The nitrate radical in the remote marine boundary layer

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Abstract. The technique of differential optical absorption spectroscopy has been used to determine the nitrate radical (NO₃) concentration in the remote marine boundary layer. The instrument was deployed in campaigns at Mace Head on the west coast of Ireland and on the north coast of Tenerife. A comprehensive set of NO₃ measurements under a wide variety of conditions was obtained. For instance, nighttime NO₃ levels at Mace Head ranged from 1 to 5 ppt in the clean marine atmosphere and from 1 to 40 ppt in semipolluted continental air masses. The nightly averaged NO₃ lifetime varied from less than 2 min to 4 hours. At Tenerife, where there was less variability in conditions, nighttime NO₃ ranged from 1 to 20 ppt, with nightly averaged lifetimes between 4 and 34 min. A photochemical box model, fully constrained by measurements of species that control the formation and removal of NO₃, was then employed to determine the major loss mechanisms of the radical. This shows that NO₃ in the clean marine air masses is very sensitive to small increases in the concentrations of dimethyl sulphide (DMS) and nonmethane hydrocarbons and that the radical is rarely in chemical steady state. At Tenerife, 80 - 90% of NO₃ was removed by reaction with DMS. However, in continental air masses with little marine influence, indirect losses of NO₃ via dinitrogen pentoxide (N₂O₅) usually dominate. It appears that in much of the North Atlantic, NO₃ is a more efficient sink for DMS compared to the hydroxyl radical (OH) during the day.

1. Introduction

The chemistry of the nighttime troposphere is usually dominated by reactions of NO₂. This radical can oxidize a number of nonmethane hydrocarbons (NMHCs) and sulphur-containing compounds such as dimethyl sulphide (DMS), and it also provides a route for the conversion of the oxides of nitrogen (NOₓ = NO + NO₂) to nitric acid (HNO₃) [see, e.g., Wayne et al., 1991]. The important nighttime reactions of NO₃ in the troposphere are summarized in Figure 1. The radical is formed in the atmosphere by the relatively slow oxidation of NO₂ by O₃, which appears to be the only primary source of NO₃ in the troposphere:

(R1) O₃ + NO₂ → NO₃ + O₂.

NO₃ reacts with NO₂ to produce N₂O₅, which readily dissociates establishing an equilibrium with NO₃:

(R2) NO₃ + NO₂ + M → N₂O₅ + M.

This equilibrium is usually achieved rapidly at ambient temperatures, unless the NO₂ concentration is very low [Carslaw et al., 1997a]. The equilibrium concentrations of NO₂ and N₂O₅ are approximately the same for an NO₂ mixing ratio of 1 ppb at 295 K.

Due to the strong absorption of NO₃ throughout the visible region of the solar spectrum, the radical is rapidly photolyzed during the day. The lifetime of NO₃ with respect to photolysis is approximately 5 s for overhead Sun and clear-sky conditions at sea level [Orlando et al., 1993]. Furthermore, the reaction between NO₃ and NO, which will be in approximate photochemical steady state with NO₂ during daytime, is very fast. In contrast, the estimated lunar photolysis rate of NO₃ at full moon is 2 x 10⁻⁷ s⁻¹ [Solomon et al., 1993], which corresponds to a lifetime of 1400 hours. During the night there should also be negligible levels of NO (unless fresh local emissions are present), since NO will be rapidly titrated away by O₃ with a time constant of about 1 min, assuming 30 ppb O₃ at 283 K. Therefore significant levels of NO₃ can form overnight via (R1).

The major direct gas phase loss mechanisms of NO₂ tend to be the reactions of the radical with a number of NMHCs. The reactions of NO₂ with alkanes and aldehydes proceed via hydrogen abstraction and although both of these reaction pathways tend to be relatively slow [Atkinson, 1991], they lead...
to the formation of HNO₃ and peroxy radicals. Both the alkyl peroxy radicals (RO₂) and the acyl peroxy radicals (RCO₃) formed can further react with NO₃ or recombine with NO₂ to form peroxy nitrates (RO₂NO₂), which act as a reservoir for NO₃. Furthermore, the HNO₃ formed via these reactions most likely provides a permanent sink for NO₃. The reactions of NO₃ with alkenes (including isoprene and various terpenes) are generally much faster than reactions with the alkanes. These proceed via the addition of NO₃ to a carbon-carbon double bond, followed by recombination with O₂ to yield a peroxy radical [Wayne et al., 1991]. The peroxy radicals formed by this reaction can then react with species such as NO, NO₂, and other peroxy radicals with the probable formation of organic nitrates as reasonably stable end products [Platt and Heintz, 1994].

NO₃ also reacts readily with sulphur-containing compounds and a reaction of particular importance in the marine boundary layer (MBL) is the reaction with DMS. Since DMS and NO₂ can often have quite similar concentrations in the MBL, their concentrations can be tightly coupled as they control each other [Allan et al., 1999]. The mechanism of the NO₃ + DMS reaction has received much attention [Ravishankara et al., 1997], and it is now agreed that the reaction proceeds via hydrogen abstraction followed by recombination with O₂ [Butkovskaya and LeBras, 1994, and references therein]:

(R3) NO₃ + CH₂SCH₂ → HNO₃ + CH₂SCH₂
(R4) CH₂SCH₂ + O₂ + M → CH₂SCH₂O₂ + M
(R5) CH₂SCH₂O₂ + NO₃ → CH₂S + CH₂O + NO₂ + O₂.

In the absence of NO during the night, (R5) will lead to the removal of a second NO₃ [Le Bras et al., 1993]. This will affect the turnover lifetime of NO₃ (vide infra) but not the rate of removal of NO₂. As we have discussed previously [Allan et al., 1999], other direct loss routes for NO₂ such as its self-reaction and thermal decomposition are too slow to be significant in the atmosphere. The heterogeneous uptake of NO₃, recently studied in the laboratory by Rudich et al. [1996], is also unlikely to be important under most conditions in the MBL.

Due to the equilibrium between NO₃ and N₂O₅, any loss of N₂O₅ will result in the removal of NO₃. One such indirect pathway is the homogeneous gas phase reaction (R6) N₂O₅ + H₂O → 2HNO₃.

Mentel et al. [1996] have recently measured k₆(293 K) to be about 2.5 × 10⁻²² cm³ molecule⁻¹ s⁻¹. The reaction was also shown to have a second-order component with respect to H₂O. This could be explained either by reactions occurring on the walls of the reactor, or by the second H₂O acting as a third body, or by reaction with H₂O dimers. In view of this uncertainty and our previous analysis [Allan et al., 1999] which showed that the [H₂O]² component would only make a modest contribution to NO₃ removal in the MBL, we have not included this in the model described below.

The heterogeneous uptake of N₂O₅ on aerosols can also make a substantial contribution to the indirect removal of NO₃ and the conversion of NO₃ into aqueous HNO₃ [Carslaw et al., 1997b; Allan et al., 1999]. Furthermore, the uptake of N₂O₅ on sea-salt particles can lead to the release into the gas phase of photolabile halogen species such as ClO₂ [e.g., Behnke et al., 1997, and references therein]. Although this reduces the overall effectiveness of N₂O₅ heterogeneous reactions as a sink for NO₃, these reactions provide a route for halogen activation [e.g., Seisel et al., 1997].

A very useful and simple diagnostic for analyzing field observations of NO₃ is to calculate the atmospheric turnover lifetime of the radical [Noxon et al., 1980; Platt et al., 1980]. If NO₃ is in steady state, where its rate of removal through a variety of direct and indirect processes is equal to its rate of formation via (R1), then the lifetime is given by

\[ \tau(\text{NO}_3) = \frac{[\text{NO}_3]_{ss}}{k_{\text{het}}(\text{NO}_3)} \tag{1} \]

where [NO₃]ₙ is the concentration assumed to be in steady state. Note that under conditions of very low NO₃, steady state conditions may not be achieved over most of the night [Carslaw et al., 1997a]. The reciprocal of this lifetime can then be compared with that calculated from the sum of the first-order loss processes involving NO₃ and N₂O₅ [Allan et al., 1999]:

\[ \tau(\text{NO}_3)^{−1} \geq \sum_i k(\text{NO}_3 + \text{HC}_i)[\text{HC}_i] + k(\text{NO}_3 + \text{DMS})[\text{DMS}] \]

\[ + k(\text{NO}_3 + \text{RO}_2)[\text{RO}_2] + k(\text{NO}_3 + \text{NO})[\text{NO}] + k_{\text{het}}(\text{NO}_3) \]

\[ + (k_6[\text{H}_2\text{O}] + k_{\text{het}}(\text{N}_2\text{O}_5))K_2[\text{NO}_2] \] \tag{2}

where the summation is over i reactive hydrocarbons HCᵢ, k₆(NO₃) and k₆(N₂O₅) are the first-order rate coefficients for heterogeneous loss of these species, and K₂ is the equilibrium constant for (R2). In principle, the equality will hold if all the removal processes for NO₃ have been accounted for. The application of (2) requires simultaneous measurements of O₃, NO₃, NO, reactive hydrocarbons, DMS, peroxy radicals, the aerosol volumetric surface area (ASA), temperature, and relative humidity. Although a number of studies have been carried out on NO₃ in the MBL [e.g., Heintz et al., 1996; Yvon et al., 1996; Carslaw et al., 1997b; Allan et al., 1999], few of these have had the complete set of ancillary data with which to investigate in detail the chemical processes occurring at night.

In this paper we will report the results of three intensive field campaigns to study NO₃ in the remote MBL at a midlatitude and a subtropical site, where relatively clean conditions could be observed, in contrast to most previous studies (vide supra). Furthermore, the requisite ancillary measurements
were available during much of the fieldwork reported here, allowing the use of a fully constrained photochemical box model. This will be employed here to determine which of the removal processes discussed earlier are important in the different air mass types encountered in the MBL, as well as examining the diurnal variations in the oxidation rate of DMS and the removal of NO₂.

2. Measurement Campaigns

NO₂ was measured by the technique of differential optical absorption spectroscopy (DOAS) (see Plane and Smith [1995] for a review of this technique) during the three intensive field campaigns. The first two campaigns were conducted at the Mace Head Atmospheric Research Station (MHARS) on the west coast of Ireland. The East Atlantic Summer Experiment (EASE'96) took place during July/August 1996, and the East Atlantic Spring Experiment (EASE'97) during April/May 1997. The MHARS, operated by University College Galway, is situated in County Galway on the west coast of Ireland (53° 19' 34" N, 9° 54' 14" W) at an altitude of 10 m above sea level. The location of this site, as shown in Figure 2, provides the opportunity to study northern hemispheric background air masses originating from the North Atlantic Ocean within a clean air sector of 180° to 300°. The site is also exposed to European continental emissions during high-latitude anticyclonic conditions and to clean polar air masses arising from midlatitude cyclones in the North Atlantic. The station is 88 km to the west of Galway city which is the nearest source of urban pollution, 150 km from the main Atlantic shipping routes and over 80 km from the transatlantic air corridors.

The DOAS instrument used to measure the concentration of NO₂ was installed in a nearshore building, and the retroreflector array was placed on a small island 4.2 km to the west of the site, as shown in Figure 2. This arrangement provided a total path light of 8.4 km at a height of approximately 25 m above sea level, and almost entirely within the MBL. Ancillary chemical and physical parameters measured during EASE'96 and EASE'97, and which are used in the present study, included NO, NO₂, O₃, NMHC, DMS, HCHO, ASA and meteorological data. Details of the instruments and sampling protocols are given in Table 1.

The third measurement campaign was carried out on the island of Tenerife during June/July 1997 as part of a larger experiment, the North Atlantic Regional Aerosol Characterization Experiment (ACE2) [Raes et al., 2000]. The aim of the campaign was to use a hill cap-cloud as a natural flow through reactor in order to study aerosol processing by a MBL cloud (see Bower et al. [2000] for an overview of this campaign). Although a total of six sites on Tenerife were used for ground-based measurements during the experiment, only three are relevant to the work described here. The DOAS instrument was situated at Benijo (28°40' N, 16°5' W) on the north coast (Figure 2), at an altitude of 75 m above sea level. The light beam was directed westward across Taganana Bay for a distance of 4.65 km to the retroreflector array, resulting in a total pathlength of 9.3 km almost entirely within the MBL. The array was placed on a cliff 250 m above sea level, so that the average height of the beam was 163 m above sea level. The second site was an empty house situated in the village of Taganana on the north coast at an altitude of 220 m. This served as a site for upwind gas and aerosol measurements below cloud base but away from the shoreline. The third site was a disused lighthouse on the shoreline at Punta del Hidalgo on the north coast (Figure 2). The tower was 55 m high with the majority of instruments located at the base of the tower. A sampling stack erected for the experiment enabled instruments to sample air drawn down the stack from the top of the tower. The ancillary data used for the present study included NO, NO₂, and O₃ from Taganana, and ASA, DMS, and meteorological data from Punta del Hidalgo. Although DMS, ASA, and local wind direction were also available from Taganana, the measurements obtained at the lighthouse were preferred for the following reasons: continuous DMS measurements for the whole period were not available from Taganana, the ASA and DMS measurements obtained at the lighthouse were preferred over those obtained at Taganana because the lighthouse was located closer to the source of the background aerosol loading, and the local wind direction measured at Taganana was strongly influenced by the local topography. Further information on the ancillary data is provided in Table 1.

3. DOAS Measurements of NO₃

The DOAS instrument, which measures the concentration of a species from its optical absorption over a pathlength of several kilometers, has been described in detail previously.
Table 1. Ancillary Measurements Required for NO₃ Analysis and Also as Inputs for the Constrained Model

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Technique / Instrument</th>
<th>Detection Limit / Time</th>
<th>Investigators / Reference</th>
</tr>
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| NO, NO₂ (1996) | Eco Physics chemiluminescent detector and photolytic converter | 50 ppt NO and NO₂ / 1 min | B. J. Bandy and S. A. Penkett (University of East Anglia (UEA))
| NO, NO₂ (1997) | NOₓ, four-channel chemiluminescence analyser | 5 ppt NO, 20 ppt NO₂ / 1 min | S. Bauguitte and S. A. Penkett (UEA)
| O₃ | Monitor Labs Model 8810 UV photometer | 1 ppb / 1 min | G. Spain, S. O’Doherty, and P. Simmonds (University of Bristol)
| Aerosol size distribution (1997) | Scanning mobility particle sizer, optical particle counters (ASASP-300, FSSP-100, and OAP) fluorescence | 5 nm-150μm radius / 1 min | C. D. O’Dowd and M. H. Smith (University of Sunderland); see O’Dowd et al. [1999]
| HCHO | automated gas chromatograph (GC) / flame ionization detector | Species-dependent detection limit ranging from 2 to 5 ppt / 1 hour | G. G. McFadyen and N. Cape (Institute of Terrestrial Ecology (ITE))
| CO₂ to C₆ NMHC and DMS | 2π radiometer | 1 min | G. G. McFadyen and N. Cape (ITE)
| | radiometer | 1 min | P. S. Monks (University of Leicester)
| | Automated weather system (AWS) | 1 min | G. G. McFadyen and N. Cape (ITE)
| NO, NO₂ (Taganana) | Eco Physics chemiluminescent detector and photolytic converter | 50 ppt NO and 100 ppt NO₂ / 1 min | G. G. McFadyen and N. Cape (ITE)
| O₃ (Taganana) | Monitor Labs ML9800 UV photometer | 0.5 ppb / 1 min | G. G. McFadyen and N. Cape (ITE)
| DMS (Hidalgo) | GC / flame photometric detector | 10 ng(S) m⁻³ / 30 min | M. Mangoni (IE-JRC Ispra)
| HCHO (Taganana) | fluorescence | 20 ppt / 1 min | P. Laj (FISBAT)
| Fine aerosol size distribution (Taganana) | Double dual mobility particle sizer (DMPS) system | 3.2 - 400 nm diameter / 10 min | P. P. Aalto and M. Kulmala (University of Helsinki)
| Fine aerosol size distribution (Hidalgo) | DMPS | 6.5 - 500 nm diameter / 10 min | R. Van Dingenen (IE-JRC Ispra)
| Coarse aerosol size distribution (Taganana) | ASASP-X | 110 nm - >3 μm / 1 min | C. Bradbury and T. Choularton (UMIST)
| NOₓ (Taganana) | 2π radiometer | 1 min | G. G. McFadyen and N. Cape (ITE)
| T and RH (Taganana) | Vaisala HMP505Y probe | 1 min | K. N. Bower and M. Flynn (UMIST)
| Wind direction (Hidalgo) | - | 10 min | F. McGovern and R. Van Dingenen (IE-JRC Ispra)

[b] ACE2 Database.
[c] Environment Institute, EC Joint Research Centre, Ispra.
[d] Inst. per lo Studio dei Fenomeni Fisici e Chimici della Bassa ed Alta Atm.
[e] University of Manchester Institute of Science & Technology.

[e.g., Carslaw et al., 1997a, 1997b; Allan et al., 1999]. The instrument consists of a Newtonian telescope (f/6, 31.5 cm diameter) which houses the optics for both transmitting light from a xenon arc lamp into the atmosphere and receiving light from a distant reflector that is used to fold the light path. The received light is then coupled to a spectrometer via a fiber optic cable and dispersed onto a photodiode array detector (PDA). Two important modifications were made for these field campaigns. First was the use of an array of retroreflectors to improve the accuracy of the folded light and hence permit longer light paths through the atmosphere to be employed. The array consists of 14 solid Suprasil quartz corner cubes, each with a diameter of 6 cm and a precision of 5 arc sec. They are mounted together on a supporting plate in a
modification was the use of a mode mixer on the 600 µm diameter Suprasil quartz multimode fiber optic cable. This was used to obtain a uniform intensity distribution at the fiber exit, independent of the distribution at the entrance [Stutz and Platt, 1997].

NO₃ was determined from the B²E' - X²A₁' absorption band centered at 662 nm. The transmitted light was directed through a 630 nm cut-on filter to prevent photolysis of NO₃ at wavelengths below 590 nm in the DOAS beam, and a 590 nm cut-on filter was also positioned in the receiver to prevent contamination in the spectrometer from second-order scattered sunlight. The spectrometer (0.5 m f/6.9 Czerny-Turner design) was used with a grating of 1200 groves mm⁻¹, providing a wavelength range of approximately 35 nm across the 1024-element PDA. The entrance slit of the spectrometer was set to a width of 600 µm and a height of 200 µm, corresponding to a resolution of about 0.6 nm. This was measured using the emission line at 659 nm from a low-pressure Neon lamp and corresponds to a sampling ratio of 19 diodes per full width at half maximum. The detector was cooled to -20°C using a four-stage Peltier cooler in order to minimize the dark current, allowing exposure times of up to 10 s in poor visibility.

A measurement of NO₃ required three different spectra to be collected: atmospheric + scattered light (A); scattered light (S) and lamp + atmospheric + scattered light (L). S spectra were recorded by shutting the xenon lamp. L spectra were obtained by opening an optical bypass which diverts a fraction of the transmitted beam directly into the receiving optics. The three spectra were taken in turn during a 1 min period, with each accumulation lasting 20 s. The cycle was then repeated for 10 min, with each type of spectrum being co-added. This procedure was introduced to reduce the effects of fluctuations in the lamp, atmosphere, or scattered light. A processed spectrum is then obtained from (A - S)(L - A), which is the spectrum transmitted through the atmosphere divided by the unattenuated lamp spectrum. This division largely removes not only the spectral features of the xenon lamp, but also the diode-to-diode variability in light sensitivity and the étaloning caused by the protective surface on the PDA. A further advantage is that since all three spectra contain the same dark leakage current and analog to digital offset of the PDA, the differences A - S and L - A effectively remove these.

The routine for deconvolving the processed spectra has been described in detail elsewhere [Plane and Nien, 1992; Plane and Smith, 1995]. The spectrum is smoothed using a fast Fourier transform (FFT) [Press et al., 1986] with a high-pass frequency filter, and the underlying trend line, containing the slowly varying component of the spectrum, is obtained from an FFT with a low-pass filter. This filtering technique removes high-frequency noise, arising from the diode-to-diode variability and read-out noise, and the broader spectral trends caused by Rayleigh and Mie scattering in the atmosphere, and detector étaloning which has not completely cancelled out in the processed spectrum. The logarithm of the broad trend (Iₑ') divided by the smoothed spectrum (I) gives the differential optical density spectrum. The total optical density (OD) at each wavelength in the spectrum is equal to the sum of the ODs of each of the individual species which absorb in the region of interest. To derive the concentration of each atmospheric species, an array of reference differential optical density spectra is created from the literature cross sections of the individual species. The reference spectra are made up to represent a typical atmospheric concentration and are then treated in the same way as the atmospheric spectra before being used in the fitting routine. All of the relevant reference spectra are then fitted to the atmospheric spectrum simultaneously using a least squares fitting routine employing singular value decomposition (SVD) [Press et al., 1986]. The fitting routine also allows the shifting and stretching of the reference spectra which is required to account for any spectral drift of the instrument between calibrations. The best fit is achieved when all known features are removed leaving a structureless residual spectrum.

The main absorbers in the 645-680 nm region are NO₃ and H₂O, and so both species are fitted in the analysis routine. The reference spectrum for NO₃ was calculated using the cross sections reported by Yokelson et al. [1994]. Because some of the rotational lines in the H₂O bands are close to saturation at the optical densities of H₂O typically encountered over an optical path of several kilometers in the boundary layer, the absorption bands do not exhibit Beer-Lambert behavior. Therefore following Alwell and Jones [1996], an H₂O absorption cross section was calculated from the high-resolution HITRAN database [Rothman et al., 1992], using the code of Drayson [1976] for the conditions of relative humidity, temperature, and atmospheric pressure at which the atmospheric DOAS spectrum was obtained. The cross section was then degraded to the spectral resolution of the DOAS spectrometer and converted into a reference spectrum.

Figure 3 illustrates the deconvolution procedure applied to an atmospheric spectrum containing an optical absorption due to NO₃. The concentration of NO₃ during the daytime is negligible due to its rapid photolysis. Thus a daytime reference spectrum (Figure 3a) taken about an hour before sunset or an hour after sunrise is divided into the nighttime spectrum, also shown in Figure 3a, to remove the water (311) overtone vibrational bands which peak at 651.5 nm. The result of this division is illustrated in Figure 3b and clearly shows the remaining NO₃ absorption at 662 nm. However, the division spectrum still contains residual structure due to incomplete removal of the water bands. The extent to which these water bands remain depends on how much the water vapor concentration changes between day and night. The division spectrum in Figure 3b is then smoothed using a fast Fourier transform (FFT) with a high-pass frequency filter, and the broad trend line is obtained by using an FFT with a low-pass filter (see Figure 3b). The logarithm of the broad trend line divided by the smoothed spectrum results in the differential optical density spectrum in Figure 3c. Figures 3e and 3f illustrate the differential cross sections of the NO₃ and H₂O references which are fitted simultaneously to the atmospheric spectrum (Figure 3c) using the least squares SVD fitting routine. The residual spectrum obtained after removing the fit is illustrated in Figure 3d. The retrieval shown in Figures 3a to 3d is for a fairly large mixing ratio of NO₃ (24.7 ± 0.7 ppt obtained at Mace Head on May 29, 1997, at 0345) normally associated with semipolluted conditions. Figures 3g and 3h are included to illustrate the ability of the technique to retrieve much smaller mixing ratios (in this case 1.9 ± 0.2 ppt obtained at Mace Head on May 20, 1997, at 0500) which is required for measurements in cleaner marine air.
4. Results and Discussion

Measurements of NO₃ were obtained on 7 nights during EASE’96 and on 25 nights during EASE’97. A further 14 nights of NO₃ observations were made along the north coast of Tenerife during June/July 1997. Figures 4a and 4b illustrate typical examples of NO₃ profiles obtained during EASE’96 and EASE’97 in various types of airmass. The entire NO₃ data set obtained in Tenerife is shown in Figure 4c. A rather striking feature is the night-to-night variability, particularly in the Mace Head observations. In order to understand this, we have classified the data using back trajectory analysis into sectors of air mass origin. For Mace Head these will be referred to as Atlantic (A), polar marine (P), easterly continental (EC), and northerly continental (NC). A typical 5 day back trajectory for each of these sectors is shown in Figure 5. In the case of Tenerife, back trajectory analysis shows two types of air mass dominated, clean maritime and European outbreak (air which has been over the European continent within the previous 5 days) [Verwer et al., 2000]. However, even European outbreak air spends 2-3 days over the Atlantic before reaching Tenerife (Figure 5) and is indistinguishable in terms of NO₃ levels.

By grouping the data obtained into these sectors, time profile plots of [NO₃], [NO₂], and rNO₃ can be derived for
Mace Head and Tenerife, as shown in Figure 6. These plots show the hourly median value of the data set for each sector, where the error bars are the associated 25th and 75th percentiles. The data have been plotted in this way to reduce the effect of data points at the extremes, where one very high or low mixing ratio can have a significant influence on the mean value. Although O$_3$ is important in the formation of NO$_3$, and hence in the calculated lifetime, it has not been included in the figure as there tends to be little significant variation in O$_3$ during the course of the night.

There are several noteworthy points in Figure 6. As expected, the largest concentrations of NO$_3$ were observed in easterly continental conditions because of the high levels of NO$_x$ (average $= 1200 \pm 700$ ppt, where the 700 ppt is the associated standard deviation). Significantly lower NO$_3$ levels were present during northerly continental periods (NO$_x = 250 \pm 100$ ppt) and in clean Atlantic conditions (NO$_x = 150 \pm 100$ ppt). Interestingly, τNO$_3$ is similar for all three sets of conditions, varying between 1 and 20 min and remaining approximately constant between sunset and sunrise (approximately 2000 and 0500 hours at Mace Head and 2000 and 0600 hours at Tenerife). This suggests that a nighttime steady state was achieved under these conditions, where the production and loss of NO$_3$ were balanced. In contrast to this were the data
obtained during the extremely clean polar episodes. Levels of up to 5 ppt of NO$_3$ were observed with nightly averaged NO$_2$ levels ranging from as little as 25 to 80 ppt. The NO$_3$ can be seen to increase gradually during the course of the night up to a maximum level reached only a few hours before sunrise. This can be seen more clearly in the time profile of $\tau$NO$_3$, which builds up to exceed 1 hour during these periods. This indicates that steady state was not achieved until well into the early morning; although the NO$_2$ levels are extremely low, there are no rapid loss processes for NO$_3$ in this very clean air. In the case of Tenerife, the NO$_2$ record exhibits peaks around 1900 hours and in the early morning, which are caused by local traffic at Taganana. In contrast, the lower NO$_2$ levels between 2000 and 0300 hours, and hence the calculated $\tau$NO$_3$ values during this period, should be representative of background Atlantic air, and lie between the values observed in Mace Head Atlantic and Polar air.

Figure 5 shows polar plots of $\tau$NO$_3$ as a function of local wind direction, at the two locations. In the case of Mace Head, the majority of the points associated with a strong continental influence (wind direction 30°-180°) lie within the 1 - 10 min range. By contrast, the majority of the points obtained in the 260°-30° wind sector lie between 10 and 100 min. In the case of Tenerife, most of the data falls in the N-NE sector, in accord with the long-range trajectories (Figure 5), and the majority of calculated lifetimes are in the range of 1 - 40 min. The bold circles in these polar plots indicate what $\tau$NO$_3$ would be if the only removal process of NO$_3$ was the direct gas phase reaction with DMS, where the DMS concentration used in each case is the average value measured during the respective campaigns. Note that the reaction NO$_3$ + DMS is assumed to consume a second NO$_3$ through (R5). Comparison with the measured $\tau$NO$_3$ shows that reaction with DMS is the major removal process at Tenerife and at Mace Head in the westerly sector between 240° and 30°, whereas other removal processes must dominate at Mace Head in the easterly sector from 30° to 240°.

The attribution of loss processes can be considered in more detail by plotting a frequency distribution of measured $\tau$NO$_3$ (in 5 min intervals) during each campaign, and comparing this to the distribution of lifetimes calculated for loss by DMS, NMHCs, and heterogeneous reaction on aerosols. The advantage of this form of analysis is that it partially overcomes the temporal and spatial problem of comparing the DOAS measured NO$_3$, averaged over a column of about 4 km through the boundary layer, with in situ measurements of the other species. Figures 8a to 8c show the measured $\tau$NO$_3$ frequency distributions for Mace Head (Polar and Atlantic marine data), Tenerife, and Mace Head (northerly and easterly continental data), respectively. The distributions for the three cases are rather different. For Mace Head (marine) the distribution is much less peaked, with a most likely lifetime of 15 - 20 min (Figure 8a). The distributions for Tenerife and Mace Head (continental) both have a most probable lifetime of only 5 - 10 min, but the Tenerife distribution (Figure 8b) exhibits a much longer tail. Comparison with the calculated $\tau$NO$_3$ distribution...
for loss by total DMS chemistry (DMS + CH$_2$SCH$_2$O$_2$) again shows three contrasting cases. For Mace Head (marine) the measured distribution is much broader and there does not appear to be a significant correlation. This is not surprising because the low levels of DMS observed at Mace Head during the campaigns suggest that a number of other removal processes need to be considered. In contrast, the Tenerife data (Figure 8b) show a very good correlation between the distributions, reinforcing the conclusion from the polar plot in Figure 7 that much of the NO$_3$ chemistry is dominated by its reaction with DMS and CH$_2$SCH$_2$O$_2$.

At the other extreme the continental data from Mace Head (Figure 8c) shows two distinctly separate distributions, as would be expected since DMS is unlikely to play a significant role in air masses originating from the continent. However, if the indirect loss processes of N$_2$O$_5$ and the direct removal of NO$_3$ via reactions with NMHCs and ASA uptake are included, then the calculated tNO$_3$ distribution is very similar to that of the measured tNO$_3$ (Figure 8d), suggesting that all these loss mechanisms are significant. For the loss due to ASA, the uptake rate was calculated with uptake coefficients of 0.003 for N$_2$O$_5$ and NO$_3$ [Allan et al., 1999].

Finally, we consider the detailed time-dependent behavior of NO$_3$, using a zero-dimensional constrained photochemical box model of the MBL [McFiggans et al., 2000]. Briefly, the model contains 80 chemical species undergoing 153 gas phase and 23 photochemical reactions, and describes 19 processes of heterogeneous uptake and wet/dry deposition. The model treats chemical species in three different categories. The first group of species are allowed to vary freely throughout the simulation; their coupled continuity equations are solved using a variable stepsize fourth-order Runge-Kutta integrator [Press et al., 1986]. Second are the species whose lifetimes are too short to consider in this manner without the model becoming excessively stiff. Instead, the steady state concentrations of species such as O($^1$D), O($^3$P), CH$_3$, C$_2$H$_6$, CH$_3$O, OH, and H are calculated in a separate iterative routine. Using an appropriate convergence limit (normally 0.01% change in concentration between iterations) and recalculating the steady state every simulated minute, this approximation introduces negligible errors. The third group includes species whose concentrations are available from experimental field observations. A constrained time step procedure is used to simulate the fluctuations of these species. For this method the field data are first averaged or interpolated to a 1-min frequency (after the removal of concentration spikes from local transient events, where necessary). The concentrations of the constrained species are then read in at the appropriate simulation time and interpolated for each integration step over the next minute. Therefore these species are not assigned
continuity equations and integrated, and their fluctuations do not determine the size of the integration time step. This technique avoids large step changes in concentrations and the associated risk of numerical instability that could arise if the model was successively halted and reinitialized.

For this study the model was constrained by all the species whose concentrations were measured in the field campaigns, except for NO3 which was predicted and then compared with the observations. The constrained species included (where available) CH4, CO, NO2, NO, O3, DMS, NMHCs, HCHO, and ASA. Although the individual oxidation pathways of the measured hydrocarbons were not treated explicitly in the model, the observed hydrocarbon data were used to define a generic alkene and an alkane. For each of these species a weighted rate constant was calculated from the individual NMHC concentrations (unsaturated or saturated) and their individual rate constants with OH and NO3. The model was also constrained by measured physical parameters including temperature, radiometric data, and relative humidity.

A significant uncertainty in the model is the treatment of the aerosol uptake of NO2 and also the reaction of NO2 with water vapor [Allan et al., 1999]. For the present study, $\gamma_{NO2}$ was fixed at 0.003, an average determined from the work of Rudich et al. [1996] for the uptake of NO2 onto the surfaces of NaCl solutions. In the case of $N_2O_5$, two values for $\gamma_{NO3}$ were used depending on the air mass type. In marine air masses experienced at Tenerife and during the Mace Head polar periods, $\gamma_{NO3}$ was set to 0.03, a value determined for the uptake of $N_2O_5$ onto surfaces of NaCl solution [Behnke et al., 1997]. For modeling the continental air mass episodes experienced at Mace Head, $\gamma_{NO3}$ was set to a value of 0.003 suggested from the work of Allan et al. [1999]. For the reaction of $N_2O_5$ with water vapor a value for $k_7$ of $2.5 \times 10^{-22}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was used [Montiel et al., 1996].

The photochemical box model was first run for the period of J185-199 during ACE2. Since NMHCs were not measured during this campaign, typical average mixing ratios of the alkanes and alkenes observed in clean marine air at Mace Head were used. These were 1350 ppt for the alkanes (weighted rate coefficient with NO3 = $3.6 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$), and 150 ppt for the alkenes (weighted rate coefficient = $3 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$). Figure 9a shows the NO3 predicted by the constrained model compared with the NO3 measurements during this period. With the exception of the night of J194-195, there is very good agreement between the modeled and observed NO3. The short-term variability in NO3 tends to be controlled by the levels of NO2, especially the peaks around sunset and sunrise which generally appear in both the NO3 and NO2 time series.

The various loss mechanisms of NO3 are compared in Figure 9b. This shows nightly profiles, averaged over all modeled days, of the percentage losses for the different pathways. The major removal pathway for NO3 is via its reaction with DMS (80-90%), as suggested by the analysis of the lifetime data (Figure 8b). Due to the dominance of DMS the predicted NO3 is not sensitive to changes in $\gamma_{NO3}$ and $\gamma_{N2O5}$, the gas phase reaction of $N_2O_5$ with H2O, or modest changes in the assumed NMHC concentrations. There is clearly a discrepancy between the measured and modeled NO3 on the night of J194-195. The reasons for this are not known. However, if DMS is set to zero in the model then good agreement is obtained, which suggests that the observed DMS at the lighthouse may not on this occasion have been present in the air mass sampled by the DOAS lightpath (which was about 10 km away; Figure 2).

A more complicated situation occurs at Mace Head, where different air mass types were sampled (see above). Of particular interest are the polar periods, where there is evidence that NO3 may not be in steady state (Figure 6). Taking the night of J127-128 as a case study, the box model was used to calculate the time-integrated NO3 concentration, [NO3]$_{int}$, as before. The constrained species in the model were also used to calculate the steady state NO3 concentration ([NO3]$_{ss}$) by inserting the upper limit of $[NO3$ from (2) into (1). Figure 10a compares the observed NO3 concentration with [NO3]$_{ss}$ and [NO3]$_{int}$ during this night. The variation in $[NO3$ is also illustrated. There is generally good agreement between the observed NO3 and [NO3]$_{ss}$ over the night. However, [NO3]$_{ss}$ deviates by up to a factor of 3 from the observations during the first part of the night until about 0100 hours. After this the measured concentrations and the two model profiles agree well, all showing a drop in [NO3] which occurs 2 hours before sunrise and is therefore not related to photolysis of the radical. On investigation of the NO3 losses predicted by the model (Figure 10b) there is a sharp increase in the contribution of DMS after midnight. Indeed, during this period the DMS changed from...
Figure 8. Frequency plots comparing the calculated lifetime of NO3 from (2) to the observed NO3 lifetime calculated from (1): Figures 8a, 8b and 8c compare the observed lifetime to that calculated assuming only DMS chemistry for Mace Head (marine), Mace Head (Continental), and Tenerife, respectively; Figure 8d compares the observed lifetime with that calculated by combining all losses given in (2) for Mace Head continental conditions.

Figure 9. (a) Modeled versus measured NO3 for the period of J185-199; (b) an average loss profile derived for each important mechanism from all the nights modeled, where ASA indicates the loss to aerosol surfaces.
Figure 10. (a) Modeled (steady state and time integrated) and measured NO₃ from Mace Head for the night of J127-128, 1997. Also shown is the calculated steady state lifetime of NO₃. (b) Percentage loss of NO due to each important mechanism, where ASA indicates the loss to aerosol surfaces.

Under the semipolluted conditions of this night all of the major loss mechanisms for NO₃ play a significant role, as shown in Figure 12b (this was suggested by the earlier analysis of the τNO₃ frequency distribution in Figures 8c and 8d). The reactions DMS + NO₃ and N₂O₅ + H₂O are the dominant loss processes, although aerosol uptake and reactions with NMHCs are still significant. The DMS component arises from the low mixing ratio of DMS (< 12 ppt for the night) present in this air mass, presumably entrained while passing over both the North and Irish Seas. Since the total loss rate remained relatively constant over the night, [NO₃]ₚ correlates closely with [NO₂]. Variable τNO₃ calculated from (2) is mostly less than 10 min, which is in good agreement with the average lifetime of 9 min calculated from (1).

All of the loss mechanisms shown in Figure 12b contribute to the removal of NOₓ from the atmosphere in the form of HNO₃, or as complex organic nitrates in the case of various alkenes. By using the measured ancillary data with the NO₃ and OH predicted by the model, it is possible to compare the production rates of HNO₃ for both day and night during this period. During the day this simply equates to the reaction of OH + NO₂, whereas at night all the NO₃ removal mechanisms shown in Figure 12b need to be considered. Figure 13 illustrates the variation in the production rates of HNO₃ over a period of the 2 days for which the model was run. During this period the majority of HNO₃ was produced during the day, although NO₃ chemistry makes a significant contribution, largely through the gas phase reaction of N₂O₅ with H₂O. The integrated contributions of OH and NO₃ to HNO₃ formation indicate that OH is around 2.6 times more efficient at removing NO than NO₃: the 24 hour average removal rates are 5.0 x 10⁶ and 1.9 x 10⁵ molecule cm⁻³ s⁻¹, respectively. Moreover, the contribution from NO₃ should be at least equal to that from OH under similar conditions during autumn and winter months when there are more hours of darkness.
NMHCs, and that the radical is often not in a steady state to contribute up to 80% of the removal of NO₃.

Due to the wide range of conditions experienced, the nightly averaged NO₃ lifetime varied from less than 2 min through to 4 hours. The very long lifetimes are associated with very clean air masses of polar origin where the NO₃ had not reached steady state. The levels of NO₃ observed at Tenerife ranged from 1 to 20 ppt, with NO₃ lifetimes in the range of 4 to 34 min. Both simple NO₃ lifetime analysis and a fully constrained box model show that 80 - 90% of NO₃ removal at Tenerife is caused by reaction with DMS, where the average DMS mixing ratio (+ standard deviation) was 44 ± 28 ppt. These results are in accord with our previous study during spring at the Weybourne Atmospheric Observatory in north Norfolk (England) [Carslaw et al., 1997b], where the DMS was found to contribute up to 80% of the removal of NO₃.

The behavior of NO₃ observed at Mace Head was more varied due to the variety of air mass types sampled. The constrained model shows that the NO₃ in the clean marine air masses is very sensitive to small changes in DMS and NMHCs, and that the radical is often not in a steady state between production and loss. In easterly continental air masses, the contribution to HNO₃ formation from NO₃ chemistry is significant and would be more so for similar conditions during the winter when shorter days with reduced photolysis and longer nights are more characteristic. Read 2.0E+06 as 2.0 x 10⁶.

5. Conclusions

The levels of NO₃ observed at Mace Head during spring and summer ranged from 1 to 40 ppt. Mixing ratios as high as 5 ppt were observed in the clean marine atmosphere, with higher mixing ratios in semipolluted continental air masses. Due to the wide range of conditions experienced, the nightly averaged NO₃ lifetime varied from less than 2 min through to 4 hours. The very long lifetimes are associated with very clean air masses of polar origin where the NO₃ had not reached steady state. The levels of NO₃ observed at Tenerife ranged from 1 to 20 ppt, with NO₃ lifetimes in the range of 4 to 34 min. Both simple NO₃ lifetime analysis and a fully constrained box model show that 80 - 90% of NO₃ removal at Tenerife is caused by reaction with DMS, where the average DMS mixing ratio (± standard deviation) was 44 ± 28 ppt. These results are in accord with our previous study during spring at the Weybourne Atmospheric Observatory in north Norfolk (England) [Carslaw et al., 1997b], where the DMS was found to contribute up to 80% of the removal of NO₃.

The behavior of NO₃ observed at Mace Head was more varied due to the variety of air mass types sampled. The constrained model shows that the NO₃ in the clean marine air masses is very sensitive to small changes in DMS and NMHCs, and that the radical is often not in a steady state between production and loss. In easterly continental air masses the indirect losses of NO₃ via N₂O₅ dominate, and the model appears to confirm the finding of Allan et al. [1999] that \( \gamma \text{N}_2\text{O}_5 \) is at least a factor of 10 smaller for continental aerosols compared with sea-salt particles.

From this study it has been shown that in clean Atlantic air observed at both Mace Head and Tenerife, the mean nighttime mixing ratio of NO₃ ranges from 1 to 7 ppt (\( \approx 2.6 \times 10^{-9} \) - \( 2.3 \times 10^{-8} \) molecule cm\(^{-3} \)). This corresponds to diurnal mean mixing ratios of 0.5 - 3.5 ppt (assuming an average of 12 hours of darkness). This is in sensible accord with the diurnal average of 3.9 ppt recently determined from measurements made on the island of Rügen in the Baltic Sea [Heintz et al., 1996].

In comparison, the measured daytime average OH concentration at Mace Head during 1997 was \( 1.4 \times 10^7 \) molecule cm\(^{-3} \) (D. J. Creasey, University of Leeds, personal communication, 1998), or a diurnal average of \( 7 \times 10^7 \) molecule cm\(^{-3} \). This compares well with the estimated 24 hour global average OH concentration of \( 8.1 \times 10^7 \) molecule cm\(^{-3} \) [Prinn et al., 1992].

An important reaction in the marine environment is the oxidation of DMS by NO₃ at night and OH during the day. Comparing the rate constants for the reaction of DMS with NO₃ and OH (1.1 x 10⁻¹² and 4.8 x 10⁻¹² cm³ molecule⁻¹ s⁻¹ at 283 K, respectively [DeMore et al., 1997]) shows that the concentration of NO₃ would have to be approximately a factor of 5 larger in order to compete with the OH reaction. The range of NO₃ concentrations measured in the present study are in fact 18 - 130 times larger, indicating that NO₃ is the more efficient sink for DMS under these conditions. It should be noted that the maximum average nighttime mixing ratio of DMS encountered during the campaign at Tenerife was of the order of 50 ppt on average, with NO₃ levels in the range 100 - 300 ppt. These levels of NO₃ were also typical of the Atlantic air arriving at Mace Head. Assuming that these values occur over much of the north Atlantic, then with DMS ∼ 50 ppt the oxidation of DMS will be faster at night. This agrees with the model results from Allan et al. [1999], where it was shown that when the NO₃ concentration is greater than about 60% of DMS, then DMS will be oxidized more rapidly by NO₃ than by OH. Many of the reactions of NO₃ with other NMHCs have rate constants that are between 10 and 1000 times slower than the equivalent reactions with OH [DeMore et al., 1997]. However, the existence of NO₃ at the levels observed in this study will make the rates of some of these reactions more comparable between day and night.

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