measurements can be found in Smith et al. (2006) and Saiz-Lopez et al. (2005). Two companion papers describe OH and  $\text{HO}_2$  day-time chemistry (Sommariva et al., 2006) and peroxy radical ( $\text{HO}_2$  and  $\text{HO}_2 + \text{RO}_2$ ) chemistry (Fleming et al., 2005) during NAMBLEX.

Section 2 of the paper briefly describes the models and the measurements used in this work. Sections 3 and 4 discuss the model-measurements comparisons of OH,  $\text{HO}_2$ ,  $\text{HO}_2 + \text{RO}_2$  and of  $\text{NO}_3$ ,  $\text{NO}_3 + \text{N}_2\text{O}_5$ , respectively. Section 5 contains a detailed rate of production and destruction analysis and Sect. 6 an analysis of one particular

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night of NAMBLEX (31 August–1 September). Finally, Sect. 7 contains the summary and the main conclusions of this work.

## 2 Models and measurements

The models used in this work are described in detail in Sommariva et al. (2006). They were built following the guidelines detailed in Carslaw et al. (1999) and in Sommariva et al. (2004) and using version 3.1 of the Master Chemical Mechanism (MCM, <http://mcm.leeds.ac.uk/>).

Four base models, with different degrees of chemical complexity, were used to study the impact of hydrocarbons, oxygenates and peroxides on the calculated concentrations of radicals. All the models were constrained to 15 min averages of measured concentrations of CO, CH<sub>4</sub>, H<sub>2</sub>, O<sub>3</sub>, NO, NO<sub>2</sub>, HCHO, selected NMHCs, H<sub>2</sub>O and to measured temperature and photolysis rates ( $j(\text{O}^1\text{D})$ ,  $j(\text{NO}_2)$ ,  $j(\text{HONO})$ , both channels of  $j(\text{HCHO})$ ,  $j(\text{CH}_3\text{COCH}_3)$ ,  $j(\text{CH}_3\text{CHO})$ ). The constraints of the different models used in this work are shown in Table 1.

The NMHCs data were linearly interpolated to 15 min. The measured species were: ethane, propane, i-butane, n-butane, i-pentane, n-pentane, n-hexane, n-heptane, ethene, propene, acetylene, trans-2-butene, but-1-ene, i-butene, cis-2-butene, 1,3-butadiene, isoprene, benzene, toluene, ethylbenzene, m-xylene + p-xylene, o-xylene plus three oxygenates (acetaldehyde, methanol, acetone) and two peroxides (H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OOH) (Lewis et al., 2005). SO<sub>2</sub> was not measured and was set to a constant value of 55 ppt (Berresheim et al., 2002).

No peroxides measurements were available after 30 August. Even before 30 August their concentrations, and in particular [CH<sub>3</sub>OOH], were often below or close to the detection limit (0.02 ppb, Morgan and Jackson (2002)). HCHO was measured with two techniques (Still et al., 2005). The University of East Anglia (UEA) measurements were used to constrain the model, because they were made closer to the radical measurements than the Leeds measurements. HCHO data were not available after August

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21, therefore the models for the following days were not constrained to HCHO, which was instead calculated. Also, measurements of chloroform ( $\text{CHCl}_3$ ) were not available before 3 August. The omission of peroxides, formaldehyde and chloroform did not influence significantly the calculated concentrations of radicals at night. In the models which were not constrained to the concentrations of oxygenates and hydroperoxides concentrations (“clean” and “full” models), these species were calculated as intermediates and the calculated concentrations were, especially for species with longer lifetimes, more than an order of magnitude less than the measured concentrations, because of the importance of transport.

Dry deposition terms were also included using the values of Derwent et al. (1996) except for peroxides ( $1.1 \text{ cm s}^{-1}$  for  $\text{H}_2\text{O}_2$  and  $0.55 \text{ cm s}^{-1}$  for organic peroxides), methyl and ethyl nitrate ( $1.1 \text{ cm s}^{-1}$ ) and HCHO ( $0.33 \text{ cm s}^{-1}$ ) (Brasseur et al., 1998). Dry deposition velocity for  $\text{CH}_3\text{CHO}$  and other aldehydes was assumed to be the same as that for HCHO. A clear diurnal cycle of the boundary layer (BL) was not always recognizable during NAMBLEX and often the synoptic pattern dominated over the local conditions (Norton et al., 2006). On many days during the campaign the boundary layer was roughly constant throughout the day with heights of 700–1500 m, while on a few days, such as 9 August, the BL showed a diurnal variation with a height of 1000–1500 m during the day and 400–500 m during the night.

Heterogeneous uptake was calculated using Eq. (1) assuming irreversible loss of gas-phase species on aerosol.

$$k_{\text{het}} = \frac{A\bar{v}\gamma}{4} \quad (1)$$

where  $A$  is the total aerosol surface area,  $\bar{v}$  is the mean molecular speed and  $\gamma$  is the temperature dependent gas/surface reaction probability. The values of  $\gamma$  used for  $\text{HO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$  were 0.006 (at 298 K), 0.004 and 0.032, respectively (Gratpanche et al., 1996; Allan et al., 1999; Behnke et al., 1997).

The models were used to calculate OH,  $\text{HO}_2$ , total peroxy radicals ( $\text{HO}_2 + \text{RO}_2$ ),  $\text{NO}_3$  (or  $\text{NO}_3 + \text{N}_2\text{O}_5$ ) for several nights of the campaign. The model results were compared

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to the measurements. OH and HO<sub>2</sub> were measured by laser-induced fluorescence (LIF) using the FAGE (Fluorescence Assay by Gas Expansion) technique. During the night the detection limits for the two radicals were  $6 \times 10^4$  and  $1 \times 10^6$  molecule cm<sup>-3</sup>, respectively (Smith et al., 2006). Total peroxy radicals (HO<sub>2</sub>+RO<sub>2</sub>) were measured by the PERCA (Peroxy Radical Chemical Amplifier) technique with a detection limit of about 0.5 ppt. The FAGE and the PERCA instruments are described in Smith et al. (2006) and Fleming et al. (2005), respectively.

NO<sub>3</sub> was measured by Differential Optical Absorption Spectroscopy (DOAS). The DOAS instrument was located about 100 m from the shore with the retro-reflector on an island about 4 km west of Mace Head. The total light path was 8.4 km and NO<sub>3</sub> was measured in the 645–680 nm spectral region with a detection limit of 0.4–0.5 ppt (Saiz-Lopez et al., 2005). A Cavity Ring-Down Spectrometer (CRDS) was also present at Mace Head. It was located about 25 m inland from the DOAS. The CRDS measured NO<sub>3</sub> and NO<sub>3</sub>+N<sub>2</sub>O<sub>5</sub> in the spectral region 655–675 nm with an estimated light path of ~20 km and a detection limit of approximately 1 ppt, depending on the aerosol loading (Bitter et al., 2005). The details of the two instruments are given in Saiz-Lopez et al. (2005); Bitter et al. (2005).

The modelling of the night-time chemistry in the marine boundary layer was concentrated on a few nights, which can be divided roughly in two periods. The semi-polluted period at the beginning of August (1–5 August), and the unpolluted period during the rest of the campaign (Heard et al., 2005). The semi-polluted period was characterized by comparatively high concentrations of NO<sub>x</sub>, CO, and NMHCs (Table 2). Acetylene, an anthropogenic marker, was 2 to 3 times higher than during other periods of the campaign. The five-day back trajectories showed that the air masses arriving at Mace Head were coming from east-northeast, passing over Northern England and Ireland (Norton et al., 2006). Most of the rest of the campaign and particularly the night 31 August–1 September was characterized by comparatively unpolluted conditions, with low NO<sub>x</sub> and hydrocarbons concentrations (Table 2) and air masses of oceanic origin coming from west, north-west and south-west. More details on the chemical conditions

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during NAMBLEX can be found in [Heard et al. \(2005\)](#) and a complete discussion of the meteorology during the campaign can be found in [Norton et al. \(2006\)](#).

### 3 OH, HO<sub>2</sub> and RO<sub>2</sub>

OH and HO<sub>2</sub> were measured during one night (31 August–1 September). OH was always below the instrumental detection limit ( $6 \times 10^4$  molecule cm<sup>-3</sup>). Late evening and early morning measurements showed concentrations of the order of  $1\text{--}2 \times 10^5$  molecule cm<sup>-3</sup>, about twice as much as the modelled concentration during the night (Fig. 1(a)). The model overestimated the measurements at sunset, but underestimated them at sunrise suggesting the presence of an OH source unaccounted for or underestimated by the model, such as HONO ([Smith et al., 2006](#)).

HO<sub>2</sub> concentrations of the order of  $1\text{--}3 \times 10^7$  molecule cm<sup>-3</sup> were detected, similar to previous measurements in Mace Head during two nights of the EASE97 campaign ( $1.5\text{--}5 \times 10^7$  molecule cm<sup>-3</sup>, [Salisbury et al. \(2001\)](#)). The models overestimated HO<sub>2</sub> by about 30–40% (Fig. 1(a)). Compared to daytime, when the model overestimated the measurements by about a factor of 2 ([Sommariva et al., 2006](#)), the agreement between the model and the measurements is reasonably good and well within the combined uncertainties of the model and of the instrument (25–30% and 50%, respectively, [Sommariva et al., 2004](#)).

PERCA measurements were taken every night during the campaign. The comparisons with the model results are shown in Fig. 1(b) and Fig. 2(a). The agreement between modelled and measured HO<sub>2</sub>+RO<sub>2</sub> was within 15–30% during most of the modelled nights. Contrary to the day-time, the model showed a tendency to underestimate the PERCA measurements during the night (see Fig. 4b in [Fleming et al., 2005](#)). During the night 20–21 August the model underestimated the measurements by about 50% (Figs. 1(b)–2(a)). On some occasions measured [HO<sub>2</sub>+RO<sub>2</sub>] increased throughout the night, which appeared to be related to NO<sub>x</sub> events, but was not always reproduced by the model (e.g. 17–18 August). [Fleming et al. \(2005\)](#) showed that the

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measured peroxy radicals concentration during the night was generally higher at higher  $[\text{NO}_x]$ .

The speciation of modelled peroxy radicals during NAMBLEX, showed that  $\text{CH}_3\text{O}_2$  was the dominant radical during the night. In the unpolluted period  $\text{CH}_3\text{O}_2$  was up to 60% of  $\text{HO}_2 + \text{RO}_2$ , while  $\text{HO}_2$  was about 20% of  $\text{HO}_2 + \text{RO}_2$ . This was approximately the reverse of the day-time proportion and in good agreement with the results of the EASE97 campaign by [Salisbury et al. \(2001\)](#). During the semi-polluted period  $\text{CH}_3\text{O}_2$  was up to 40% of  $\text{HO}_2 + \text{RO}_2$ , while  $\text{HO}_2$  was about 40% of  $\text{HO}_2 + \text{RO}_2$  indicating a faster production of inorganic radicals in presence of higher  $\text{NO}_x$  and NMHCs concentrations. The modelled  $\text{HO}_2 / (\text{HO}_2 + \text{RO}_2)$  ratio was about 50% higher than the measured ratio, as a consequence of the overestimation of  $\text{HO}_2$  ([Fleming et al., 2005](#)).

Comparing the results of the different models (Table 1) it is clear that the difference between the “full”, “fulloxy” and “fulloxyper” models was negligible (Figs. 1 and 2(a)), indicating that additional constraints of oxygenates and peroxides did not influence significantly the concentrations of  $\text{HO}_2$  and  $\text{RO}_2$ . However for the “clean” model, which was constrained only to CO and  $\text{CH}_4$ , calculated concentrations of  $\text{HO}_2$  (Fig. 1(a)) and  $\text{HO}_2 + \text{RO}_2$  (Figs. 1(a) and 2(a)) were about an order of magnitude lower than the concentrations calculated by the “full” and “fulloxy” models. This was due to the fact that the only peroxy radical of the “clean” model was  $\text{CH}_3\text{O}_2$ , which mainly came from  $\text{CH}_4$  oxidation, a very slow reaction at night ( $k_{\text{CH}_4 + \text{NO}_3} < 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , [Atkinson et al., 2003](#)).

Similar results were obtained during the baseline periods of the SOAPEX-2 campaign in the Southern Hemisphere using a model similar to the “clean” model ([Sommariva et al., 2004](#)). On one occasion (15–16 February 1999), late evening and early morning measurements of OH and  $\text{HO}_2$  were made, showing late evening concentrations of  $\text{HO}_2$  about a factor of two larger than the predictions of the “clean” model (Fig. 2(b)). The model underestimated  $\text{HO}_2 + \text{RO}_2$  by about almost an order of magnitude, a similar factor to that found when using the ‘clean’ model for NAMBLEX (Fig. 1(b)). Since the more detailed models (“full”, “fulloxy” and “fulloxyper”) provide

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much better agreement with the NAMBLEX observations of  $\text{HO}_2+\text{RO}_2$ , this observation suggests that even in the extremely clean conditions of Cape Grim (Sommariva et al., 2004)  $\text{CO}$  and  $\text{CH}_4$  alone cannot account for the radical budget and even low concentrations of NMHCs play a significant role.

## 4 $\text{NO}_3$

The nitrate radical was measured for many nights during NAMBLEX by DOAS and CRDS (Saiz-Lopez et al., 2005; Bitter et al., 2006<sup>1</sup>). Data from the CRDS instrument were available only for the initial semi-polluted period of the campaign when the concentrations were higher (Table 2). The model-measurements comparisons are shown in Fig. 3.

The models always underestimated the DOAS measurements of  $[\text{NO}_3]$ , on average by about a factor of 4–5 up to a factor of 10 (Figs. 3(b)–3(c)). On some nights, like 18–19 and 19–20 August, the modelled concentrations of  $\text{NO}_3$  were up to 60 times lower than the DOAS measurements. This was similar to the results obtained for the one night in the SOAPEX-2 campaign which was modelled (15–16 February 1999) and for which  $\text{NO}_3$  measurements were available (Fig. 2(b)).

The agreement between modelled  $\text{NO}_3$  and  $\text{NO}_3+\text{N}_2\text{O}_5$  and the measurements by CRDS was generally better (Fig. 3(a)). Modelled concentrations were typically within 30–50% of the measurements, with the model showing a tendency to underestimate the measurements. Note that on the night 1–2 August the high CRDS measurements before midnight (Fig. 3(a)) were subject to a larger uncertainty than the measurements taken later in the night, due to the higher aerosol optical depth (Bitter et al., 2006<sup>1</sup>).

A detailed comparison between the DOAS and CRDS measurements and a discussion of the possible reasons for the different  $[\text{NO}_3]$  measured by the two instruments

<sup>1</sup>Bitter, M., Ball, S. M., Povey, I. M., Jones, R. L., Saiz-Lopez, A., and Plane, J. M. C.: Measurements of  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{OIO}$ ,  $\text{I}_2$ , water vapour and aerosol optical depth by broadband cavity ringdown spectroscopy during the NAMBLEX campaign, in preparation, 2006.

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is presented in Bitter et al. (2006)<sup>1</sup>. An important point to note is that while the DOAS measurements were averages over a long path (8.4 km at Mace Head) crossing a branch of sea, the CRDS measurements were point measurements made about 100 m from the shore (Heard et al., 2005). The fact that the model-DOAS discrepancy was similar in such diverse conditions as SOAPEX-2 (Sommariva et al., 2004) and NAMBLEX (Table 2) in contrast with the good agreement between the model and the CRDS point measurements suggests that the zero-dimensional approach used in this work might not be suitable to model DOAS measurements.

Under the relatively low  $[\text{NO}_2]$  conditions at Mace Head,  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  rapidly equilibrate (R3) and any loss of  $\text{N}_2\text{O}_5$  resulted in the removal of  $\text{NO}_3$  from the system.  $\text{N}_2\text{O}_5$  can be removed by reaction with  $\text{H}_2\text{O}$  and by uptake on aerosol. Previous studies have shown that, under certain conditions (semi-polluted air masses with little marine influence), removal of  $\text{N}_2\text{O}_5$  can be a major loss pathway for  $\text{NO}_3$  (Allan et al., 1999, 2000). Semi-polluted conditions were experienced at the beginning of the NAMBLEX campaign (1–2 August). To test the impact of  $\text{N}_2\text{O}_5$  uptake on modelled  $[\text{NO}_3]$  the model was run with an uptake rate coefficient for  $\text{N}_2\text{O}_5$  equal to 0.016 (in the base model  $\gamma_{\text{N}_2\text{O}_5}=0.032$ ). The effect on modelled  $[\text{NO}_3]$  was negligible (model “fulloxy-n2o5” in Fig. 3(a)), showing that the model was not very sensitive to  $\text{N}_2\text{O}_5$  heterogeneous uptake under these conditions.

An important issue in night-time chemistry is the concentration of nitric oxide. NO rapidly reacts with radicals, for which there are few night-time sources, and with ozone. With 30 ppb of  $\text{O}_3$ , NO has a lifetime of about 1 min at 283 K. Its concentration is therefore expected to be extremely low during the night. However, this is not always the case, since NO local sources might be present. During NAMBLEX, NO concentrations above the detection limit of the instrument (3–4 ppt) were often detected during the night. The night-time average mixing ratio was about 15–20 ppt during the semi-polluted period and about 6.5–7 ppt during the unpolluted period. This suggests the presence of a local source of NO, possibly emissions from the soil during the night.

The emission of NO from soils might provide an important  $\text{NO}_3$  sink (via the  $\text{NO}+\text{NO}_3$

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reaction), particularly in Ireland, because of the presence of peaty soils around Mace Head (Williams and Fehsenfeld, 1991; Williams et al., 1992; Regina et al., 19998). Since the DOAS sampled over the sea, while the CRDS sampled over the land, local NO soil emissions might explain the difference between the two instrument's measurements and the underestimation of the DOAS observations by the model. This hypothesis is discussed in more detail in Bitter et al. (2006)<sup>1</sup>, who used a simple box model to show how NO emitted over land could suppress NO<sub>3</sub> at the levels observed by CRDS but, as the air mass was advected over the sea and away from the NO source by offshore winds, the concentration of NO<sub>3</sub> would steadily increase to the levels observed by DOAS. Conversely under a sea-breeze, the higher NO<sub>3</sub> concentrations maintained over the sea are rapidly titrated by the NO emissions at the shore when the air mass arrives over the land (Bitter et al., 2006)<sup>1</sup>.

The “clean” and the “fulloxy” models were therefore run with measured NO during the day and [NO]=0 during the night to understand the impact of nitric oxide on modelled NO<sub>3</sub> and to see if this could explain the discrepancy between the model and the DOAS measurements. The results of these test runs are shown in Fig. 4. Also shown are the results of model runs with [DMS]=0 and with both [NO] and [DMS]=0.

Figure 4 suggests that setting [DMS] to zero did not have a significant effect on the calculated NO<sub>3</sub>, except when the models were also constrained to zero [NO]. In fact, when the models were constrained to measured NO, the main fate of NO<sub>3</sub> was the reaction with NO. The models showed that when both [DMS] and [NO] were set to zero, NO<sub>3</sub> mainly reacted with NMHCs. These reactions were slower, resulting in a higher [NO<sub>3</sub>] and the models became more sensitive to DMS. Therefore, when both [DMS] and [NO] were set to zero, [NO<sub>3</sub>] became 3–4 times larger than when NO was present. However, this was not enough to increase the calculated [NO<sub>3</sub>] up to the values measured by the DOAS and caused an overestimation of the CRDS measurements (about 40–50% and up to a factor of 3).

Another issue which might be significant in explaining the differences between the DOAS, the CRDS and the models is the vertical profile of NO<sub>3</sub>. Saiz-Lopez et al. (2005)

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observed a positive vertical  $\text{NO}_3$  gradient over Mace Head, which they attributed in part to the temperature and  $\text{NO}_2$  vertical profile and in part to the reaction of  $\text{NO}_3$  with DMS, whose concentration was higher near the sea surface (Purvis et al., 2005). The  $\text{NO}_3$  gradient could also cause a downward motion of  $\text{NO}_3$  over the ocean. This could in part explain the fact that the DOAS measurements were higher than the CRDS measurements (Bitter et al., 2006)<sup>1</sup>. In fact, while the heights of the CRDS and of the DOAS telescope were roughly the same, the DOAS retro-reflector was located at a higher position, so the average height of measurement for DOAS measurements was greater than that of the CDRS. A significant vertical gradient in  $[\text{NO}_3]$  would compromise the zero-dimensional model used in this study and lead to poor prediction of the measured  $[\text{NO}_3]$ .

## 5 Analysis of the radical fluxes

The rates of production and destruction of modelled OH,  $\text{HO}_2$  and  $\text{NO}_3$  were calculated for the nights 1 and 2 August, characterized by semi-polluted conditions and higher  $[\text{NO}_3]$ , and 31 August and 1 September, characterized by unpolluted conditions and lower  $[\text{NO}_3]$  (Table 2). The objective of the analysis was to identify the most important reactions and the processes driving the night-time chemistry under those conditions. The “fulloxy” model was used as reference. The results of the rate of production and destruction analysis are shown in Fig. 5 for  $\text{HO}_x$  during the night 31 August–1 September and in Fig. 6 for  $\text{NO}_3$  during the nights of 1–2 August and 31 August–1 September.

There were essentially two interacting chain cycles, one directly linking OH to  $\text{HO}_2$  via CO, the other proceeding via  $\text{RO}_2$ , with  $\text{CH}_3\text{O}_2$  as the main immediate precursor of  $\text{HO}_2$ . The time constant of the former was quite short, of the order of 1 s, and was largely determined by the OH reactions shown in Fig. 5(a), primarily involving CO, but also HCHO,  $\text{O}_3$  and  $\text{H}_2$ . The route through  $\text{CH}_3\text{O}_2$  involved not only reaction of OH with  $\text{CH}_4$ , but also with NMHCs. There were also two other, longer time constants associated with the chain cycle, involving the conversion of  $\text{CH}_3\text{O}_2$  to  $\text{HO}_2$  by reaction

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with NO and of HO<sub>2</sub> to OH by reaction with O<sub>3</sub> and NO, with the latter decreasing in importance with time. If there was no source term, the coupled radical pool would slowly decay, via both peroxy-peroxy and OH+NO<sub>2</sub> reactions. There was, however, a radical source (mainly of OH and CH<sub>3</sub>O<sub>2</sub>), provided by Criegee intermediates formed from O<sub>3</sub>+alkene reactions (mainly propene, c-2-butene, t-2-butene, c-2-pentene, t-2-pentene), that helped to maintain the radical concentrations, although there was generally a slow decrease with time. The decomposition of CH<sub>3</sub>SO<sub>3</sub> to give SO<sub>3</sub> and CH<sub>3</sub>O<sub>2</sub> and the reaction of CH<sub>3</sub>CO<sub>3</sub> with NO provided additional CH<sub>3</sub>O<sub>2</sub> sources.

Fleming et al. (2005) calculated the fluxes of radicals from alkenes+O<sub>3</sub> and alkenes+NO<sub>3</sub> during several nights of the NAMBLEX campaign. They showed that ozone reactivity dominated the formation of radicals most of the nights, except when the NO<sub>3</sub> concentration was high, such as in the semi-polluted period at the beginning of the campaign. This is in broad agreement with the results of the reaction rate analysis discussed above (it must be noted that Fleming et al. (2005) used [NO<sub>3</sub>] as measured by DOAS, which was typically an order of magnitude higher than the modelled [NO<sub>3</sub>] used here).

On the night of 1-2 August, the main formation and destruction routes for NO<sub>3</sub> were NO<sub>2</sub>+O<sub>3</sub> and NO<sub>3</sub>+NO<sub>2</sub> respectively (Fig. 6). The NO<sub>3</sub>+NO<sub>2</sub>⇌N<sub>2</sub>O<sub>5</sub> equilibration was rapid but led to a net sink for NO<sub>3</sub>, because of the loss of N<sub>2</sub>O<sub>5</sub> by hydrolysis and heterogeneous uptake. On 31 August–1 September, the N<sub>2</sub>O<sub>5</sub> loss was less significant than on 1–2 August, so that the forward and reverse steps in the equilibration balanced. The main losses of NO<sub>3</sub> on both nights were the reactions with NO and with DMS. On the unpolluted night 31 August–1 September the two reaction rates were comparable ( $\sim 5 \times 10^3$  molecule cm<sup>-3</sup> s<sup>-1</sup>), while on the semi-polluted night 1–2 August the reaction with NO was about a factor of 4 faster (Fig. 6). In fact, on this night the concentration of NO was generally higher (about a factor of 3 during the night), as polluted air arrived at Mace Head from the north-east, and the DMS concentration was lower. Other sinks for NO<sub>3</sub> were the reactions with a range of NMHCs (mainly alkenes like but-1-ene and t-2-butene and aromatics like phenol and catechols) and peroxy radicals (HO<sub>2</sub> and

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CH<sub>3</sub>O<sub>2</sub>).

## 6 A case-study night

Measurements of HO<sub>2</sub>, HO<sub>2</sub>+RO<sub>2</sub> and NO<sub>3</sub> were all made on the night between 31 August and 1 September. OH was also measured, but was always below the detection limit. A large spike of NO<sub>2</sub> occurred in the middle of the night allowing the couplings between the species and the cycles of HO<sub>x</sub> and NO<sub>3</sub> to be studied.

Between 22:00 and 24:00 on 31 August the measured concentration of NO<sub>2</sub> rose from its “normal” value of 40 ppt to about 300 ppt. The concentration of NO did not change as much (Fig. 7). The spike appeared to be related to a change in the local wind direction from ~200°(S-SW, from the open sea) to ~150°(S-SE, along the coastline). The most probable explanation was a local source of NO<sub>2</sub>, which was brought to the instrument as the wind shifted direction. Figure 8 shows the reactions of the most important species in the night-time chemistry on 31 August–1 September (Sect. 5) and their connections via ozone and NO. O<sub>3</sub> in particular had a double role. It converted HO<sub>2</sub> to OH, and also reacted with NO<sub>2</sub> to generate NO<sub>3</sub>. NO<sub>2</sub> was produced from NO, through its reactions with CH<sub>3</sub>O<sub>2</sub> and HO<sub>2</sub>. NO<sub>3</sub> and NO<sub>2</sub> were linked through the reaction NO<sub>3</sub>+NO and through the equilibrium of N<sub>2</sub>O<sub>5</sub>. Ozone, nitrogen oxides (NO, NO<sub>2</sub>, NO<sub>3</sub>) and OH, HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> were therefore interconnected and a change in the concentration of one of these species, namely NO<sub>2</sub>, quickly propagated through the cycles to affect all the others.

The fluxes during the NO<sub>2</sub> event (23:00) and under “normal” conditions (24:00) are shown in Fig. 8. It can be seen that with high [NO<sub>2</sub>] the rate of O<sub>3</sub>+NO<sub>2</sub> was about 6 times faster than with low [NO<sub>2</sub>]. This caused an increment in [NO<sub>3</sub>] and the rapid consumption of ozone. With higher NO<sub>3</sub> concentration the rates of the reactions with DMS and NO (to regenerate NO<sub>2</sub>) increased by a factor of 8 and 3, respectively. The consequence was a decrease in ozone by about 30% and of NO by almost a factor of 4, which is clearly visible in the measurements (Fig. 7). With less O<sub>3</sub> and NO present, the

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conversion between  $\text{HO}_2$  and OH slowed down to about half its normal rate. While OH continued to be produced by the decomposition of the Criegee intermediates (mainly  $\text{CH}_3\text{CHOO}$ ), the decrease in the propagation rates lead to a decrease in  $[\text{OH}]$ .

The measurements reflected these changes. In correspondence to the  $\text{NO}_2$  spike the concentration of NO and  $\text{O}_3$  decreased (Fig. 7) and the concentration of  $\text{NO}_3$  showed a slight increase (Fig. 3(c)). The DMS profile showed an initial increase until 22:30, which was then followed by a fast decline until midnight, due to the reaction with  $\text{NO}_3$  (Fig. 7).

## 7 Conclusions

Night-time measurements of radicals were made during a field campaign (NAMBLEX) in a marine environment in the Northern Hemisphere. OH was always below the detection limit ( $6 \times 10^4$  molecule  $\text{cm}^{-3}$ ), but  $\text{HO}_2$  concentrations of  $1\text{--}3 \times 10^7$  molecule  $\text{cm}^{-3}$  were measured during one night (31 August–1 September).  $\text{HO}_2 + \text{RO}_2$  and  $\text{NO}_3$  were measured on several nights. On the night of 31 August–1 September simultaneous measurements of  $\text{HO}_2$ ,  $\text{HO}_2 + \text{RO}_2$  and  $\text{NO}_3$  were available, together with many other supporting measurements, allowing a thorough study of night-time chemistry. The radicals concentrations were calculated using a set of zero-dimensional box-models, based on the Master Chemical Mechanism and constrained to measured species and parameters.

The agreement between the model and the measurements was reasonably good for  $\text{HO}_2$ , with a tendency to overestimate the measurements by less than 40%. The agreement with  $\text{HO}_2 + \text{RO}_2$  was more variable, but within 15–30% during most of the nights. A model containing only CO and  $\text{CH}_4$  chemistry always underestimated both  $[\text{HO}_2]$  and  $[\text{HO}_2 + \text{RO}_2]$  by about an order of magnitude, showing that most of the peroxy radicals generated during the night derived from the oxidation of NMHCs. The most important peroxy radicals were  $\text{HO}_2$  (20% on unpolluted nights and 40% on semi-polluted nights) and  $\text{CH}_3\text{O}_2$  (60% on unpolluted nights and 40% on semi-polluted nights).

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The measurements indicated that the radical concentrations remained more or less constant throughout the night, suggesting a nocturnal radical source. The model showed that reaction of  $O_3$  with alkenes (mainly propene, butenes and pentenes) was a slow but steady source of OH during the night which compensated the slow removal of radicals via the formation of peroxides from peroxy-peroxy reactions.

The model consistently underestimated  $[NO_3]$  measured by DOAS by a factor of 5–10 or more. The agreement with the CRDS measurements during NAMBLEX was much better, within 30–50%. Scavenging of  $NO_3$  by NO over land was explored as one of the possible explanations for the discrepancy between the two instruments and with the model. Reaction with NO was the main loss process for  $NO_3$  during the night 31 August–1 September, followed by the reaction with DMS. When the model was run with  $[NO]=0$ ,  $NO_3$  mainly reacted with DMS resulting in an increase in modelled  $NO_3$  of about 50%. With  $[DMS]=0$ , modelled  $NO_3$  increased by about 70–80% and the main losses for the nitrate radical became the reactions with a variety of alkenes, aromatics and peroxy radicals or the uptake on aerosol. The only source of  $NO_3$  was the reaction of  $NO_2$  with  $O_3$ .

On 31 August–1 September a spike of  $NO_2$  of up to 300 ppt allowed an examination of the coupling between  $NO_3$  and  $HO_x$ . The increase in  $NO_2$  caused an acceleration of the reaction with  $O_3$ , increasing the production of  $NO_3$  (and hence the rates of its reactions with DMS and NO) and depleting  $O_3$ . The decrease in NO and  $O_3$  caused a slowing of the  $HO_2 \rightarrow OH$  conversion rate.

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**Table 1.** Models used in this work.

Base Models	Constraints
“clean”	H <sub>2</sub> , O <sub>3</sub> , NO, NO <sub>2</sub> , HCHO and H <sub>2</sub> O, temperature, photolysis rates. CO, CH <sub>4</sub>
“full”	as “clean” + 22 hydrocarbons, DMS, CHCl <sub>3</sub>
“fulloxy”	as “full” + 3 oxygenates
“fulloxyper”	as “fulloxy” + 2 peroxides
Test Models	Constraints
“fulloxy-n2o5”	as “fulloxy” with $\gamma_{\text{N}_2\text{O}_5} = 0.016$
“fulloxy-no”	as “fulloxy” with [NO] = 0
“fulloxy-dms”	as “fulloxy” with [DMS] = 0
“fulloxy-dms-no”	as “fulloxy” with [NO] and [DMS] = 0

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**Table 2.** Average (20:00–05:00) measurements on some selected nights during NAMBLEX. Concentrations in molecule  $\text{cm}^{-3}$ , temperature in  $^{\circ}\text{C}$ .

Measurements	1–2 Aug	18–19 Aug	19–20 Aug	20–21 Aug	31 Aug– 1 Sep
$\text{O}_3$	$7.8 \times 10^{11}$	$7.0 \times 10^{11}$	$6.1 \times 10^{11}$	$5.8 \times 10^{11}$	$8.8 \times 10^{11}$
NO	$3.2 \times 10^8$	$1.5 \times 10^8$	$2.0 \times 10^8$	$1.3 \times 10^8$	$9.2 \times 10^7$
$\text{NO}_2$	$7.1 \times 10^9$	$1.8 \times 10^9$	$3.2 \times 10^9$	$6.1 \times 10^9$	$1.6 \times 10^9$
$\text{CH}_4$	$5.0 \times 10^{13}$	$4.7 \times 10^{13}$	$4.8 \times 10^{13}$	$4.7 \times 10^{13}$	$4.6 \times 10^{13}$
CO	$4.0 \times 10^{12}$	$2.2 \times 10^{12}$	$2.0 \times 10^{12}$	$2.0 \times 10^{12}$	$3.0 \times 10^{12}$
$\text{H}_2$	$1.4 \times 10^{13}$	$1.3 \times 10^{13}$	$1.3 \times 10^{13}$	$1.3 \times 10^{13}$	$1.3 \times 10^{13}$
HCHO (UEA)	$1.7 \times 10^{10}$	$3.1 \times 10^9$	$3.5 \times 10^9$	$5.6 \times 10^9$	–
HCHO (Leeds)	$3.9 \times 10^{10}$	$1.5 \times 10^{10}$	$1.4 \times 10^{10}$	$1.8 \times 10^{10}$	–
Propene	$6.0 \times 10^8$	$3.6 \times 10^8$	$5.3 \times 10^8$	$5.8 \times 10^8$	$2.5 \times 10^8$
DMS	$6.4 \times 10^8$	$2.6 \times 10^9$	$1.0 \times 10^9$	$1.1 \times 10^9$	$1.1 \times 10^9$
Acetylene	$7.2 \times 10^9$	$1.5 \times 10^9$	$1.9 \times 10^9$	$1.5 \times 10^9$	$3.5 \times 10^9$
Acetaldehyde	$2.3 \times 10^{10}$	$1.2 \times 10^{10}$	$1.1 \times 10^{10}$	$9.9 \times 10^9$	$6.5 \times 10^9$
Temperature	17.5	13.8	12.8	14.3	14.1

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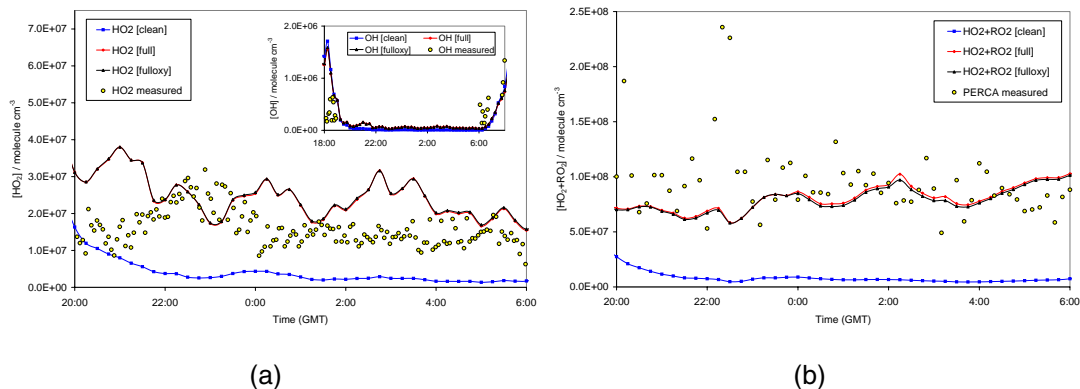
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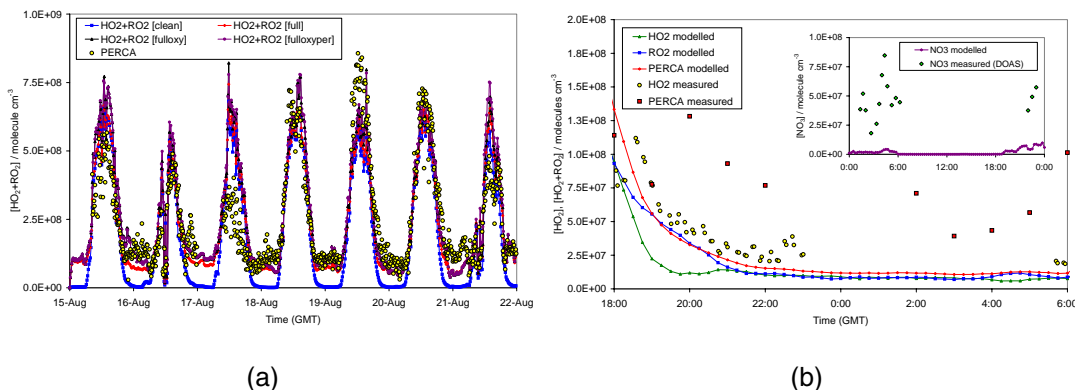


**Fig. 1.** Model-measurement comparison for OH,  $\text{HO}_2$  (a) and  $\text{HO}_2+\text{RO}_2$  (b) during the night 31 August–1 September.

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**Fig. 2.** Model-measurement comparison for  $\text{HO}_2$  and  $\text{HO}_2 + \text{RO}_2$  during the period 15–21 August of NAMBLEX (a). Model-measurement comparison for  $\text{NO}_3$ ,  $\text{HO}_2$  and  $\text{HO}_2 + \text{RO}_2$  during the night 15–16 February 1999 of SOAPEX-2 (b). The equivalent of the “clean” model was used for the SOAPEX-2 campaign (Sommariva et al., 2004).

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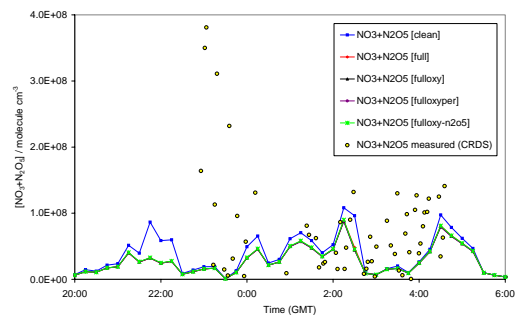
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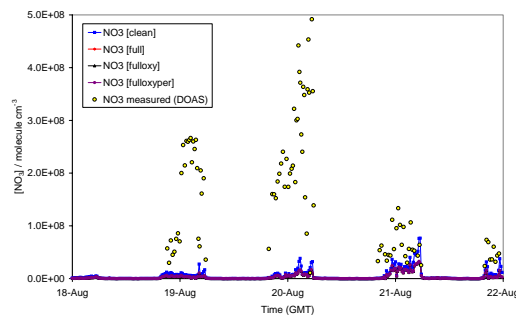
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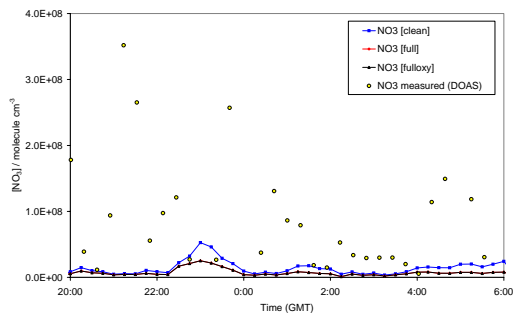
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(a)



(b)



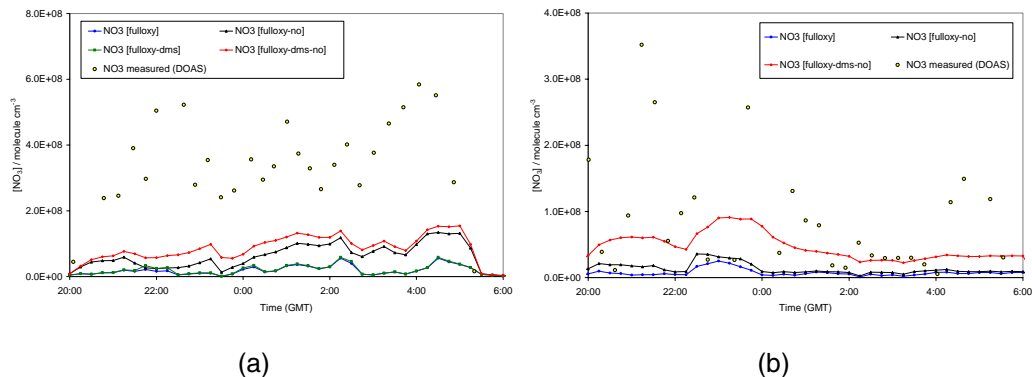
(c)

**Fig. 3.** Model-measurement for  $\text{NO}_3+\text{N}_2\text{O}_5$ , also showing the impact of  $\text{N}_2\text{O}_5$  uptake, during the night 1–2 August (a) and for  $\text{NO}_3$  during the period 18–22 August (b) and the night 31 August–1 September (c).

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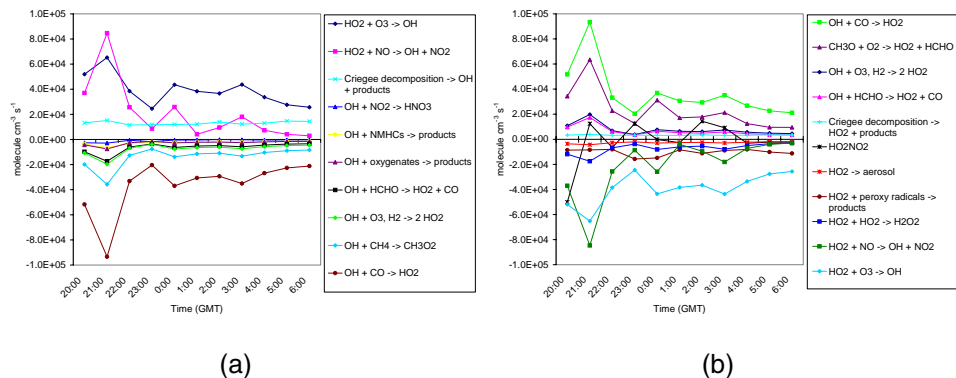


**Fig. 4.** Model-measurement comparison for  $\text{NO}_3$  showing the impact of  $[\text{NO}]=0$  and  $[\text{DMS}]=0$  during the night 1–2 August **(a)** and 31 August–1 September **(b)**.

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**Fig. 5.** Rates of production and destruction of OH (a) and HO<sub>2</sub> (b) during the night of 31 August–1 September.

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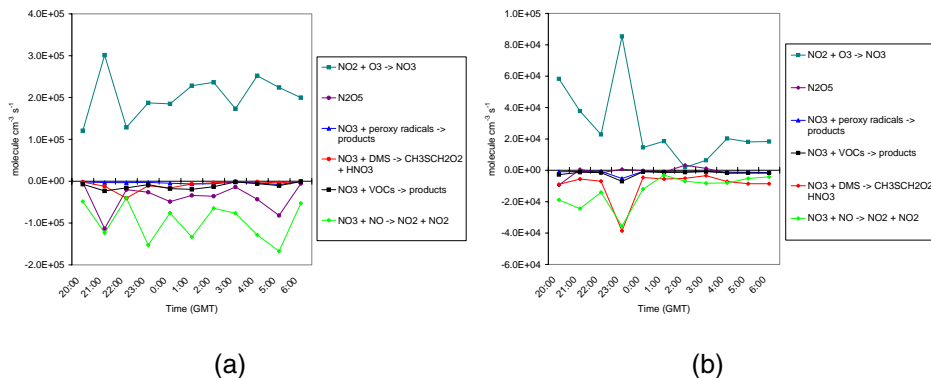
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**Fig. 6.** Rates of production and destruction of  $\text{NO}_3$  during the night of 1–2 August (a) and during the night of 31 August–1 September (b).

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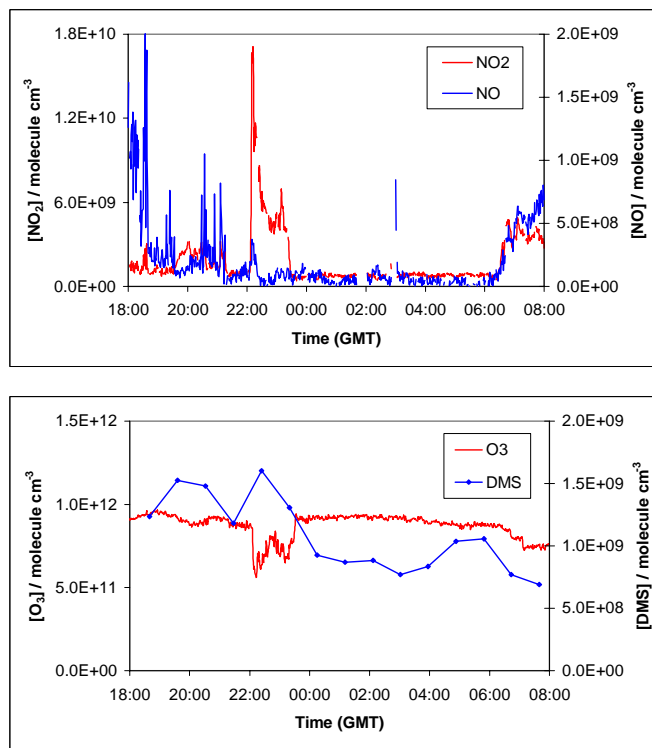
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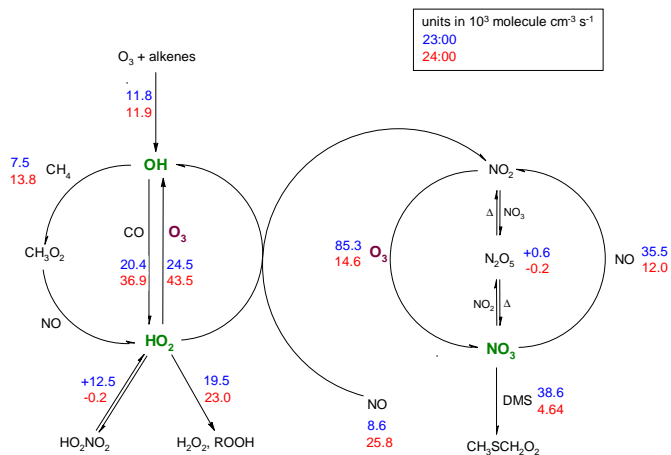


**Fig. 7.** O<sub>3</sub>, DMS and NO<sub>x</sub> concentrations measured during the night of 31 August–1 September.

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**Fig. 8.** Radical fluxes during the night of 31 August–1 September at 23:00 (in the middle of the NO<sub>2</sub> spike) and 24:00 (after the NO<sub>2</sub> spike).

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