



Chemical and meteorological influences on the lifetime of NO₃ at a semi-rural mountain site during PARADE

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Abstract. Through measurements of NO₂, O₃ and NO₃ during the PARADE campaign (PARTicles and RADicals, Diel observations of mechanisms of oxidation) in the German Taunus mountains we derive nighttime steady-state lifetimes (τ_{ss}) of NO₃ and N₂O₅. During some nights, high NO₃ (~ 200 pptv) and N₂O₅ (~ 1 ppbv) mixing ratios were associated with values of τ_{ss} that exceeded 1 h for NO₃ and 3 h for N₂O₅ near the ground. Such long boundary-layer lifetimes for NO₃ and N₂O₅ are usually only encountered in very clean/unreactive air masses, whereas the PARADE measurement site is impacted by both biogenic emissions from the surrounding forest and anthropogenic emissions from the nearby urbanised/industrialised centres. Measurement of several trace gases which are reactive towards NO₃ indicates that the inferred lifetimes are significantly longer than those calculated from the summed loss rate. Several potential causes for the apparently extended NO₃ and N₂O₅ lifetimes are examined, including additional routes to formation of NO₃ and the presence of a low-lying residual layer. Overall, the most likely cause of the anomalous lifetimes are related to the meteorological conditions, though additional NO₃ formation due to reactions of Criegee intermediates may contribute.

1 Introduction

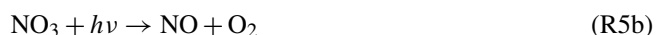
NO₃ and N₂O₅ are key species in the chemical removal of NO_x and of several hydrocarbons at night (Wayne et al., 1991; Atkinson and Arey, 2003). Traditionally, NO₃ is considered to be formed mainly by the reaction of NO₂ with O₃ (Reaction R1) with negligible contributions e.g. from reaction between OH and HNO₃ (Reaction R2) or the photolysis of halogen nitrates (XONO₂), where X may be Br or Cl (Reaction R3). N₂O₅ is produced in an association reaction between NO₃ and NO₂ (Reaction R4a), with which it is in thermal equilibrium (Reactions R4a, b).



The production rate of NO₃ is therefore usually assumed to be the product of the NO₂ and O₃ concentrations and the rate constant (k_1):

$$P(\text{NO}_3) = k_1[\text{NO}_2][\text{O}_3]. \quad (1)$$

In general, equilibrium between N₂O₅, NO₃ and NO₂ is reached rapidly following sunset and holds until sunrise (Brown et al., 2003). During the day, NO₃ is photolysed (with a lifetime of a few seconds) to give NO₂+O (Reaction R5a, ~90 %) or NO+O₂ (Reaction R5b, ~10 %) (Johnston et al., 1996) and also reacts quickly with NO (Reaction R6) so that NO₃ and N₂O₅ mixing ratios are usually below the detection limit of most instruments. During the night, in the absence of light to regenerate it from NO₂ (Reaction R7) and with sufficient distance from emissions sources, NO levels approach 0 (due to Reaction R8) and NO₃ and N₂O₅ can accumulate in the atmosphere.



The mechanism and rate of removal of NO₃ and N₂O₅ from the atmosphere depend on the type of air mass. In areas impacted by local anthropogenic activity, NO can be a major sink of NO₃. The rate constant for this reaction of $2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson et al., 2004) results, for example, in a chemical lifetime for NO₃ of about 16 s in the presence of 100 pptv of NO. NO₃ mixing ratios measured in situ at ground level in cities are sometimes low due to the high mixing ratio of NO. However, a few tens of kilometres downwind of urban areas or several tens of metres aloft, where [NO] can be significantly lower due to reduced mixing of ground-level emissions and titration by O₃, NO₃ mixing ratios can reach up to several hundred pptv and N₂O₅ up to a few ppbv (Asaf et al., 2009; Brown et al., 2009). Downwind of industrial activity, especially that related to petroleum production and storage, observed NO₃ lifetimes are limited by the presence of reactive hydrocarbons (Geyer et al., 2003; Stutz et al., 2010; Brown et al., 2011; Crowley et al., 2011).

In rural and forested environments, NO can be emitted from soils but is in general much less concentrated than in urban areas, and its mixing ratio is often close to 0 at night. In these environments, biogenic volatile organic compounds (BVOCs) can contribute a substantial fraction of the NO₃ reactivity. Unsaturated BVOCs such as monoterpenes have large rate constants for reaction with NO₃, e.g. $\sim 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for limonene and $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for α -pinene and β -pinene (Atkinson and Arey, 2003). In heavily forested areas with high monoterpene emission rates, NO₃ lifetimes may be reduced to a few tens of seconds (Rinne et al., 2012; Mogensen et al., 2015), resulting in efficient conversion of NO_x to organic nitrates and formation of secondary organic aerosol (Hallquist et al., 1999; Fry et al., 2014).

In the absence of any known, significant gas-phase reaction, the main sink of N₂O₅ at night is heterogeneous hydrolysis on aqueous aerosols, clouds and surfaces. The formation of particle-phase HNO₃ by this route results in repartitioning of NO_x from the gas to the condensed phase. Deposition of the particle nitrate formed is a substantial, permanent loss process for NO_x, resulting in reduced rates of photochemical O₃ production. Furthermore, if the aerosol particles contain chloride, the uptake of N₂O₅ can result in release of ClNO₂ and subsequently Cl atoms, which may enhance the rates of oxidation of hydrocarbons (Behnke et al., 1997; Osthoff et al., 2008; Bertram and Thornton, 2009; Thornton et al., 2010; Sarwar et al., 2012). The N₂O₅ uptake coefficient (overall efficiency of transfer from gas to particle phase) is largest for aqueous aerosols but depends on the composition of the aerosol (nitrate, sulfate and organic content) and humidity and possible organic coatings (Riemer et al., 2009) and is thus highly variable in time and space. Losses of NO₃ to aerosol or other surfaces are generally considered to be minor compared to its gas-phase losses and indirect losses via N₂O₅ uptake. In environments such as clean marine air masses where reactive partners for NO₃ are absent, lifetimes can become large and N₂O₅ losses to aerosol or surfaces may control the NO₃ levels via the equilibrium (Reactions R4a, b) (Heintz et al., 1996; Martinez et al., 2000).

Over the continents during the night, when the earth's surface does not receive energy by solar radiation, it cools down and the convective mixing which usually takes place during the day stops. This results in formation of a shallow, weakly mixed nocturnal boundary layer, with strong vertical stratification. Under such conditions, pronounced vertical gradients in NO₃ and N₂O₅ mixing ratios have been observed (von Friedeburg et al., 2002; Stutz et al., 2004; Brown et al., 2007) with ground-level emissions (both biogenic and anthropogenic) often resulting in lower NO₃ and N₂O₅ lifetimes, with cleaner air aloft (e.g. in the residual layer or free troposphere) often resulting in higher values. In all these different environments, the emission/formation rates of VOCs and aerosols and subsequent mixing are thus the key parameters controlling the NO₃ and N₂O₅ lifetimes.

In this paper, we describe a subset of an extensive suite of measurements obtained in the PARADE (PARTicles and RADicals, Diel observations of mEchanisms of oxidation) campaign (August–September 2011) at the top of a ~825 m high mountain situated between an urbanised flatland area and a forested mountainous area. A first campaign at this site (Crowley et al., 2010) during May 2009 found maximum NO₃ lifetimes of 10 to 15 min with mixing ratios up to 50 pptv for NO₃ and 500 pptv for N₂O₅. From the results of this first campaign it was concluded that at near-zero nighttime NO mixing ratios, the NO₃ lifetime was most likely controlled by emissions of BVOCs, which were, however, not measured. The heterogeneous loss of N₂O₅ was found to be only of limited importance in controlling NO₃ lifetimes. During PARADE, several hydrocarbons, both biogenic and an-

thropogenic, were measured as well as NO and also aerosol surface area (ASA) and chemical composition. We compare NO₃ lifetimes calculated using a steady-state approximation (based on the NO₃ production rate and mixing ratio) with those derived from the summed reactivity of individual trace gases and surfaces. For several campaign nights, we found that the steady-state lifetime significantly exceeded the lower limit of the NO₃ lifetime calculated from the summed reactivity and investigate potential causes of this.

2 Campaign location and measurement techniques

2.1 Site description

The PARADE campaign took place at the Taunus Observatory located on top of the Kleiner Feldberg mountain (50.22° N, 8.45° E) 825 m above sea level (a.s.l.). Local sites at the base of the mountains are at elevations of 120 ± 50 m. The station is used permanently by the environment and geological agency of the state of Hessen (HLUG) and the German weather service (DWD). The site has already been described (Handisides, 2001; Crowley et al., 2010), and only a short summary is given below. Directly (1–2 km) to the north-north-east and the south-east of the site are two similarly high mountains (Großer Feldberg at 878 m and Altkoenig at 798 m a.s.l.). The area in the north-west to north-east sector may be described as a relatively sparsely populated, partially forested rural region, whereas the south-west to south-east sector contains significant urban infrastructure including the densely populated cities of Frankfurt (~ 20 km to the south-east) and Mainz and Wiesbaden (20–30 km to the south-west). The site is directly surrounded (100 m radius) by a mix of coniferous trees (mainly spruce) and shrubs. Within a radius of 5 km from the site, the region is dominated by forest (coniferous, broad-leaved and mixed), especially to the north-east which has the lowest contribution from local agriculture and urban emissions. This is displayed in the land-use pie charts found in Fig. S1 in the Supplement. The same figure indicates that over a distance of 50 km, a significant fraction (~ 50 %) of the land area is used for agriculture.

The largest urban influence is found in the south-east sector for both 5 and 50 km distances to the site. In the northern sectors, the closest cities are located between 60 and 90 km away from the site and are significantly less populated than Frankfurt, Mainz and Wiesbaden. The heavily populated and industrialised *Ruhrgebiet* is about 130 km towards the north-west.

During the PARADE campaign, most instruments were located in the permanent laboratory facilities at the site. A platform on top of the building was used to house some instruments and the inlets outside at a height (from the ground) of about 8 m. Measurements central to this study (NO, NO₂, NO₃, N₂O₅, O₃, VOCs) were sampled via co-located in-

Table 1. Instruments deployed during PARADE.

Species	Instrument	Inlet position
NO ₃ and N ₂ O ₅	CRDS	Tower
NO ₃	LP-DOAS	Roof*
NO ₂	CRDS	Tower
NO	CLD	Tower
VOCs	GC-MS/GC-FID	Tower
O ₃	AirPointer	MoLa
Aerosol surface area	FMPS/APS	MoLa

* The telescope of the LP-DOAS set-up was located on the roof, about 2 m below the inlets of the point measurements. The retroreflectors were at different heights at a distance of ~ 1.5 km towards the north (see Sect. 2.2.4).

lets (< 5 m horizontal separation, < 1 m vertical separation). Aerosol measurements were made from a mobile laboratory (MoLa) (Drewnick et al., 2012) with its inlet at 10 m height, about 15 m distant from the main building. The instruments deployed are listed in Table 1, operational details, measurement uncertainties and detection limits are given in the next section. The MoLa also provided meteorological data (wind speed, wind direction, temperature, pressure relative humidity (RH) and global radiation) at 1 s resolution. The values were in generally good agreement with the lower frequency data sets reported by the DWD and HLUG.

2.2 Instrumentation

Below, we describe the instruments (and their overall uncertainties) used to make the critical measurements related to the calculation of NO₃ lifetimes. NO₂ and O₃, important for calculation of NO₃ production rates, were measured by multiple instruments, with good agreement. A comparison of three NO₂ data sets, including the one used here, is described in Thieser et al. (2016). Several O₃ data sets agreed to within about 10 % and the choice of data set for e.g. NO₂ or O₃ would not change the conclusions of this work.

2.2.1 NO₂, NO₃ and N₂O₅ measurements by cavity ring-down spectrometer (CRDS)

The two-channel thermal dissociation CRDS measuring NO₃ and N₂O₅ was deployed at this site during a previous campaign (Schuster et al., 2009; Crowley et al., 2010). Briefly, the CRDS uses a laser diode tuned to 662 nm to directly measure NO₃ in one channel at ambient temperature and the sum of (NO₃ + N₂O₅) in a second channel which is held at ~ 100 °C, converting N₂O₅ to NO₃ (plus NO₂). Zeroing is performed by addition of NO (Reaction R6). The mixing ratio of N₂O₅ is then calculated from the difference in mixing ratios observed in each cavity. The CRDS instrument was located outside on the platform on top of the building in order to reduce inlet loss of NO₃. Air is drawn through a 1 m length of 0.5 in. (OD) PFA tube at 50 standard L min⁻¹ and sampled (18 standard L min⁻¹) from the centre of the flow

via 0.25 in. PFA tubing into the two cavities of the CRDS. This set-up keeps inlet residence times short (≈ 0.1 s) and also helps avoid sampling of coarse particles and droplets. Corrections were applied to account for the losses of NO₃ on the filters, on the walls of the automatic filter changer and during passage through the cavities. The overall NO₃ transmission was $\sim 68\%$ (Crowley et al., 2010). The instrument detection limit was 2 pptv in 1 s for NO₃ and approximately 5 pptv for N₂O₅. The total uncertainty was $\sim 15\%$ for both NO₃ and N₂O₅, with the largest contributions arising from uncertainty in the NO₃ cross section (Orphal et al., 2003; Osthoff et al., 2007) and NO₃ losses.

During PARADE, NO₂ was measured using several instruments. We use data obtained using CRDS with a 405 nm diode laser as recently described in detail (Thieser et al., 2016). The instrument was zeroed using dry, synthetic air and corrections were made for humidity differences between the zero air and ambient. Typical ring-down times were ~ 30 μ s and the instrument has a detection limit for NO₂ of ≈ 20 pptv in 1 min and an accuracy of 6% where the dominant contribution is uncertainty in the NO₂ cross sections (Voigt et al., 2002).

2.2.2 VOC measurement by GC

VOCs were measured using two gas-chromatographic instruments with a mass spectrometer (GC-MS) and a flame ionisation detector (GC-FID). The GC-MS measured biogenic and aromatic hydrocarbons with online adsorption/thermal desorption (Markes International) connected to a gas chromatograph (Agilent GC 6890A) and a mass selective detector (Agilent MSD 5973 inert). The time resolution was ~ 1 h (35 min sampling time), and detection limits were around 1 pptv with an uncertainty of 10–15%.

The GC-FID measured non-methane hydrocarbons (NMHC) using two coupled gas chromatographs (GC 5000 VOC and GC 5000 BTX; AMA instruments, Ulm, Germany). GC 5000 VOC was used for measurement of C₂–C₆ NMHCs and BTX for C₆–C₁₂. The detection limits ranged from 1 to 5 pptv, exceptions being ethane, ethene, propene, benzene and toluene with values of 8, 16, 9, 14 and 48 pptv respectively. The GC-FID was calibrated using a multi-gas mixture (National Physical Laboratory). Total uncertainty is close to 10% for most trace gases with the exception of 1-pentane (15%). The time resolution of the measurement is 60 min and the mixing ratio represents an average over a sampling period of 20 min.

2.2.3 NO, O₃ and CO₂

NO measurements were made with a modified commercial chemiluminescence detector (CLD 790 SR). Operation of this instrument during the PARADE campaign has recently been described (Li et al., 2015). The detection limit for this instrument is 4 pptv in 2 s with a total uncertainty of 4%. The

O₃ data set used in this work was obtained by a commercial AirPointer from Recordum Messtechnik GmbH. It was located in the MoLa and has a detection limit of ~ 1 ppbv (Drewnick et al., 2012) and an accuracy of 5%. The O₃ inlet was situated a few metres above the MoLa, itself located 15 m metres away from the main tower. CO₂ was measured using non-dispersive differential broadband infrared absorption (LICOR 6262).

2.2.4 NO₂, O₃ and NO₃ measurements by long-path differential absorption spectroscopy (LP-DOAS)

In addition to the co-located point measurements described above, NO₂, O₃ and NO₃ were also measured by LP-DOAS over a light path of ~ 3 km. The telescope was situated on the same roof as the CRDS instruments (835 m a.s.l.) and was connected with a glass fibre to the laboratory where the light source, spectrometer and other components were located. Three reflectors were positioned at different heights (896.5, 927 and 959 m a.s.l.) to the north-north-east of the telescope on a tower at the Großer Felberg mountain (see Sect. 2.1) at a distance of 1.48 km from the light source. A fourth reflector was positioned on the Großer Feldberg mountainside at a distance of 1.23 km from the light source at 872 m a.s.l. A schematic showing the light paths in relation to the site topography is shown later when we discuss the results. The overall measurement accuracies are 2, 2 and 10% for NO₂, O₃ and NO₃ respectively and are dominated by uncertainties in the absorption cross sections used.

2.2.5 Particle properties

Particle size information was obtained using MoLa instruments (see above). A fast mobility particle sizer (FMPS 3091, TSI, Inc.) and an aerodynamic particle sizer (APS 3321, TSI, Inc.) as well as an optical particle counter (OPC 1.109, Grimm) covered a particle size range from 5.6 nm to 32 μ m. Aerosol was sampled at ambient RH and no correction was applied for hygroscopic growth. The ASA used for calculating rates of trace gas uptake was calculated from the combined FMPS and APS data sets or from the FMPS data alone (5–9 September). Generally, the bulk of the surface area ($> 75\%$) was found in particles of diameter < 450 nm as measured by the FMPS.

2.2.6 Radiosoundings

The planetary boundary-layer height was determined from radiosondes (GRAW, DFM-06), measuring temperature, relative humidity and position as already described for this campaign (Berkes et al., 2015). Each day, 4 to 10 radiosondes were launched from the summit of the Kleiner Feldberg starting approximately 1 h before sunrise and ending 1 h after sunset. From these data, the potential temperature was calculated and used to determine the type of the boundary layer (stable, neutral, turbulent).

3 Results and discussion

3.1 Meteorological conditions

During the 25 days of the PARADE campaign, the meteorological conditions were quite variable (see Fig. 1). As previously outlined (Phillips et al., 2012), the campaign can be separated broadly into three periods which are associated with different air-mass origins and the arrival of cold fronts. The first part of the campaign from 15 August to 26 August was characterized by a relatively high temperature (up to 25 °C) during the day and a variable day-to-day humidity and wind direction. The air originated from the sector between south and west, and back trajectory calculations using HYSPLIT (Draxler and Rolph, 2011) showed that it was located over the continent during the previous 48 h. Exceptions to this pattern occurred on a few days when air masses passed over the English Channel. The marine influence could be traced through the presence of enhanced ClNO₂ (measured using chemical ionisation mass spectrometry) during the night and early morning (Phillips et al., 2012).

The arrival of a cold front originating from the Atlantic on the evening of the 26 August marks the beginning of the second period of the campaign. Immediately following the arrival of this front, the daytime temperature decreased approximately by 10 °C and from 26 to 27 August the relative humidity was close to 100 % and the mountaintop was frequently in clouds. The average daily temperature then slowly increased to reach 20 °C on 3 September in the afternoon. Back trajectories of 48 h showed that from 28 August to 1 September the air was influenced by the Atlantic and the Benelux region. From 1 to 3 September, the 48 h air-mass origin was much closer to the site and stayed over the European continent. The arrival of another front on the evening of 2 September caused the temperature to drop again by 5 °C. Until the end of the campaign, the air originated from the UK and was characterised by low levels of solar radiation and high humidity as the mountaintop was frequently in clouds and fog.

3.2 NO₂, NO₃ and N₂O₅ mixing ratios

The NO₃, N₂O₅ and NO₂ time series as well as that of O₃, NO and ASA are shown in Fig. 2. The mixing ratios of all measured nitrogen species were highly variable due to the close proximity of anthropogenic activity and its spatial/temporal heterogeneity (Crowley et al., 2010; Phillips et al., 2012). NO₂ mixing ratios were well above the detection limit during the whole campaign and ranged from 0.5 to more than 20 ppbv, with a campaign average of 2.7 ppbv during the day and 2.6 ppbv during the night. The highest, plume-like values of > 15 ppbv were spread over time periods of a few hours, occurred both day and night and were associated with polluted air masses arriving from the south-east (direction of Frankfurt). During passage of the cold fronts (vertical,

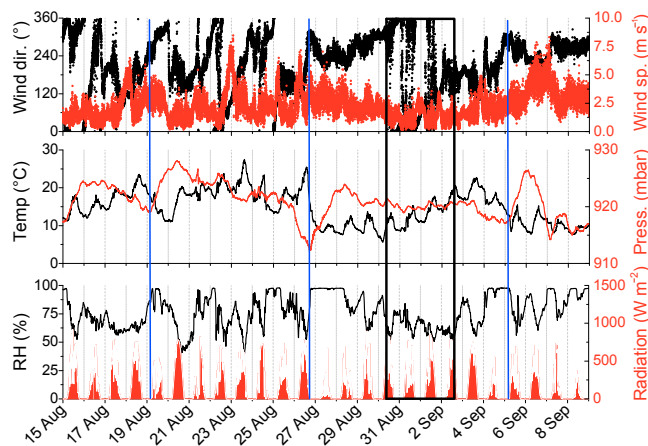


Figure 1. Meteorological parameters measured during the PARADE campaign. The vertical blue lines represent the arrival of cold fronts. The black box corresponds to the time period in which the longest NO₃ steady-state lifetimes were measured.

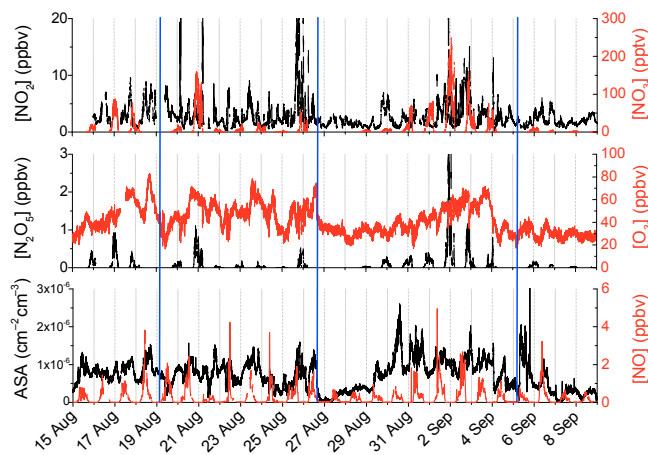


Figure 2. NO₂, NO₃, N₂O₅, O₃ and NO volume mixing ratios and aerosol surface area (ASA) measured during the PARADE campaign. The vertical, blue lines represent the arrival of cold fronts.

blue lines in Fig. 2) the mountaintop was often in cloud with measured relative humidity close to 100 %. No N₂O₅ or NO₃ could be detected on these nights and O₃ levels were reduced to background levels of ~ 25 ppbv during the following days. The low levels of solar radiation and photochemical activity reduced the maximum daytime mixing concentrations of NO to ~ 0.5 ppbv.

As NO₂ is necessary for the formation of NO₃ and N₂O₅ (Reactions R1 and R4) and also because high levels are indicative of more polluted air masses which are usually associated with shorter NO₃ lifetimes, we examine the dependence of NO₂ on the local meteorological situation in more detail. A conventional wind rose is displayed in Fig. 3a; in Fig. 3b we plot the relative count frequency of the NO₂ mixing ratios indexed against wind direction. The north-east sec-

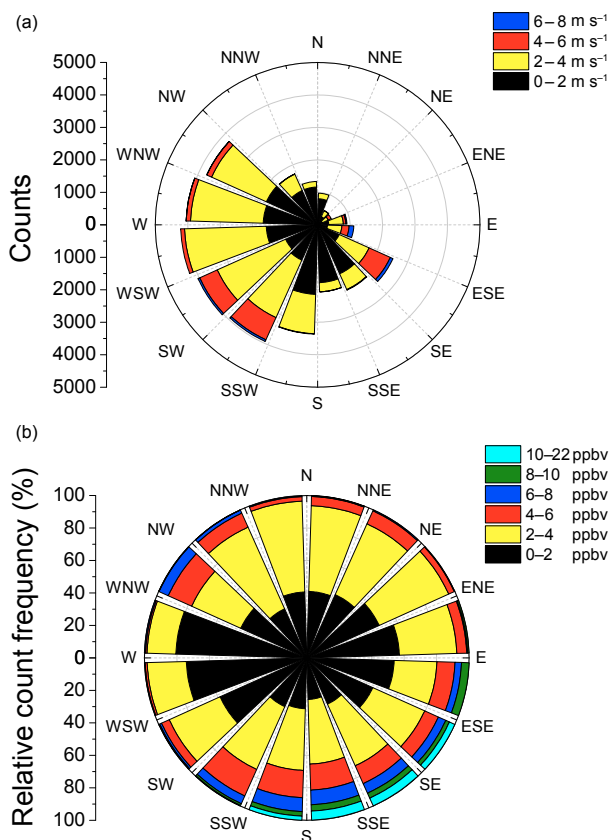


Figure 3. (a) Wind rose indicating the predominant wind direction and speeds throughout the campaign. (b) Relative count frequency of NO₂ mixing ratios against wind direction. Mixing ratios higher than 10 ppbv were encountered only for wind directions between east-south-east and south-south-west, reflecting the impact of the major local urban centres.

tor was the least represented with a time coverage of just 6 h. The most frequently encountered wind direction was west (≈ 200 h) but it is also where low NO₂ mixing ratios (< 2 ppbv, in black) were most frequently encountered. The sector east to south-south-west was characterised by frequent high NO₂ mixing ratios. It is the only sector which was associated with NO₂ mixing ratios greater than 10 ppbv, which reflects emissions originating from the three local cities of Frankfurt, Mainz and Wiesbaden. High NO_x levels measured in this sector were associated with the highest levels of anthropogenic hydrocarbons such as toluene.

[NO₃] and [N₂O₅] were highly variable during a single night and also from one night to the next, ranging from below the detection limit to 250 pptv for NO₃ and 3 ppbv for N₂O₅, which is significantly greater than previously measured at this site (Crowley et al., 2010). Precipitation periods were associated with [NO₃] and [N₂O₅] below the detection limit, which is likely a result of N₂O₅ uptake to droplets. The high variability in both [NO₃] and [N₂O₅] is partly due to the variability in their production rate. Figure 4 plots the

mixing ratio of NO₃ (measured at night and at relative humidity lower than 97 %) and its production rate ($P(\text{NO}_3)$, in pptv s⁻¹; Fig. 4b) as calculated using Eq. (1) against the local wind direction. Both production rate and mixing ratio of NO₃ show higher values for air masses coming from the Frankfurt and the Mainz/Wiesbaden sectors.

3.3 NO₃ and N₂O₅ lifetimes

The steady-state method for estimating the lifetime of NO₃ is based on the assumption that, after a certain time following sunset, the NO₃ and N₂O₅ concentrations in a single air-mass build-up to a quasi-constant value. Steady state is reached when the sum of direct and indirect loss rate constants of NO₃, $L(\text{NO}_3)$ in s⁻¹, balances its production rate, $P(\text{NO}_3)$, so that

$$[\text{NO}_3]_{\text{ss}} = \frac{P(\text{NO}_3) + T_{\text{in}}(\text{NO}_3)}{L(\text{NO}_3) + T_{\text{out}}(\text{NO}_3)}, \quad (2)$$

where $P(\text{NO}_3)$ and $L(\text{NO}_3)$ are terms for NO₃ chemical formation and loss respectively and $T_{\text{in}}(\text{NO}_3)$ and $T_{\text{out}}(\text{NO}_3)$ represent the influence of transport of NO₃. Generally, the terms $T_{\text{in}}(\text{NO}_3)$ and $T_{\text{out}}(\text{NO}_3)$ are regarded as insignificant for radical species with chemical lifetimes on the order of minutes rather than hours or days. The simpler form, Eq. (3), for the steady-state approximation has therefore been used frequently in analysing NO₃ measurements (Noxon et al., 1980; Platt et al., 1980; Allan et al., 1999) and has been examined in detail (Brown et al., 2003). At steady state, the NO₃ lifetime (τ_{ss}) is then

$$\tau_{\text{ss}}(\text{NO}_3) = \frac{[\text{NO}_3]}{k_1[\text{NO}_2][\text{O}_3]} = \frac{1}{L_{\text{ss}}(\text{NO}_3)}. \quad (3)$$

The term $L_{\text{ss}}(\text{NO}_3)$ is the loss term of NO₃ corresponding to the steady-state lifetime. The loss term $L(\text{NO}_3)$ is the sum of processes removing NO₃ and is often simplified as in Eq. (4):

$$L(\text{NO}_3) \approx k_6[\text{NO}] + \sum ([\text{VOC}]_i k_i) + 0.25 K_{\text{eq}}[\text{NO}_2] \bar{c} \text{ASA} \gamma_{\text{N}_2\text{O}_5}, \quad (4)$$

where k_6 is the rate constant for Reaction (R6) (2.6×10^{-11} cm³ molecule⁻¹ s⁻¹ at 298 K; Atkinson et al., 2004) and K_{eq} is the equilibrium constant describing the relative concentrations of NO₃ and N₂O₅ under equilibrium for any given NO₂ concentration and temperature and is given by $K_{\text{eq}} = k_4/k_{-4}$. \bar{c} is the mean thermal velocity of N₂O₅, k_i is the rate constant for reaction of NO₃ with a VOC, and $\gamma_{\text{N}_2\text{O}_5}$ is the uptake coefficient for N₂O₅ to aerosol with particle ASA (cm² cm⁻³). Expressions (3) and (4) ignore loss of NO₃ via heterogeneous uptake and loss of N₂O₅ via gas-phase reactions, both of which are generally considered negligible, and consider NO₃ production path through oxidation of NO₂ by O₃ only. Later, we shall discuss the potential impact of other NO₃ production pathways.

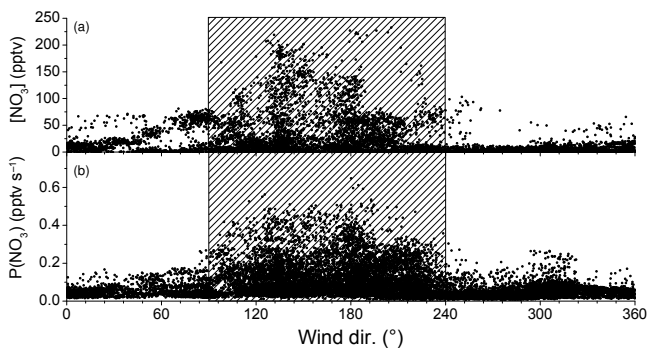


Figure 4. [NO₃] and NO₃ production rate, $P(\text{NO}_3)$ from Reaction (R1), vs. wind direction. The grey areas correspond to the Frankfurt–Mainz–Wiesbaden sector. Temperature-dependent rate constants ($\text{NO}_2 + \text{O}_3$), used to calculate the NO₃ production term, were taken from an evaluation of kinetic data (Atkinson et al., 2004).

Implicit to this analysis is the assumption that steady state is achieved when the air mass reaches the measurement site. The strongest local sources of NO₂ and O₃ are likely to be the urban centres of Frankfurt, Mainz and Wiesbaden, all ~20 km distant in the southern sectors. As outlined above, there are no close, strong, continuous sources of anthropogenic pollution in the northern sectors. The NO₃ production rate as a function of wind direction in Fig. 4 confirms that the whole northern sector is relatively low in NO₃ precursors.

With typical wind speeds of between 2 and 5 m s⁻¹ the transport times are at least 1 h from the major pollution sources. The time required to achieve steady state depends on the NO₃ production term and the overall loss frequency and is shorter when $P(\text{NO}_3)$ is low and the removal rate high. Numerical simulations were performed to test the validity of the steady-state approximation (Brown et al., 2003) and details are given in the Supplement (Fig. S2). The results indicate that achievement of steady state can indeed take longer than 1 h, when NO₃ lifetimes are long, especially when considering air masses with high NO₂ and O₃ e.g. as occasionally encountered from the southern sectors. During the first hours of nighttime, use of Eq. (3) may thus result in *underestimation* of the steady-state lifetime of NO₃.

The NO₃ lifetime can also be calculated from the production rate of NO₃ and the time derivatives of [NO₃] and [N₂O₅] as in Eq. (5) and thus does not require steady state to have been acquired (McLaren et al., 2010). The lifetime calculated via derivatives, $\tau_{\text{DER}}(\text{NO}_3)$, is given by

$$\tau_{\text{DER}}(\text{NO}_3) = \frac{[\text{NO}_3]}{k_1 [\text{NO}_2][\text{O}_3] - \frac{d[\text{NO}_3]}{dt} - \frac{d[\text{N}_2\text{O}_5]}{dt}} \quad (5)$$

As in the steady-state approximation, this method assumes that only chemical losses impact on NO₃ and N₂O₅ mixing ratios (negligible transport in and out of the sampled air

mass) and that the sink terms are constant over the time step considered.

The campaign time series of the steady-state NO₃ lifetime is presented in Fig. 5a. The night-to-night variability of $\tau_{\text{ss}}(\text{NO}_3)$ is very high throughout the 3 weeks of the campaign, with an average value of 200 s (± 100 s) for NO₃. The longest lifetimes (~1 h for NO₃) were observed during 3 consecutive nights on 30 and 31 August and 1 September.

In Fig. S3 in the Supplement, we plot the NO₃ steady-state lifetime, $\tau_{\text{ss}}(\text{NO}_3)$ and the lifetime calculated using the derivatives method, $\tau_{\text{DER}}(\text{NO}_3)$. Both calculations agree well for the lowest NO₃ lifetimes (first period of the campaign from 15 to 26 August). This is expected, as the steady-state condition is readily fulfilled when the losses of NO₃ (or N₂O₅) are rapid. During the nights 30 and 31 August and 1 September, $\tau_{\text{ss}}(\text{NO}_3)$ is up to 2 times greater than $\tau_{\text{DER}}(\text{NO}_3)$. This is clearly not related to the effects outlined above which apply to the first hours of darkness but, as we discuss later, is associated with deviation from steady state during these periods. The derivatives method does not provide data for the whole campaign. $\tau_{\text{DER}}(\text{NO}_3)$ is sometimes very scattered and sometimes negative, which arises from noise on the derivative terms. However, on average, the ratio $\tau_{\text{ss}}(\text{NO}_3) / \tau_{\text{DER}}(\text{NO}_3)$ was 0.99 with ~66 % of the lifetimes agreeing within 30 %. The analysis and discussion below are based on the lifetimes obtained by the steady-state analysis.

The wind rose in Fig. 5b indicates that high values of $\tau_{\text{ss}}(\text{NO}_3)$ (~1 h) were encountered irrespective of wind direction. This is initially surprising, as long NO₃ lifetimes values are not expected in air masses originating from the highly polluted sectors.

The short-term (hour-to-hour) variability was very high, as already described in Crowley et al. (2010) for this site. They describe the evolution of $\tau_{\text{ss}}(\text{NO}_3)$ over a single night in which the lifetime increased slowly after sunset to reach a roughly constant value around midnight. As steady state was predicted to be achieved on a much shorter timescale, and because other loss processes involving NO or heterogeneous loss of N₂O₅ were too slow, the increase in [NO₃] and $\tau_{\text{ss}}(\text{NO}_3)$ was interpreted as being due to a slow decrease in the concentration of VOCs, though measurements of VOCs were not available to confirm this. During the PARADE campaign a number of VOCs and the ASA were measured, allowing us to calculate the overall loss rate constant of NO₃ using Eq. (4). As only a subset of the suite of organic species likely to be present at the site was measured, this calculation will provide a lower limit for the overall NO₃ loss rate (and thus an upper limit for its real lifetime).

3.3.1 Loss of NO₃ via reaction with NO

With an average O₃ mixing ratio of about 40 ppbv, the NO lifetime at night is about 5 min, so that, in the absence of local sources and photochemical degradation of NO₂, the NO mixing ratio will be close to 0 within an hour of sunset. This

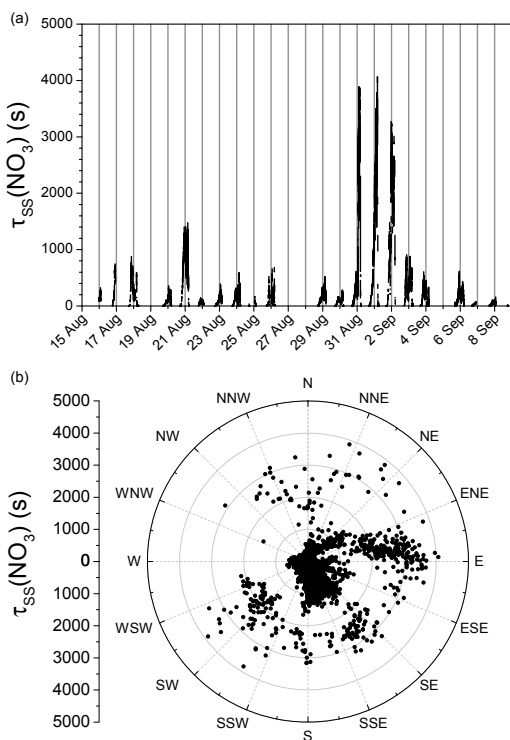


Figure 5. (a) $\tau_{ss}(\text{NO}_3)$ calculated according to Eq. (3). (b) $\tau_{ss}(\text{NO}_3)$ vs. wind direction.

was the case for most of the nights during PARADE and NO measurements were below the (5 pptv) detection limit. On some nights, however, as exemplified in Fig. 6, 10–20 pptv of NO were measured, and between 21:00 UTC and sunrise $\tau_{ss}(\text{NO}_3)$ (Fig. 6a, black line) was consistent with that calculated from the NO reactivity as $k_6[\text{NO}]$ (Fig. 6a, red line). During the period from 19:00 to 21:00 UTC the lifetime of NO₃ attributable to reaction with NO, $\tau(\text{NO})$ is greater than $\tau_{ss}(\text{NO}_3)$, which may be due both to non-acquisition of steady state (for the first hour or so) and a contribution of other loss processes.

Figure 6 shows that the non-zero NO mixing ratios encountered on this night were in air masses associated with low wind speeds and may be a result of vehicle use on local roads or soil emissions.

3.3.2 Heterogeneous removal rate

The overall loss rate constant for NO₃ contains a contribution from indirect loss via the heterogeneous removal of N₂O₅ to particles as described by Eq. (4). In Fig. 7, we plot the calculated loss rate constant (s^{-1}) for NO₃ resulting from the uptake of N₂O₅ to particles (L_{HET} in blue) and compare it to the overall loss rate constant in steady state (L_{ss} , open circles) for two different nights. A simple temperature-dependent value of the uptake coefficient ($\gamma = 0.244 - 7.9 \times 10^{-4}T$) was used

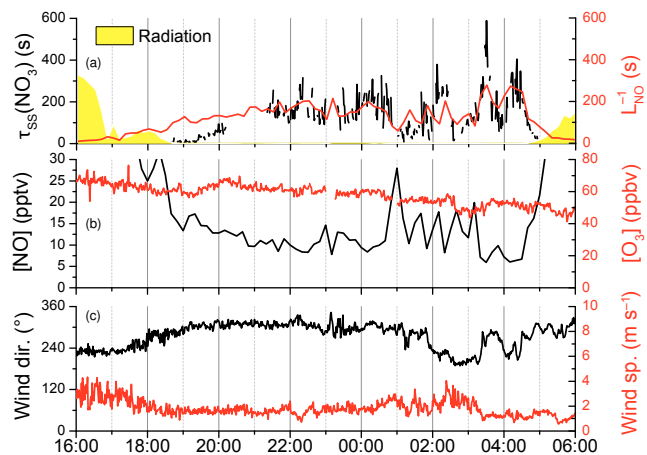


Figure 6. (a) $\tau_{ss}(\text{NO}_3)$ and inverse loss rate constant (L_{NO}^{-1}), for loss of NO₃ via reaction with NO during the night of 23 August. Panels (b) and (c) display the associated [NO], [O₃], wind speed and wind direction data.

as recommended by IUPAC (Ammann et al., 2013). This expression is based on laboratory studies and results in a value at 283 K of $\sim 2 \times 10^{-2}$, which is larger than uptake coefficients obtained by analysis of both laboratory and field data in which the particle is not purely inorganic (Brown and Stutz, 2012). During periods when the NO₃ lifetime is long (e.g. $\tau_{ss}(\text{NO}_3) > 2000$ s or $L_{ss}(\text{NO}_3) < 5 \times 10^{-4} \text{ s}^{-1}$) as on the second period of the night of the 30 August (Fig. 7b), when using the γ parameterisation above, the losses of N₂O₅ to particles can account entirely for the observed lifetimes or even exceed the steady-state reactivity, which may be the result of using a high value for γ . On this night, NO was below the instrumental detection limit and was not considered for NO₃ losses. During periods when the NO₃ lifetime is shorter (e.g. on 5 September, Fig. 7a) the indirect, heterogeneous loss represents only a small fraction of the overall loss. More sophisticated parameterisations of the uptake coefficient, including e.g. the nitrate and chloride content of the particles and the existence of organic coatings (Bertram and Thornton, 2009), often fail to reproduce in situ measurements (Bertram et al., 2009) and indicate that γ is a large source of uncertainty in these calculations. However, even the use of values as large as 0.1 does not reproduce the shorter lifetimes and, as previously discussed for this site (Crowley et al., 2010), the remaining losses are likely due to direct reactions of NO₃ with VOCs.

3.3.3 Loss of NO₃ via reaction with VOCs

The VOCs measured during PARADE are listed in Table 2 together with their rate constants (at 298 K) for reaction with NO₃. Among the trace gases listed, only a few of them (at high concentrations or with large rate constants for reaction with NO₃) contributed significantly to the loss of NO₃ and

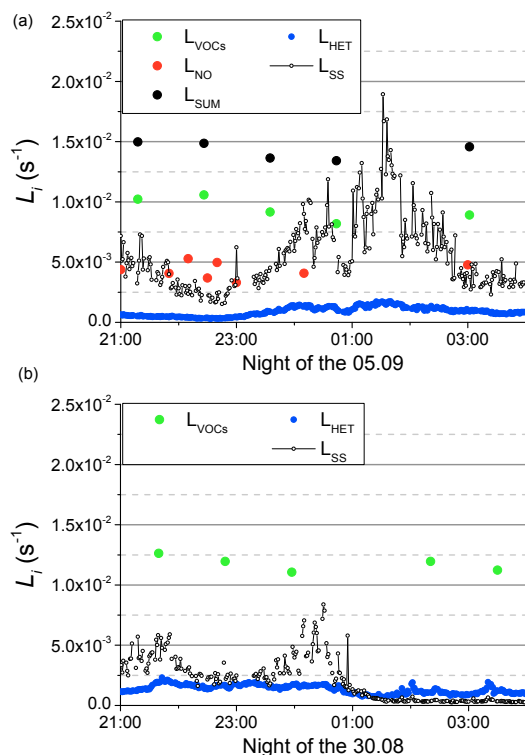


Figure 7. (a) Individual ($L_{\text{VOCs}} = \sum k_i[\text{VOC}]_i$, $L_{\text{NO}} = k_6[\text{NO}]$ and L_{HET}) and summed NO₃ loss terms (L_{SUM}) for the night of 5 September, together with the loss rate constant of NO₃ in steady state (L_{SS}). (b) Individual ($L_{\text{VOCs}} = \sum k_i[\text{VOC}]_i$, $L_{\text{NO}} = k_6[\text{NO}]$ and L_{HET}) and summed NO₃ loss terms (L_{SUM}) for the night of the 30 August, together with the inverse of the steady-state lifetime of NO₃ (L_{SS}). L_{VOCs} , L_{NO} , L_{HET} and L_{SS} are given in the original time resolutions (respectively 30, 10, 1 and 1 min). To calculate L_{SUM} , high-resolution L_{NO} and L_{HET} were interpolated to the L_{VOCs} time grid.

are highlighted in bold. Further discussion will focus on these VOCs. Apart from isoprene (up to 200 pptv), the mixing ratios of VOCs which are reactive towards NO₃ were generally below 100 pptv (see Supplement, Fig. S4). A clear diel cycle was observed for isoprene and during the warmer first and last parts of the campaign daytime mixing ratios were up to 5 times higher than during the night. For the monoterpenes the diel cycle was less pronounced and on two nights (4–5 September and 5–6 September) large mixing ratios were observed during the night (e.g. > 50 pptv for myrcene and limonene), which were not accompanied by increases in isoprene. As expected, during colder, rainy periods, the BVOCs were less abundant and showed a weaker diel variation.

For each monoterpene, the NO₃ loss rate constant for reaction with VOCs ($L_i = k_i[\text{VOC}]_i$ where k_i is the rate constant for each VOC) is plotted together with the steady-state NO₃ total reactivity ($L_{\text{SS}}(\text{NO}_3)$) and the VOCs summed reactivities (including alkanes and alkenes) in Figs. 7 and S5. The rate coefficients for reaction of NO₃ with the VOCs were de-

rived from the temperature-dependent expressions given by IUPAC and were calculated at each time step of the data set. Figure S5 shows that, over almost the whole campaign, the steady-state loss rate constants L_{SS} (open circles) are significantly lower than those calculated by summing the individual contributions of the VOCs (L_{VOCs} , dashed line). Indeed, during the 3 nights in which very long NO₃ lifetimes were encountered, L_{SS} is approximately 4 to 5 times lower than that expected from the summed VOCs. In other words, within the steady-state framework used here and using the NO₃ production term, $k_1[\text{NO}_2][\text{O}_3]$, the observed mixing ratios and lifetimes of NO₃ are incompatible with the VOC measurements.

The divergence between the steady-state loss rates and that obtained by summing the losses with each VOC is exacerbated when one considers that the VOCs measured in PARADE cover only a fraction of those present in the air so that L_{VOCs} must strictly be regarded as a lower limit. As exemplified in Figs. 7 and S5, summing the individual loss rate constants due to reaction of NO₃ with NO (L_{NO}), the complete set of VOCs (L_{VOCs}) and indirect loss via heterogeneous uptake of N₂O₅ to available particles (L_{HET}) results in an air-mass reactivity that is larger than that derived from the steady-state calculations, i.e. the NO₃ lifetime is longer than expected (or its concentration higher). Generally, the opposite is observed and missing reactivity is assigned e.g. to VOCs that were not measured. Below, we examine possible explanations for this, including the breakdown of the steady-state assumption, the potential role of other chemical routes to NO₃ generation and meteorological effects.

3.3.4 NO₃ production rate

So far, our calculations have been based on the assumption that NO₃ is generated solely in the reaction between NO₂ and O₃ (Reaction R1, see Sect. 3.3). If NO₃ is only formed via Reaction (R1), the uncertainty associated with $P(\text{NO}_3)$, propagated from those of [NO₂] and [O₃] is approximately 8 %. The good agreement between several devices for measurement of both NO₂ and O₃ indicates that the term $k_1[\text{NO}_2][\text{O}_3]$ is indeed well defined. As indicated in Sect. 1, other sources of NO₃ are known but are generally regarded as negligible. The reaction of OH with HNO₃ (Reaction R2) generates NO₃ at ~ 100 % yield but, even assuming nighttime concentrations of hydroxyl radicals of 1×10^5 molecule cm⁻³ and 2 ppbv of HNO₃, the NO₃ production rate is only ~ 1 % of that from Reaction (R1). In the absence of sunlight, the formation of NO₃ from the photolysis (Reaction R3) of halogen nitrate, XONO₂ (where X = Cl, Br or I), will not contribute at nighttime. A further possible source of nighttime NO₃ and cause for error in steady-state lifetime estimations could be the rapid recycling of NO₃ from the products formed in its initial reaction with BVOCs, as has been seen for the OH radical (Lelieveld et al., 2008; Taraborrelli et al., 2012). The organic nitrates formed as first-generation products when NO₃ reacts with biogenic VOCs

Table 2. VOCs measured using GC-MS and GC-FID during PARADE.

GC-MS VOCs	$k(\text{NO}_3 + \text{VOC})^a$	Maximum mixing ratio (pptv)	GC-FID VOCs	$k(\text{NO}_3 + \text{VOC})^a$	Maximum mixing ratio (ppbv)
Isoprene	7.0×10^{-13}	220	Ethane	$< 1 \times 10^{-17}$	7.2
α -Pinene	6.2×10^{-12}	170	Ethene	2.1×10^{-16}	15
Myrcene	1.1×10^{-11}	70	Propane	$< 7 \times 10^{-17}$	2.5
Limonene	1.22×10^{-11}	130	Propene	9.5×10^{-15}	20
p-Cymene	1.0×10^{-15} b	20	<i>i</i> -Butane	1.1×10^{-16} b	1.3
Benzene	$< 3 \times 10^{-17}$ b	230	<i>n</i> -Butane	4.6×10^{-17}	1.4
Toluene	7.0×10^{-17} b	420	<i>cis</i> -2-Butene	3.5×10^{-13}	0.6
Ethylbenzene	$< 6 \times 10^{-16}$ b	80	<i>i</i> -Pentane	1.62×10^{-16} b	1
<i>m</i> -Xylene	2.6×10^{-16} b	130	<i>n</i> -Pentane	8.7×10^{-17} b	1
<i>p</i> -Xylene	5.0×10^{-16} b	65	1-Pentene	1.5×10^{-14} b	1.9
<i>o</i> -Xylene	4.1×10^{-16} b	75	Butadiene	1.0×10^{-13} b	10.6

^a Rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) at 298 K taken from the latest evaluation (Atkinson et al., 2006; Ammann et al., 2016) unless noted otherwise.

^b Rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) taken from Atkinson and Arey (2003).

are, however, believed to be chemically stable and there is no obvious pathway for rapid re-release of NO₃ once formed.

We now consider a further nighttime process forming NO₃ via the oxidation of NO₂ by stabilised Criegee intermediates (sCIs), which are formed in the atmosphere by the reaction of O₃ with biogenic and anthropogenic alkenes (Johnson and Marston, 2008). This may be especially relevant when observing apparently long NO₃ lifetimes (i.e. high concentrations) in the presence of reactive VOCs.

The possibility of NO₃ generation via sCI reaction with NO₂ was first raised several years ago (Fenske et al., 2000; Presto and Donahue, 2004), though in the early studies, which were unable to detect Criegee radicals directly, uncertainties regarding the products and the rate constant were large. In recent work (Welz et al., 2012) on the reaction between the simplest sCI (CH₂O₂) and NO₂, a large rate constant ($7_{-2}^{+3} 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) was determined. The authors hypothesised that the reaction between other sCI and NO₂ might have similar rate constants. A further study (Stone et al., 2014) reports a rate constant ($1.5 \pm 0.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the same reaction and detected HCHO as product, consistent with an O-atom transfer from sCI to NO₂ to form NO₃. Subsequently, the formation of NO₃ (and N₂O₅) resulting from the photolysis at 248 nm of a mixture of CH₂I₂, O₂ and NO₂ was attributed to the reaction between CH₂O₂ and NO₂ (Ouyang et al., 2013). Whether sCI can contribute significantly to nighttime NO₃ formation or not depends on the assumption that all sCIs react with a similar rate coefficient to CH₂O₂, that NO₃ is formed at high yield and that sufficient sCIs are present in the nighttime boundary layer. In Table 3, we assess the three reactions that could have contributed to NO₃ formation during PARADE. We take a generic rate coefficient for sCI + NO₂ that lies between the literature determinations (Welz et al.,

2012; Stone et al., 2014) and assume 100 % product yield for formation of NO₃.

Table 3 shows that, whereas the reaction between OH and HNO₃ can safely be neglected, the reaction between sCI and NO₂ can represent a significant fraction of the total rate of production of NO₃ if sCIs are present at ~ 0.1 pptv during night. This reflects the fact that, although Criegee radicals are expected to be present at concentrations 4–6 orders of magnitude less than those of O₃, the rate constant for reaction with NO₂ is ~ 5 orders of magnitude larger.

The rate of formation of sCIs in the boundary layer depends on both the concentration and nature of the organics reacting with O₃ to form it and is expected to be very variable. Likewise, the sink reactions of sCIs are difficult to predict, though reactions with water vapour, SO₂ and NO₂ are expected to be important (Vereecken et al., 2012). Boundary-layer mixing ratios of sCIs are thus associated with great uncertainty. Based on a steady-state approach, sCI mixing ratio up to 0.03 pptv have been calculated for the PARADE campaign (Bonn et al., 2014), i.e. within the range of values used in Table 3. Recent measurements in a Boreal forest environment estimated sCI mixing ratios to be 0.0025 to 0.04 pptv (Taipale et al., 2014) and sCIs have been tentatively identified (Mao et al., 2012) as the source of an interfering signal in ambient measurements of OH that may approach 0.2 pptv (Novelli et al., 2014). As not all ambient sCIs will decompose to OH within such instruments, the wider implication is that pptv amounts of sCI may be present.

To calculate the influence of sCI-induced formation of NO₃ during the PARADE campaign we recalculated the NO₃ production rate assuming two different sCI concentrations at the limits of the range listed in Table 3 and using the rate constant given. In Fig. 8 we display the calculated steady-state lifetime without sCI reactions forming NO₃ (black symbols) and the effect of using a low sCI concentration (τ_{LSCI} , blue

Table 3. Reactions producing NO₃.

Reaction	Mixing ratio first reactant	Mixing ratio second reactant	Rate coefficient (298 K) ^a	$P(\text{NO}_3)^b$
O ₃ + NO ₂	20–50 ppbv	0.5–5 ppbv	3.5×10^{-17}	$(0.9\text{--}220) \times 10^{-3}$
OH + HNO ₃	$(1\text{--}10) \times 10^{-2}$ pptv	0.5–5 ppbv	1.5×10^{-13}	$(1.9\text{--}190) \times 10^{-5}$
sCI + NO ₂	0.01–0.1 pptv	0.5–5 ppbv	5.0×10^{-12}	$(0.6\text{--}6) \times 10^{-3}$

^a Units of cm³ molecule⁻¹ s⁻¹. ^b Units of pptv s⁻¹.

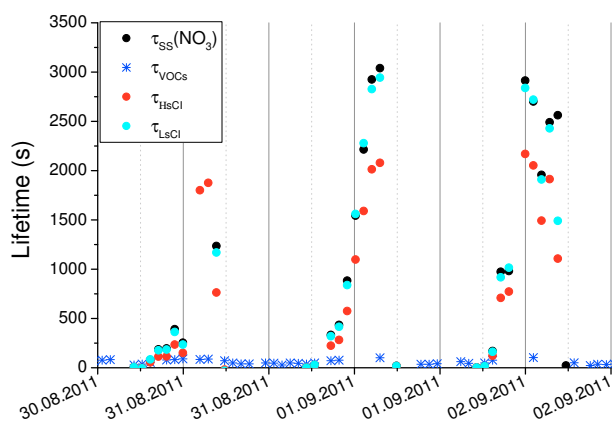


Figure 8. NO₃ steady-state lifetimes calculated using different production terms. Black data points: only NO₂ + O₃ forms NO₃. Blue circles: additional formation from 0.01 pptv sCI reacting with NO₂. Red data points: additional formation from 0.1 pptv sCI reacting with NO₂. The inverse of L_{VOCs} is indicated by the blue stars. Similar to Fig. 7, all data were interpolated to the VOC time axis; hence the low time resolution.

symbols) or a high concentration (τ_{HsCl} , red symbols). The resultant reduction in the calculated steady-state lifetime of NO₃ is significant when using the higher values of [sCI]. For example, on 31 August, the largest value of $\tau_{\text{ss}}(\text{NO}_3)$ would be reduced from 3000 s (black data points) to 2000 s (red data points) when assuming 0.1 pptv of sCI. However, in order to bring the steady-state lifetime into agreement with that based on the VOC measurements (green symbols), a sCI mixing ratio of 4 pptv would be required. Our present knowledge of Criegee formation and loss mechanisms under atmospheric conditions precludes accurate assessment of their role in forming NO₃ at nighttime, though sCI mixing ratios as large as 4 pptv appear (at present) unlikely, though not impossible.

3.3.5 Meteorological considerations

We have shown that, while uncertainties in some parameters required for calculation of NO₃ lifetimes exist, they are likely to be insufficient to explain the high concentrations (and lifetimes) of NO₃ during the nights of 30 August to 1 September.

Close examination of the NO₃ lifetime on these nights (e.g. Fig. 9) reveals an especially strong gradient, with $\tau_{\text{ss}}(\text{NO}_3)$ values increasing e.g. by 500 to 600 % over the course of an hour. Simultaneously, $\tau_{\text{ss}}(\text{N}_2\text{O}_5)$ values (not shown) increase by 200 %. The smaller increase in $\tau_{\text{ss}}(\text{N}_2\text{O}_5)$ is due to a simultaneous decrease of [NO₂] by 50 %, thus shifting the equilibrium towards NO₃. The large gradient in $\tau_{\text{ss}}(\text{NO}_3)$ cannot be attributed to a decrease in the mixing ratios of reactive trace gases, which were much less variable (see above). We therefore consider the possibility that the long lifetimes observed on these nights are related to sampling air masses from a low-lying residual layer (i.e. from above a particularly shallow nocturnal boundary layer) which, especially at low wind speeds, is decoupled from ground emissions of NO_x and VOCs, allowing NO₃ and N₂O₅ to build up to higher levels and would also help to explain the lack of dependence on wind direction.

The hypothesis that sampling of residual-layer air is responsible for the long steady-state lifetimes of NO₃ and their apparent incompatibility with the VOC measurements is examined in detail in Fig. 9. Here, the time profiles of $\tau_{\text{ss}}(\text{NO}_3)$, NO₂, O₃, CO₂, and ASA and some meteorological parameters are plotted for the night of 30 August. The night from 30 to 31 August can be divided into two distinct periods. Between 21:00 and 00:30 UTC (first period) $\tau_{\text{ss}}(\text{NO}_3)$ was roughly constant at an average value of about 150 s. After this, we observed a large increase in the NO₃ steady-state lifetime between ~00:30 and 01:30 UTC, followed by period 2 (01:30 UTC until dawn) in which $\tau_{\text{ss}}(\text{NO}_3)$ was consistently close to 3000 s.

The transition from the shorter (period 1) to longer (period 2) lifetimes is accompanied by a decrease in the NO₂ mixing ratio from about 2.5 to 1 ppbv, a ~2 ppmv decrease in CO₂, an increase in O₃ from ~15 to 25 ppbv and a ~30 % increase in particle surface area. Changes in the local wind direction (at ~20 m height) between the clean northern sector to the anthropogenically polluted south sector during this second period did not impact the NO_x levels or the NO₃ lifetime.

These observations are consistent with air from the residual layer being sampled during the second period. Higher levels of O₃ and particles, formed during the previous day in the turbulently mixed boundary layer, are expected in the residual layer compared to the shallow, nocturnal boundary

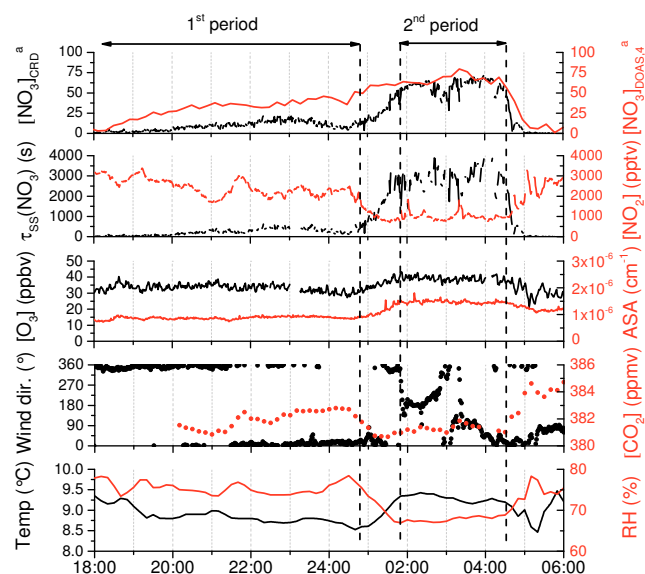


Figure 9. Detailed view of the night of the 30 August indicating two periods corresponding to different NO_3 lifetime regimes. The trends in NO_3 lifetime, CO_2 , NO_2 , O_3 , RH and aerosol surface area (ASA) indicate a transition from boundary-layer to residual-layer air between $\sim 00:30$ and $01:30$ UTC in the morning. Sunrise was at about $05:00$ UTC. ^a Units of pptv.

layer in which dry deposition is important for both. Conversely, levels of NO_2 , formed from oxidation of ground-level NO emissions are expected to be higher in the lower levels (Stutz et al., 2004; Brown et al., 2007) and thus decrease when sampling air from the residual layer. The second period is also marked by a significant drop in relative humidity (from ~ 80 to 65%) and an increase in the temperature of $\approx 1^\circ\text{C}$. The former is expected as relative humidity decreases above the nocturnal boundary layer. A correlation between increasing NO_3 lifetimes and temperature has been observed previously (Crowley et al. 2010) and was attributed to downward movement of higher air masses during an inversion.

Figure 10a and b show profiles of the potential temperature and relative humidity within the first period at 19:00 UTC and within the second period at 04:00 UTC from 30 to 31 August. The temporal development of the temperature and the relative humidity profiles agrees well with the near-surface observations. The profiles of the potential temperature show a change from stable stratification (potential temperature increase with height) to neutral stratification (potential temperature is constant with height) which is an additional indication that the measurements within period 2 were obtained within the residual layer. The same temporal development of the potential temperature profiles was observed 24 h later (Fig. 10a, b), when again the NO_3 lifetime was enhanced. On both nights, the lack of a switch in sign of the RH gradient with height at 04:00 UTC contrasts with the profiles at 19:00 and 06:00 UTC which show clear evidence for a switch from

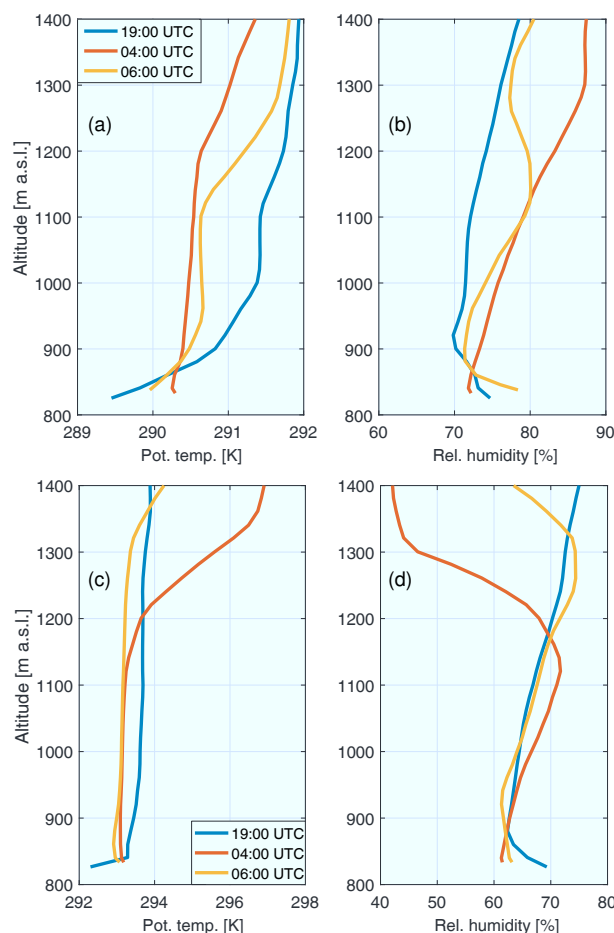


Figure 10. Vertical profiles of the potential temperature (a) and the relative humidity (b) during the first period on 30 August at 19:00 UTC (blue), as shown in Fig. 9, and on 31 August at 04:00 UTC (red) and 06:00 UTC (orange, after sunrise) during the second period. (c, d) Same as above but for 31 August to 1 September.

boundary layer to residual layer some 50 to 100 m above the summit. Between 31 August and 2 September we observed no nocturnal build-up of CO_2 , which strongly contrasts the periods prior to and after this period (see Fig. S6) and again indicates that this period with the longest NO_3 lifetimes is associated with residual-layer air.

When sampling from the residual layer, we would expect that the observed increase in O_3 and ASA and simultaneous decrease in NO_2 and RH would be accompanied by a decrease in those biogenic trace gases, which are reactive towards NO_3 . Indeed, if we take the measured NO_3 mixing ratio of 200 pptv on 2 September, we calculate that the lifetime of biogenics such as limonene should be of the order of only a few minutes in the residual layer. The simultaneous measurement of both high NO_3 steady-state lifetimes and terpene mixing ratios can now be explained if we consider that the terpene emissions are only local, i.e. from trees that are close

to the top of the mountain (and our inlet) and thus also within the residual layer. Such local emission (e.g. within 30 m of the inlet) does not allow the NO₃+terpene chemistry to go to steady state so that only a fraction of the NO₃ (and terpene) are consumed. The extent of reaction will be related to the location of the emission relative to the inlet and local wind speeds and is likely to be highly variable.

So far, we have assumed that NO₃ (or N₂O₅) levels aloft (i.e. in the residual layer) are enhanced w.r.t. the boundary layer. As NO₃ (and also NO₂ and O₃) was measured by LP-DOAS at different heights, this data set should give some insight into the occurrence and extent of vertical gradients in NO₃ concentrations. In Fig. 9 we plot a data set obtained using the LP-DOAS. In the first period (until ~00:30 UTC), the DOAS measurements of NO₃ at the highest altitude were significantly larger (factor of ~5 at 24:00 UTC) than those measured by the CRDS. This difference in concentration disappeared during the second phase (01:30 until 04:00 UTC) when both instruments measured high NO₃, thus supporting the concept that the top of the mountain is in the residual layer during this period. Below, we compare the CRDS and DOAS measurements in more detail.

3.3.6 Comparison of NO₃ lifetimes derived from CRDS and LP-DOAS instruments

As mentioned in Sect. 2.2 the LP-DOAS measurements were conducted using a total of four light paths. For this analysis we compare data retrieved from only the lowest (835 to 872 m a.s.l.) and highest (835 to 959 m a.s.l.) levels (see Fig. 11). By comparison, the height of the CRDS inlet was ~838 m a.s.l.

We refer to the lower and higher levels as DOAS 1 and DOAS 4 respectively. Steady-state NO₃ lifetimes were calculated in the same way as described above for the CRDS data set, using the NO₂ and O₃ data obtained from the DOAS instrument at those two different levels. Because of the short horizontal (1.5 km) and vertical (~125 m) range of the DOAS light paths, the integrated temperature over both light paths is assumed to be the same as the temperature measured at the Kleiner Feldberg hilltop and these values were used to calculate the rate constant (k_1) for NO₃ production. Note that differences in temperature of a few Kelvin do not impact significantly the rate constant, k_1 .

In Fig. 12 we plot the NO₃ mixing ratios and steady-state lifetimes obtained on two different nights, 1–2 and 5–6 September, by the CRDS and LP-DOAS instruments. While the night of 5–6 September shows large differences between the mixing ratios reported by the CRDS and LP-DOAS instruments, and a strong vertical gradient in NO₃, good agreement, i.e. a weak (or 0) gradient, is observed on 1–2 September. The LP-DOAS measurements of the NO₂ (Thieser et al., 2016) and O₃ mixing ratios (Fig. 13) reveal little or no difference between the highest and lowest light paths over the whole campaign, so that the NO₃ production term

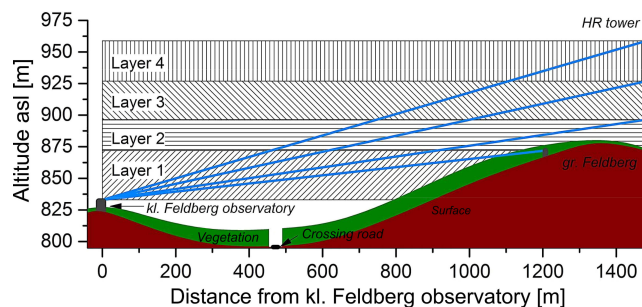


Figure 11. Schematic diagram of the LP-DOAS light paths deployed during the PARADE campaign, with the Kleiner Feldberg on the left and the Grosser Feldberg on the right. The LP-DOAS data sets used in this work are those obtained from the lower-most and upper-most light paths.

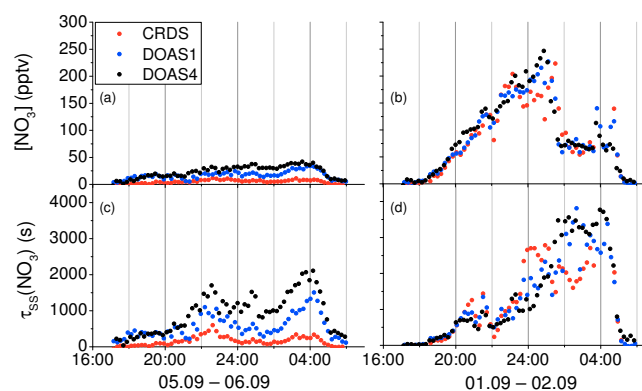


Figure 12. [NO₃] (a) and $\tau_{ss}(\text{NO}_3)$ (c) using CRDS data (red), lowest LP-DOAS light path (DOAS 1) and highest LP-DOAS light path (DOAS 4) for the night of 5–6 September. (b, d) As for the left-hand plot but showing data for the night of 1–2 September.

was roughly constant with altitude. The clear dependence of the NO₃ mixing ratio on height on 5–6 September is thus due to variation in the NO₃ loss term. Figure 12c indicates a factor of up to ~5 increase in NO₃ lifetime when comparing the LP-DOAS data at the highest level to the CRDS measurements.

In Fig. 14a we plot the campaign NO₃ mixing ratios measured by the CRDS and DOAS 4 vs. the DOAS 1 data set. As mentioned previously and illustrated in Fig. 11, the LP-DOAS light source and the CRDS inlet were co-located at a height of ~835 m whilst the LP-DOAS retroreflectors were at ~959 and 872 m. All data which were above the detection limit (10 pptv for LP-DOAS and 5 pptv for the CRDS) were included. The coloured lines (black, blue and red) represent slopes of 0.5, 1 and 2 respectively. Nearly all of the black data points [NO₃]_{DOAS4} have slopes between 1 and 2, indicating that, on average, [NO₃] is higher aloft, consistent with previous observations of positive vertical gradients in NO₃ (Stutz et al., 2004; Brown et al., 2007). At large mixing ratios, i.e. for [NO₃]_{DOAS1} > 100 pptv, the al-

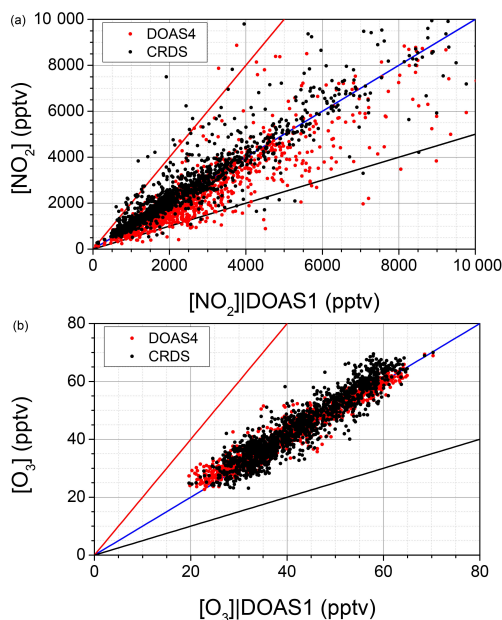


Figure 13. (a) Comparison between $[\text{NO}_2]\text{CRDS}$, $[\text{NO}_2]\text{DOAS4}$ and $[\text{NO}_2]\text{DOAS1}$ (whole campaign). (b) Comparison between $[\text{O}_3]\text{CRDS}$, $[\text{O}_3]\text{DOAS4}$ and $[\text{O}_3]\text{DOAS1}$ (whole campaign). Blue lines have a gradient of 1, red lines a gradient of 2 and black lines a gradient of 0.5.

titude dependence on the $[\text{NO}_3]$ is weaker and the black points are closer to the blue line (slope of 1). The ratio between $[\text{NO}_3]\text{CRDS}$ and $[\text{NO}_3]\text{DOAS1}$ also shows some dependence on the NO_3 mixing ratio. When the NO_3 mixing ratios are low, the ratio CRDS/LP-DOAS is also low and generally less than 0.5. In extreme cases, the $[\text{NO}_3]\text{CRDS}$ values are close to a few pptv or below the detection limit while $[\text{NO}_3]\text{DOAS1}$ measured as high as 40 to 50 pptv. To illustrate this, for NO_3 steady-state lifetimes of < 1500 (i.e. all nights except for 30 August–2 September) the average value of the $[\text{NO}_3]\text{DOAS4}/[\text{NO}_3]\text{DOAS1}$ ratio is 1.23 ± 0.07 , whereas for NO_3 steady-state lifetimes of > 1500 s we derive a $[\text{NO}_3]\text{DOAS4}/[\text{NO}_3]\text{DOAS1}$ ratio of 0.95 ± 0.05 .

Both $\tau_{\text{ss}}(\text{NO}_3)\text{CRDS}$ and $\tau_{\text{ss}}(\text{NO}_3)\text{DOAS4}$ data sets (Fig. 14b) show the same trends as the one described for $[\text{NO}_3]$. At low $\tau_{\text{ss}}(\text{NO}_3)\text{DOAS1}$ the black and red points are respectively closer to the black and red lines and as $\tau_{\text{ss}}(\text{NO}_3)\text{DOAS1}$ increases to the highest values the data points are all closer to the blue line. The apparent dependence of the NO_3 mixing ratios and lifetime on the NO_3 concentrations reflects the fact that, when NO_3 is high, both instruments are sampling the residual layer in which NO_3 levels are expected to be higher and gradients in NO_3 are expected to be weaker than found close to the surface (Brown et al., 2007).

In summary, the data shown in Fig. 9 and the LP-DOAS measurements of NO_3 at different altitudes provide compelling evidence for a low-lying residual layer (or very shallow nocturnal boundary layer) being responsible for the oc-

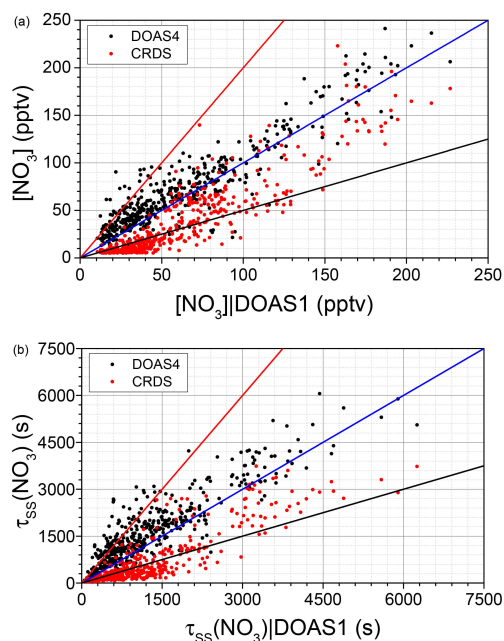


Figure 14. (a) $[\text{NO}_3]\text{CRDS}$ (red) and $[\text{NO}_3]\text{DOAS4}$ (black) vs. $[\text{NO}_3]\text{DOAS1}$. (b) $\tau_{\text{ss}}(\text{NO}_3)\text{CRDS}$ (red) and $\tau_{\text{ss}}(\text{NO}_3)\text{DOAS4}$ (black) vs. $\tau_{\text{ss}}(\text{NO}_3)\text{DOAS1}$. Coloured lines on both panels represent slopes of 0.5, 1 and 2 (black, blue and red respectively).

casional observation of high NO_3 mixing ratios seen by the ground-level CRDS instrument and the associated long steady-state lifetimes. This layer will be most stable and thus best decoupled from the underlying boundary layer when wind speeds are low. The DOAS measurement of concentration at different altitudes does not contain information about the vertical exchange and mixing itself. Any estimation of vertical mixing for a reactive trace gas like NO_3 would require a chemical model with transport, which would be difficult for such an environment with complex topography like the Kleiner Feldberg.

4 Conclusions

We observed highly variable NO_3 concentrations and lifetimes at a mountain site in south-west Germany. Measurements of NO_3 , its precursors and its sink reactions (both direct and indirect) enabled assessment of the processes (both chemical and meteorological) influencing its steady-state lifetime. We found that, during several nights, the observed steady-state lifetime was frequently larger than expected based on measured gas-phase reactants such as VOCs and NO. We have shown that an enhancement in the NO_3 production term via the reaction between Criegee and NO_2 may be significant but unlikely to explain the discrepancy. The periods with the highest apparent NO_3 lifetimes were associated with the presence of a very shallow boundary layer at the mountaintop so that the instrument inlets sampled from

the residual layer and NO₃ (and N₂O₅) mixing ratios and lifetimes were larger than those calculated from measured sources and sink terms.

Data availability

The PARADE data can be obtained on request (via John Crowley) from the owners.

The Supplement related to this article is available online at doi:10.5194/acp-16-4867-2016-supplement.

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