Nocturnal nitrogen oxides at a rural mountain-site in South-Western Germany

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Abstract

A new, two-channel instrument for simultaneous NO$_3$ and N$_2$O$_5$ monitoring was used to make the first comprehensive set of nocturnal NO$_x$ measurements (NO, NO$_2$, NO$_3$ and N$_2$O$_5$) at the Taunus Observatory, a rural mountain site (Kleiner Feldberg) in Southwestern Germany. In May 2008, NO$_3$ and N$_2$O$_5$ mixing ratios were well above the instrumental detection limit (a few ppt) on all nights of the campaign and were characterised by large variability resulting from inhomogeneously distributed sinks. The concentrations of NO$_3$, N$_2$O$_5$ and NO$_2$ were consistent with the equilibrium constant, $K_2$, defining the rates of formation and thermal dissociation of N$_2$O$_5$. A steady-state lifetime analysis showed that nocturnal NO$_x$ losses were generally dominated by reaction of NO$_3$ with volatile organic compounds in this forested region, with N$_2$O$_5$ uptake to aerosols of secondary importance. Analysis of a limited dataset obtained at high relative humidity indicated that the loss of N$_2$O$_5$ by reaction with water vapour is less efficient (> factor 3) than derived using laboratory kinetic data. The fraction of NO$_x$ present as NO$_3$ and N$_2$O$_5$ reached $\approx$20% on some nights, with night-time losses of NO$_x$ competing with daytime losses.

1 Introduction

Daytime oxidation processes (e.g. of volatile organic trace gases, VOC) are dominated by the photochemically generated hydroxyl radical (OH), which is absent (or present at much reduced levels) at night. At night-time, the nitrate radical, NO$_3$, is considered the major initiator of oxidation of certain classes of gas-phase organic compounds such as biogenic terpenes and dimethyl sulphide (Wayne et al., 1991). NO$_3$ is formed predominantly in the reaction of NO$_2$ with ozone (Reaction R1) and is converted to N$_2$O$_5$ via further reaction with NO$_2$ (Reaction R2a). Due to the thermal decomposition of N$_2$O$_5$ to NO$_2$ and NO$_3$ (Reaction R2b), the relative concentrations of NO$_3$ and N$_2$O$_5$ are closely linked (Brown et al., 2003a) and are a strong function of temperature and...
[NO₂].

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]  
(R1)

\[ \text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \]  
(R2a)

\[ \text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M} \]  
(R2b)

As a consequence of its rapid photolysis and reaction with NO (Reaction R4), the NO₃ radical is absent or at significantly reduced concentration during the day and the rapid equilibrium (Reaction R2a, R2b) ensures very low concentrations of N₂O₅ also. Apart from regions impacted by strong anthropogenic NO emissions or very close to the surface where soil emissions of NO are important, NO is rapidly converted to NO₂ via Reaction (R3) at night enabling a build up of NO₃ and N₂O₅. In rural areas NO₂, NO₃ and N₂O₅ are thus the only nocturnal nitrogen oxides apart from long lived, reservoir species such as HNO₃ or PAN.

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  
(R3)

\[ \text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2 \]  
(R4)

The lifetime of NO₃ is then controlled mainly by its reactions with certain VOC, whereas N₂O₅ (an acid anhydride) is lost mainly by heterogeneous hydrolysis on aerosol surfaces to result in aqueous phase nitrate formation:

\[ \text{NO}_3 + \text{VOC} \rightarrow \text{products} \]  
(R5)

\[ \text{N}_2\text{O}_5 + \text{aerosol} \rightarrow \text{nitrate} \]  
(R6)

Close to ground level, dry deposition could also be important for both NO₃ and N₂O₅. The sequential oxidation of NO to NO₂ to NO₃ to N₂O₅ and finally to particulate nitrate thus represents a change in the partitioning of nitrogen oxides between the NOₓ
(NO + NO₂) and NOy families (where NOy is the sum of all nitrogen oxides and includes long lived reservoir species such as HNO₃) and also the partitioning of NOy between the gas and particulate phases. Both the modification of the NOx/NOy ratio and the oxidation of VOCs by NO₃ impact on daytime photochemical rates.

Given sufficient time, a stationary state is reached for NO₃ at night in which its production (the rate of which is given by \( k_1[NO_2][O_3] \)) is approximately balanced by the sum of direct losses and indirect loss via conversion to N₂O₅ and subsequent heterogeneous removal. The turnover lifetime of NO₃ in steady state, \( \tau_{ss}(NO_3) \), which is defined as the inverse of the sum of the direct and indirect loss frequencies (\( \tau_{ss}(NO_3) = 1/(f_{dir}(NO_3) + f_{indir}(NO_3)) \)), is given by:

\[
\tau_{ss}(NO_3) = \frac{[NO_3]}{k_1[NO_2] \cdot [O_3]}
\]

In the absence of both light and NO the direct losses of NO₃ are dominated by reactions with organic trace gases (Reaction R5) so that, to a good approximation, \( f_{dir}(NO_3) = \Sigma(k_i[VOCS]) \) where \( k_i \) is the rate coefficient for reaction of NO₃ with a specific VOC of concentration [VOC]. The rate of indirect loss of NO₃ via its conversion to N₂O₅ depends on the equilibrium constant \( (K_2) \) that defines the relative concentration of NO₃ and N₂O₅ for any given temperature and amount of NO₂.

\[
K_2 = \frac{[N_2O_5]}{[NO_2] \cdot [NO_3]} = \frac{k_2}{k_{-2}}
\]

The frequency of indirect loss of NO₃ is thus given by \( f_{indir}(NO_3) = K_2[NO_2](f_{het} + f_{homo}) \). Where \( f_{het} \) is the loss frequency for N₂O₅ due to irreversible, heterogeneous uptake to aerosol surfaces and \( f_{homo} \) is the loss frequency of N₂O₅ due to gas-phase reaction with water vapour. Combining the definitions of \( f_{dir}(NO_3) \) and \( f_{indir}(NO_3) \) with Eq. (1) and ignoring loss of NO₃ or N₂O₅ by dry deposition, we derive (Geyer et al.,
2001; Aldener et al., 2006):

\[
\tau_{ss}(\text{NO}_3) \approx \frac{1}{f_{\text{dir}}(\text{NO}_3) + f_{\text{indir}}(\text{NO}_3)} \approx \frac{1}{f_{\text{dir}}(\text{NO}_3) + K_2[\text{NO}_2](f_{\text{het}} + f_{\text{homo}})}
\]  

For aerosol particles of diameter less than \( \approx 1 \) micron, \( f_{\text{het}} \) is given by:

\[
f_{\text{het}} \approx \frac{\gamma \cdot \bar{c} \cdot A}{4}
\]

where \( A \) is the aerosol surface area density (\( \text{cm}^2 \text{ cm}^{-3} \)), \( \bar{c} \) is the mean molecular velocity of \( \text{N}_2\text{O}_5 \) (23 500 cm s\(^{-1}\) at 280 K) and \( \gamma \) is the dimensionless uptake coefficient. The presently recommended kinetic expression (IUPAC) for gas-phase reaction between \( \text{N}_2\text{O}_5 \) and \( \text{H}_2\text{O} \) contains terms both linear and quadratic in \( \text{H}_2\text{O} \) concentration:

\[
\begin{align*}
\text{N}_2\text{O}_5 + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3 \\
\text{N}_2\text{O}_5 + 2\text{H}_2\text{O} & \rightarrow 2\text{HNO}_3 + \text{H}_2\text{O}
\end{align*}
\]

(R7a)  
(R7b)

with \( k_{7a} = 2.5 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and \( k_{7b} = 1.8 \times 10^{-39} \text{ [H}_2\text{O}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). As \( [\text{H}_2\text{O}] \gg [\text{N}_2\text{O}_5] \), pseudo first-order kinetics are applicable so that

\[
f_{\text{homo}} = k_{7a}[\text{H}_2\text{O}] + k_{7b}[\text{H}_2\text{O}]^2
\]

with the \( \text{H}_2\text{O} \) concentration in units of molecule \( \text{cm}^{-3} \). The relative importance of direct and indirect loss mechanisms for \( \text{NO}_3 \) depends on several factors including the concentrations of \( \text{NO}_2 \) and VOCs, the available surface area (4) and the temperature, which strongly influences both \( K_2 \), emission rates of biogenic VOCs (Geyer and Platt, 2002) and available \( \text{H}_2\text{O} \)-vapour. For this reason, the direct and indirect loss mechanisms can show large regional and seasonal dependencies, with \( \text{NO}_3 \) lifetimes close to the surface varying from minutes in areas impacted by anthropogenic or biogenic emissions to hours in remote regions (Heintz et al., 1996; Allan et al., 2000).
In this paper we describe the first deployment of a new, two-channel optical cavity based instrument for detection of NO$_3$ and N$_2$O$_5$, and also the first measurements of NO$_3$ or N$_2$O$_5$ at the Taunus Observatory, a rural mountain site in South-western Germany. Ancillary measurements of NO, NO$_2$, O$_3$ and aerosol surface area enabled us to calculate NO$_3$ and N$_2$O$_5$ lifetimes and assess some aspects of nocturnal chemistry at this site.

2 Experimental

2.1 Site description

The measurements were made at the Taunus Observatory, located at 50°13′25″ N, 8°26′56″ E and 825 m above sea level at the summit of the “Kleiner Feldberg” a mountain in the Taunus range in South-western Germany (Fig. 1). The area directly around the observatory is mainly coniferous forest (predominantly spruce). The hill top itself (50 m in radius) has been cleared of trees for meteorological measurements several times, the last time about half a century ago and only a couple of willows and some birch trees remain between the cleared area and the spruce trees. The direct vicinity of the measurement containers is covered by shrubs and blueberry plants. Because of its elevation the station is known for its quite remote character for central Germany with a few main roads and some small towns within 5 km. The observatory is impacted by pollution from the heavily populated Rhein-Main area (pop. ≈2 million) including a dense motorway system and large cities such as Frankfurt (pop. ≈700 000, 30 km SE), Wiesbaden (pop. ≈300 000, 20 km SW) and Mainz (pop. ≈200 000, 25 km SSW). The area 50–100 km north of Kleiner Feldberg is lightly populated and devoid of major industry. Wind flow patterns are influenced by the presence of two similar sized mountains: Altkönig (798 m) and Großer Feldberg (878 m) in the direct vicinity (2.7 km and 1.3 km distant, respectively). Previous measurements have shown that highest CO levels at the Taunus Observatory were associated with Easterly winds containing air
from the Frankfurt region which have been channelled between the Großer Feldberg and Altkönig mountains (Wetter, 1998) with highest levels of O$_3$ arriving with wind from the east to southeast during fine weather (Handisides, 2001). As well as the Taunus Observatory, the meteorological garden of the German weather service (DWD) and the measurement container of the State of Hessen environmental agency (HLUG) are also located at the summit of the Kleiner Feldberg.

2.2 Instrumentation

The instruments were located in the upper container of a two-container tower, with the inlet $\approx$4.5 m above the ground. In order to avoid trace gas losses (especially of NO$_3$) the inlet was constructed from a 1.4 m long, glass tube of internal diameter 10.4 cm, which was internally coated with a thin film of Teflon (FEP 100a). An industrial fan attached to the exit of the glass tube maintained a flow (at circa 700 Torr) of $\approx$20 m$^3$ min$^{-1}$ through the tube, resulting in residence times of $\approx$0.1 s to the sampling line. 18 L min$^{-1}$ air was sampled (at 90° to the main flow) from the centre of the large diameter tube via a short piece of $\frac{1}{4}''$ PFA-Teflon tubing ($\approx$15 cm) and a 2 µm pore Teflon filter to the NO$_3$/N$_2$O$_5$ instrument. A $\approx$4 m length of $\frac{1}{4}''$ PFA-Teflon tubing, sampling at $\approx$3 L/min from the centre of the inlet, transferred air to the NO/NO$_2$/O$_3$ detector (see below). Physical characterisation of the aerosol size distribution and aerosol number concentration was performed via inlets from the same container used for NO$_3$ and N$_2$O$_5$ measurements. Smaller particles were sampled through a 1 m long Tygon tube, which was mounted horizontally straight out of the container window in order to keep sampling losses as small as possible. Larger particles were sampled via a vertical glass tube extending above the roof of the upper container. This inlet was covered by a cap to prevent rain from entering.
2.2.1 NO$_3$ and N$_2$O$_5$ measurements

NO$_3$ and N$_2$O$_5$ mixing ratios were measured using a two-channel, off axis cavity-ring-down system (OA-CRD). A single channel prototype of this device was described recently (Schuster et al., 2009) and took part in a major NO$_3$/N$_2$O$_5$ inter-comparison at an environmental chamber in 2007 (Apodaca et al., 2009; Dorn et al., 2009). The major modification of the device for the present campaign was the introduction of a second cavity to enable simultaneous measurement of NO$_3$ and N$_2$O$_5$. This is the first implementation of the two-channel device in the field and it is therefore described in some detail.

The instrument and inlet configuration is shown in Fig. 2. The NO$_3$ cavity (PFA tubing, 70 cm long, volume 79 cm$^3$) was operated close to ambient temperature, whereas the summed concentration of NO$_3$ + N$_2$O$_5$ was measured in a Teflon coated Pyrex cavity (70 cm long, volume 165 cm$^3$) heated to 80 $^\circ$C. The heated cavity was located behind a $\approx$20 cm section of Teflon coated glass tubing heated to 85 $^\circ$C to quantitatively convert N$_2$O$_5$ to NO$_3$. Laboratory tests showed that, at the given flow rates and residence time in the converter, this temperature was sufficient to quantitatively dissociate N$_2$O$_5$. Note that the cavity temperature was cooler than in our prototype device, (Schuster et al., 2009) which was operated at 95 $^\circ$C. The flow rates through the cavities were 10 L(std)min$^{-1}$ (NO$_3$) and 8 L(std)min$^{-1}$ (N$_2$O$_5$ + NO$_3$), resulting in residence times of $\approx$0.4 s and 0.8 s, respectively.

The light source used was a $\approx$100 mW laser diode operated at 662 nm, close to the peak of the NO$_3$ absorption spectrum. Light exiting the cavity was filtered by a 662 nm interference filter prior to detection by a PMT. The pre-amplified PMT signal was digitised and averaged with a 10 MHz, 12 bit USB scope (Picoscope 3424) which was triggered at the laser modulation frequency of 100 Hz. Typically 256 ring-down events were recorded to result in a time resolution of $\approx$3 s. The cavity loss due to absorption at 662 nm was calculated from the change in ring-down constant in the presence of an absorber and converted to a concentration of NO$_3$ using the effective cross section of
NO\textsubscript{3} at the experimental temperature and the established relation (Berden et al., 2000; Mazurenka et al., 2005)

\[
[\text{NO}_3] = \frac{\Delta k_{rd} L}{\sigma_{\text{NO}_3} cd}
\]  

(6)

where [NO\textsubscript{3}] is the concentration of NO\textsubscript{3} (molecule cm\textsuperscript{-3}), \(k_{rd}\) is the ring-down constant (a first-order rate coefficient with units of s\textsuperscript{-1}), \(\Delta k_{rd}\) is the difference in the ring-down decay constant with and without NO\textsubscript{3}, \(L\) is the distance between the cavity mirrors (70 cm), \(d\) is the length of the cavity which is filled with absorber, \(\sigma_{\text{NO}_3}\) is the effective absorption cross section of NO\textsubscript{3} and \(c\) is the speed of light \(\approx 2.998 \times 10^{10} \text{ cm s}^{-1}\).

Temperature dependent values of \(\sigma_{\text{NO}_3}\) were taken from (Yokelson et al., 1994; Orphal et al., 2003) and convoluted with the laser emission profile to obtain effective cross sections as described previously (Schuster et al., 2009).

The ring-down constant in the absence of NO\textsubscript{3} was derived by adding \(\approx 10^{12}\) molecule cm\textsuperscript{-3} of NO (8 sccm of a 100 ppm mixture of NO in N\textsubscript{2}) to the air above the filter every 100 s for a period of \(\approx 20\) s (duty cycle of 80%). Slight drifts in the ring-down constant over the course of an hour were then removed from the dataset by fitting a polynomial to the \(\approx 36\) titration points obtained in the presence of NO. Typically, for the NO\textsubscript{3} channel the standard deviation in the fit was \(\approx 1\) ppt, whereas for the sum channel it was \(\approx 2.5\) ppt.

By variation of the mirror purge gas flow whilst monitoring the ring-down signal due to a constant flow of NO\textsubscript{2} into the cavity (NO\textsubscript{2} also absorbs at 662 nm), we were able to calculate a value of \(L/d\) of \(1.01 \pm 0.03\). Note that the ring-down time constant, \(\tau\), is equal to \(1/k_{rd}\) and for a cavity free of absorbing species was typically close to 80 \(\mu\text{s}\), indicating an effective optical path length of \(\approx 25\) km.

Loss of NO\textsubscript{3} to the filter was determined in the laboratory as described previously (Schuster et al., 2009) by flowing NO\textsubscript{3} or N\textsubscript{2}O\textsubscript{5} (generated in the reaction of NO\textsubscript{2} with O\textsubscript{3}) into the cavities with and without a filter in place. Repeated tests resulted in a clean
filter transmission of 90±3% for NO₃ and 98±2% for N₂O₅. During the campaign, the filter was usually changed at 1 h intervals to prevent significant build up of a reactive surface. We show later that leaving the filter for two hours did on one occasion result in loss of NO₃ transmission (but not N₂O₅).

The data also required correction for loss of NO₃ during transport through the cavities. This was achieved by carrying out pre- and post-campaign experiments in the laboratory in which a 11 SLM flow of air containing stable concentrations of N₂O₅ and NO₃ was passed through both cavities. By varying the relative flow rate through each cavity whilst maintaining the total flow and thus NO₃/N₂O₅ concentration, the residence time of gas in each cavity was varied. As described previously (Schuster et al., 2009) an exponential dependence of the NO₃ signal on residence time was observed, allowing loss terms of 0.25±0.05 s⁻¹ (cold cavity) and 0.11±0.05 s⁻¹ (hot cavity) to be derived. Based on known cavity residence times when sampling from the atmosphere, the corrections to the field data for cavity losses were calculated as 11±2% for both channels.

Other corrections that can be applied to the data result from chemistry within the cavities. The addition of NO to titrate NO₃ whilst measuring the ring-down constant in the absence of NO₃ (chemical zero) disturbs the equilibrium between NO₃ and N₂O₅, and leads to N₂O₅ dissociation to NO₃. The magnitude of this effect (essentially an error in the determination of the chemical zero) can be estimated in a steady state analysis from the amount of N₂O₅, the cavity temperature and the NO added as:

\[
[\text{NO}_3]_{\text{extra}} = \frac{k_{-2}[\text{N}_2\text{O}_5]}{k_4[\text{NO}]}
\]  

(7)

At a typical cavity temperature of 292 K, \(k_{-2}\) is \(\approx 0.02\) s⁻¹ and \(k_4\) is \(3.6 \times 10^{-11}\) cm³ molecule⁻¹ s⁻¹. The extra NO₃ formed in this process is \(\approx 0.2\) ppt at N₂O₅ mixing ratios of 200 ppt. As such N₂O₅ mixing ratios were always associated with NO₃ mixing ratios of 20 ppt or more, this represents an insignificant effect (sub percent).
In addition to titrating NO\textsubscript{3}, the addition of NO can lead to NO\textsubscript{2} formation via its reaction with ambient O\textsubscript{3}. As both NO\textsubscript{2} and O\textsubscript{3} absorb weakly at 662 nm, (cross sections are \(\approx2\times10^{-21}\) cm\(^2\) molecule\(^{-1}\) for NO\textsubscript{2} and \(1\times10^{-21}\) cm\(^2\) molecule\(^{-1}\) for O\textsubscript{3}) this can also have an impact on the retrieved chemical zero. The amount of NO\textsubscript{2} formed during titration, \(\delta[\text{NO}_2]\), may be approximated by:

\[
\delta[\text{NO}_2] = [\text{O}_3]\left\{1 - \exp(-k_3[\text{NO}]t)\right\}
\]  

(8)

where \(t\) is the cavity residence time (0.88 s in the N\textsubscript{2}O\textsubscript{5} + NO\textsubscript{3} cavity and 0.44 s in the NO\textsubscript{3} cavity). \(k_3\) is equal to \(4.3\times10^{-14}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 80°C (hot cavity) and \(1.8\times10^{-14}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at \(\approx290\) K (cold cavity). We assume O\textsubscript{3} is 80 ppb (the largest value measured in the campaign). For the hot cavity \(\delta\) NO\textsubscript{2}=3 ppb, and for the cold cavity just 0.6 ppb. Given the values of the NO\textsubscript{2} and O\textsubscript{3} cross sections listed above, this represents an error of just 0.15 ppt equivalents (N\textsubscript{2}O\textsubscript{5} + NO\textsubscript{3} cavity) and 0.03 ppt (NO\textsubscript{3} cavity) which are much lower than noise levels and fluctuations in the chemical zero.

Although the cold cavity was heavily insulated, we measured temperatures within the cavity that were \(\approx4–5\)°C warmer than ambient. A warming of the cavity compared to ambient air can potentially impact on the NO\textsubscript{3} measurement as a new equilibrium between N\textsubscript{2}O\textsubscript{5} and NO\textsubscript{3} may be established, leading to an overestimation of the true NO\textsubscript{3} concentration and also the NO\textsubscript{3}/N\textsubscript{2}O\textsubscript{5} ratio. As a first approximation, an upper limit to the size of this effect can be estimated from the concentration of N\textsubscript{2}O\textsubscript{5}, the known dissociation rate constant \((k_{-2})\) at the temperature of the cavity and the average residence time (\(t\)) of N\textsubscript{2}O\textsubscript{5} in the cavity.

\[
\delta[\text{NO}_3]=\delta[\text{N}_2\text{O}_5]=\delta[\text{N}_2\text{O}_5]_0\exp\left(-k_{-2}t\right)\]

(9)

At 290 K (typical ambient temperatures were 280–285 K), the thermal dissociation rate constant for N\textsubscript{2}O\textsubscript{5} is \(1.4\times10^{-2}\) s\(^{-1}\). The average residence time is taken as the time for gas to be transported half way between the T-piece connector to the centre
of the cavity and the exit and is \( \approx 0.26 \text{s} \). This estimation of the residence time takes into account the fact that we “integrate” the \( \text{NO}_3 \) concentration over the entire cavity length. These values of \( k_{-2} \) and \( t \) result in \( \approx 0.4\% \) conversion of the \( \text{N}_2\text{O}_5 \) to \( \text{NO}_3 \), which represents a maximum correction of 1.6 ppt for \( \text{NO}_3 \) when \( \text{N}_2\text{O}_5 \) was close to 400 ppt (the largest values measured in the campaign). This calculation does not take into account the fact that the formation and loss rates of \( \text{N}_2\text{O}_5 \) are not de-coupled at this temperature. As typical vales of \( \text{NO}_2 \) were 1–2 ppb (\( \approx 2–4 \times 10^{10} \text{ molecule cm}^{-3} \)) the instantaneous first-order constant for \( \text{N}_2\text{O}_5 \) formation (\( k_2[\text{NO}_2] \)) is 2.5–5 \( \times 10^{-2} \text{ s}^{-1} \), i.e. similar to its thermal dissociation rate constant. More accurate correction factors were thus obtained by numerical simulation (Curtis and Sweetenham, 1987) of the effect of a 5°C temperature jump in \( \text{NO}_2/\text{NO}_3 / \text{N}_2\text{O}_5 \) mixtures at equilibrium and at similar concentrations to those measured in the campaign. The results showed that the maximum change in \( \text{NO}_3 \) or the \( \text{NO}_3/\text{N}_2\text{O}_5 \) ratio was \( \approx 1–1.5\% \). This effect was considered too small to warrant correction to the data, though it is worth noting that long cavity residence times and larger temperature increases between ambient and cavity will result in significant systematic overestimation of \( \text{NO}_3 \) under some conditions.

The random noise limited detection limits (3 s integration per datapoint) were 1–2 ppt (\( \text{NO}_3 \)) and 4–5 ppt (\( \text{N}_2\text{O}_5 \)). As summarised by Schuster et al. (2009), when considering the above and taking into account estimated errors in the \( \text{NO}_3 \) cross section at both cavity temperatures (Yokelson et al., 1994; Orphal et al., 2003) we estimate the uncertainty to be \( \pm 15\% \) for \( \text{NO}_3 \) and at least 2 ppt. For the \( \text{N}_2\text{O}_5 \) channel these values are \( \pm 15\% \) and at least 3 ppt.

### 2.2.2 NO, NO\(_2\) and O\(_3\) measurements

The measurements of NO, NO\(_2\) and O\(_3\) were based on the chemiluminescence of the reaction between NO and O\(_3\) (Fontijn et al., 1970). The instrument is a modified commercial Chemiluminescence Detector (CLD 790 SR) originally manufactured by ECO Physics (Duernten, Switzerland). The original instrument housed two CLD chan-
nels, that were used for the detection of NO and NO$_2$. The quantitative detection of NO$_2$ is based on its photolytic conversion (Blue Light Converter, Droplet Measurement Technologies, Boulder, CO, USA) to NO, which was subsequently detected in the CLD (Kley and McFarland, 1980). A third channel was added for the measurements of O$_3$ following the design described by Ridley et al. (1992). In the present study data were obtained at a time resolution of 2 s.

In-field calibrations for NO were made on a regular basis by adding a secondary standard (2 ppmv NO in N$_2$, Air Liquide, Germany) diluted by zero air to a mixing ratio of approximately 2 ppbv. The zero air, that was also used for regular background measurements, was produced from synthetic air (Air Liquide, Germany), that was additionally filtered through a catalytic air purifier (Pt/Pd) and charcoal and purafil (KMnO$_4$/Al$_2$O$_3$) cartridges. The secondary NO standard used in the field was traced to a primary standard (NIST, USA). The efficiency of the Blue Light Converter for NO$_2$ measurements was determined by gas phase titration of NO (from the secondary standard) using an excess of O$_3$. This procedure yielded a conversion efficiency of $(46.6 \pm 2)\%$ over the campaign. The ozone channel was calibrated using a commercial O$_3$ calibrator (model TE49C, Thermo Instruments, Germany).

The detection limits for the NO and NO$_2$ measurements were 10 ppt and 80 ppt, respectively for an integration period of 2 s. The total uncertainties for the measurements of NO, NO$_2$, and O$_3$ were determined to be 10%, 10% and 5%, respectively, based on the reproducibility of in-field background measurements, calibrations, the uncertainties of the standards and the conversion efficiency of the photolytic converter.

### 2.2.3 Particle measurements

Aerosol number and size distribution was monitored using a scanning mobility particle sizer (TSI 3936), consisting of an electrostatic classifier with a $^{80}$Kr source for particle equilibrium charging and a long differential mobility analyser (TSI 3081) with a condensation particle counter (TSI 3025A) for particle detection. The sheath flow inside the electrostatic classifier was set to 6 L min$^{-1}$ and the sample flow of the ultra fine
particle counter was set to its maximum value of 1.5 L min\(^{-1}\) (high flow). This set-up allowed particle detection within the size range between 9.8 and \(\approx 300\) nm in diameter. Each size distribution measurement took 135 s, i.e. 120 s for up scan and 15 s for down scan. Four consecutive measurements were averaged afterwards to obtain a smooth result with a time resolution of ten minutes. In the absence of information regarding composition, a particle density of 1.2 g/cm\(^3\) was assumed. Larger particles with a diameter between 360 nm and 19\(\mu\)m were detected occasionally by an aerosol particle sizer (APS, TSI 3321) using a sampling flow rate of 1 L min\(^{-1}\). Typical night-time particle concentrations as measured by the SMPS were 2000–5000 particle cm\(^{-3}\) with a bi-modal distribution (maxima at \(\approx 35\) and 120 nm) with most surface area contained in particles of radius \(\approx 200–250\) nm. The APS particle measurements only functioned sporadically and revealed low concentrations of coarse particles (10–20 particle cm\(^{-3}\), with a mean diameter \(\approx 600\) nm). The APS measurements indicate that particles measured by the SMPS account for at least 65% of the total aerosol surface area and generally close to 80%.

### 2.2.4 Meteorological data

Atmospheric pressure and temperature, wind direction/speed and relative humidity were available as 10 min averaged data from the German weather service station (DWD), located \(\approx 20\) m away from the container. Global radiation was available from the local environmental agency station (HLUG) as 30 min averaged data. These measurements were also located just a few metres away. The HLUG also provided O\(_3\) measurements (30 min averages) using a UV-absorption instrument (API 400).

### 3 Observations and analysis

The measurements were carried out in May 2008, with almost complete coverage for NO and NO\(_2\) from the 9th until the 20th. O\(_3\) was measured over the same period, but
with a break for instrument repair between the 14th and 15th. The NO$_3$/N$_2$O$_5$ instrument was operated on one night prior to and 6 nights within this period. The complete trace gas and meteorological data set is displayed in Fig. 3. NO$_3$/N$_2$O$_5$ measurements typically started just before local sunset and stopped after the signals had returned to baseline levels following sunrise. The early part of the campaign (up to 15th of May) was characterised by easterly winds (12–25 km/h) cloud-free skies and daytime maximum temperatures up to 18°C. Temperatures at night generally sunk to ≈9–12°C with relative humidities of 30–45% and no precipitation. After the 15th of May, the wind direction was more variable with components from the Southwest bringing clouds and rain. NO$_2$ was present at concentrations of typically between 1 and 2 ppb at night, with excursions up to 4 ppb. Daytime mixing ratios were generally less than 10 ppb. O$_3$ was present at levels between 30 and 75 ppb, with maximum mixing ratios of ≈55–75 ppb encountered in the late afternoon, which usually decreased steadily (by 10–20 ppb) during the night. The HLUG O$_3$ mixing ratios have been multiplied by a factor 0.82 to bring them into line with the MPI measurements, which are considered to be more reliable due to frequent calibration.

The high levels of night-time O$_3$ ensured that NO levels were low and usually close to the instrumental detection limit. The conditions were therefore conducive for NO$_3$ chemistry (sufficient NO$_x$ and O$_3$ to drive formation and no NO) and both NO$_3$ and N$_2$O$_5$ were detected on all nights in which the instrument was operated, with maximum mixing ratios of ≈500 ppt and 60 ppt observed for N$_2$O$_5$ and NO$_3$, respectively. A more detailed view is given in Fig. 4, which displays data from one night only (12–13th of May). On this night, NO$_3$ and N$_2$O$_5$ mixing ratios increased above the detection limit shortly after local sunset (at ≈21:00) when both photolysis and NO levels were sufficiently reduced. The lifetime of NO in the presence of ≈60 ppb of O$_3$ is only about 1 min, so that the slow decrease in NO after 19:00 simply reflects the decrease in light intensity and the decreasing photolysis rate of NO$_2$. Maximum values of ≈25 and 70 ppt were reached by NO$_3$ and N$_2$O$_5$, respectively, both displaying great temporal variability, with fluctuations of 15–20 ppt (i.e. up to 50% signal modulation) in one minute. The
short term variability (minutes) of NO$_3$ and N$_2$O$_5$ is typical of a ground site (Brown et al., 2003b) and is driven by the sampling of air masses with different chemical histories and variable loss processes encountered by both species during transport to the site from the NO$_x$ emission region(s).

On a slightly longer time scale (10–15 min) there is evidence for variability driven by fluctuations in the NO$_2$ mixing ratio (e.g. between ≈3 a.m. and 5 a.m. on the 13th) which, together with O$_3$, defines the production rate of NO$_3$ and N$_2$O$_5$. At sunrise (≈05:30 local time) both NO$_3$ and N$_2$O$_5$ are rapidly depleted as J$_{NO_3}$ increases. The direct photolysis of NO$_3$ depletes N$_2$O$_5$ via the equilibrium (Reaction R2a, R2b) and also releases NO to further remove NO$_3$. NO is also generated in the photolysis of NO$_2$ at roughly the same time, and both NO$_3$ and N$_2$O$_5$ return to below detection limit within 1 h. The blue, vertical lines indicate at which times the Teflon filter was changed. Filter changing was conducted manually, and took ≈1–2 min. On this night, there was no evidence for loss of N$_2$O$_5$ or NO$_3$ on the filter, which would have been observable as an increase in the NO$_3$ or N$_2$O$_5$ signal directly after filter changing.

3.1 Equilibrium between NO$_2$, NO$_3$ and N$_2$O$_5$

According to Reaction (R2a) and (R2b), the relative concentrations of NO$_3$ and N$_2$O$_5$ should be controlled by the temperature dependent equilibrium constant (K$_2$) and the concentration of NO$_2$. The time for a chemical system to relax to equilibrium is the sum of the inverse forward and back rate constants, i.e., with NO$_2$ in large excess over NO$_3$:

$$\tau_{eq} = \frac{1}{k_2[NO_2] + k_{-2}}$$

At pressures close to 1 bar, the rate constant for the forward reaction ($k_2$) is circa $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, which when combined with typical NO$_2$ concentrations of 1.5 ppb ($\approx4\times10^{10}$ molecule cm$^{-3}$), gives a first-order N$_2$O$_5$ formation rate constant of 0.04 s$^{-1}$. The thermal dissociation rate constant for N$_2$O$_5$ ($k_{-2}$) is 0.0064 s$^{-1}$ at the average night-time temperature of 11±1.5°C. This results in a relaxation time to thermal
equilibrium of \( \approx 100 \text{s} \) and implies that, in the absence of very local sources or sinks of \( \text{NO}_3 \) or \( \text{N}_2\text{O}_5 \), these species should be in thermal equilibrium. Qualitative confirmation of this could be observed during measurements as even rapid changes in \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) (see discussion of variability above) closely tracked each other.

Whether equilibrium was acquired could be tested by making a point-by-point comparison of the measured \( \text{NO}_2 \) mixing ratio (interpolated onto the same time grid as the \( \text{NO}_3/\text{N}_2\text{O}_5 \) data) with that calculated from the \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) observations, the temperature and the literature value for \( K_2(T) \), which is recommended as \( K_2 = 3.0 \times 10^{-27} \exp(10990/T) \) (Sander et al., 2006). The results are shown for the night 8th–9th of June in Fig. 5. As data filter, only \( \text{NO}_3 \) mixing ratios greater than 7 ppt were considered. The black data points in the upper panel of Fig. 5 are the calculated \( \text{NO}_2 \) mixing ratios (\( \text{NO}_2\)-calc). The grey data points were calculated using the upper and lower bounds of the propagated overall uncertainty in \( \text{NO}_2\)-calc, which arises from uncertainty in the \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) mixing ratios and the uncertainty in \( K_2 \) at 285 K (factor of 1.3). The red line is the CLD measurement of \( \text{NO}_2 \). There is good agreement between the measured and calculated \( \text{NO}_2 \) mixing ratios on this night, with the major features in \( \text{NO}_2 \) around midnight, when variations between 0.5 and 3 ppb are apparent, nicely captured.

From expression (Eq. 2), a plot of the product of the \( \text{NO}_2 \) and \( \text{NO}_3 \) mixing ratios versus the \( \text{N}_2\text{O}_5 \) mixing ratio should be a straight line with the slope equal to \( K_2 \). Such a plot is shown (Fig. 6) for the same dataset (night 8th–9th of June, 01:00–03:00, \( \text{NO}_3 > 7 \text{ppt} \)). The measured \( \text{NO}_2 \) mixing ratio was converted to a concentration so that the slope is an equilibrium constant in the usual units of inverse concentration (cm\(^3\) molecule\(^{-1}\)). The temperature for each \( \text{NO}_3/\text{N}_2\text{O}_5/\text{NO}_2 \) datapoint varied from \( \approx 284 \) to 287 K during the night (see colour scale). Even though the difference between maximum and minimum temperature was only \( \approx 3 \text{K} \), it is apparent that the data points obtained at the coolest temperatures result in the largest slope (largest values of \( K_2 \)), reflecting the strong temperature dependence in \( K_2 \). The solid black lines represent the expected slopes at the extremes of the small temperature range covered, and should therefore encompass all the data. The dotted black lines use the values of \( K_2 \) at the
outer bounds of the recommended uncertainty in this parameter. Essentially all of the
data is encompassed by the dotted lines. The relevant temperature for calculating
the equilibrium constant is not necessarily that at the inlet, but that experienced by
the air mass during the last \( \approx 100 \) s (approximate relaxation time to equilibrium for the
conditions at the Kleiner Feldberg) prior to entering the inlet. As our temperatures are
those measured by the German weather service station \( \approx 20 \) m distant from our inlet
this represents a source of uncertainty in our calculations. In this context, the night-
time temperatures reported by the local environmental agency (HLUG) are \( \approx 0.5^\circ \)C
lower than reported by the DWD.

Nonetheless, by selecting data within small temperature windows we were able to
derive values of \( K_2 = 1.95 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \) (\( 284>T>283 \) K, average temperature
284.3 K) and \( K_2 = 1.44 \times 10^{-10} \text{ cm}^3 \text{ at molecule}^{-1} \) (\( 287>T>286 \) average temperature
286.8 K) with a proportional fit to the data. The uncertainty associated with these
values of \( K_2 \) derived from the field data are related to uncertainty in the NO\(_3\), N\(_2\)O\(_5\) and
NO\(_2\) measurements, which propagate to a value of \( \approx 23\% \). and, more significantly, are
impacted by the unknown temperature history of the air mass directly before sampling
(see above). The statistical errors associated with the fit were less than 1%.

The values of \( K_2 \) listed above are in very close agreement (within 2%) with recent
measurements made in the field using simultaneous detection of NO\(_2\), NO\(_3\) and N\(_2\)O\(_5\)
(Osthoff et al., 2007). They also agree (within 7%) with literature evaluations (Sander
et al., 2003) of \( 1.89 \) and \( 1.35 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \) at these respective temperatures.
We note that a later evaluation by the same panel and using the same database
(Sander et al., 2006) results in slightly worse, but, given the uncertainties involved,
acceptable, agreement.

In Fig. 7, we present equilibrium constants calculated from measured mixing ratios
of NO\(_2\), NO\(_3\) and N\(_2\)O\(_5\) for the each night of the campaign. To avoid systematic error at
low mixing ratios, data were selected so that the NO\(_3\) mixing ratio was always greater
than 5 ppt.
The temperature dependent values of $K_2$ thus calculated are compared with evaluations (JPL, 2003 and 2006) and recent field determinations (Osthoﬀ et al., 2007). Despite significant scatter in the data is it apparent that, even when neglecting the 30% overall error in our measurements of NO$_3$ and N$_2$O$_5$, the calculated values of $K_2$ are consistent with the recommended values, with slightly better agreement with the field data of (Osthoﬀ et al., 2007).

To date, there have been only a few simultaneous measurements of NO$_2$, NO$_3$ and N$_2$O$_5$. Our data at the Kleiner Feldberg support observations (Brown et al., 2003b; Aldener et al., 2006; Osthoﬀ et al., 2007) that thermal equilibrium exists at night between these three trace gases under most conditions, the possible exception being at low temperatures. Our data may also be considered to provide confirmation of the laboratory derived equilibrium constant $K_2$, which has usually been obtained by measuring individual rate constants for the forward and backward processes (Reaction R2a and R2b) via pseudo first-order analysis rather than measurement of equilibrium concentrations, which is difficult to achieve in laboratory set-ups with reactive surfaces. The notable exception to this being the work of (Osthoﬀ et al., 2007), in a well characterised, multi-channel cavity apparatus, whose laboratory derived equilibrium constants agree very well with ours (within 6%).

Conversely, assuming that the laboratory derived equilibrium constant is accurately known, we can conclude that our two-channel set-up for NO$_3$ and N$_2$O$_5$ (used for the first time in this campaign) and the associated data correction procedure can accurately measure ambient NO$_3$ and N$_2$O$_5$ mixing ratios. Poor agreement between calculated NO$_2$ concentrations (via NO$_3$, N$_2$O$_5$ and $K_2$) and those measured directly were however occasionally observed. This occurred when NO$_3$ was reactively lost at an aged Teflon filter, resulting in falsification of the N$_2$O$_5$/NO$_3$ ratio and subsequent overestimation of the NO$_2$ concentration. Although small, post filter-change discontinuities in the NO$_3$ signals were usually concealed by their large natural variability, they were clearly evident in the calculated NO$_2$ mixing ratio as short term variability in NO$_3$ and N$_2$O$_5$ were closely matched and thus cancelled. Evidence for NO$_3$ filter loss was seen in the
dataset from the 9th–10th when filter changes were performed only every two hours. Similarly, on one night (13th–14th May) the high-volume flow inlet was replaced by a 3/8" PFA tube of ≈550 cm length. This resulted in a ≈30% increase in the calculated, equilibrium amount of NO₂ over a period when NO₂ was actually stable, indicating that ≈30% of the NO₃ had been lost in the inlet. Note that the residence time in the 550 cm length of tubing was ≈0.9 s. Loss of ≈30% of the NO₃ is thus broadly consistent with the loss rate coefficient of 0.25 s⁻¹ in PFA tubing reported in the experimental section.

3.2 NO₃ and N₂O₅ lifetimes and loss rates

The NO₃ turnover lifetime (see E3) at the Taunus Observatory was highly variable with maximum values of ≈1500 s. Generally, the NO₃ lifetime was longest after ≈03:00 following a slow increase from dusk. This is most apparent (Fig. 8) on the nights of the 9th, 12th and 13th, in which the lifetime directly after dusk (at ≈20:00) remained under ≈200 s for the next ≈3 h. Figure 8 also shows the instantaneous NO₃ production ($k_1[NO_2][O_3]$) rates during each night (red lines), which were typically between 100 and 300 ppt/h and fairly constant but with some excursions to larger values due to influxes of NO₂.

Recall that the NO₃ lifetime is determined by both direct losses (e.g. gas-phase reaction with biogenic organics) and indirect loss processes involving N₂O₅. The slow increase in NO₃ lifetime after dusk may thus have been due to either a decrease in gas-phase reactivity after dusk or due to a decrease in surface area or reactivity of aerosol. As the NO levels were reduced to below the detection limit in just a few minutes after dusk, the slow rate of build up of NO₃ and N₂O₅ was not due to a reduction in its concentration during this period. Alternatively, an increase in lifetime could also be related to a stabilisation of the lower atmosphere by adiabatic cooling, which would reducing turbulence and thus dry deposition rates. The observation on most nights of the campaign of a clear increase in wind speed following sunset, does however not support this possibility.

Before examining aspects of the NO₃ lifetime in more detail it is worthwhile es-
establishing whether a stationary state analysis was applicable for this dataset. Stationary state is formally achieved when the rate of change of NO$_3$ and N$_2$O$_5$ are zero, i.e. $d\text{NO}_3/dt = k_1[\text{NO}_2][\text{O}_3] + k_{-2}[\text{N}_2\text{O}_5] - k_2[\text{NO}_2][\text{O}_3] - f_{\text{dir}}(\text{NO}_3)[\text{NO}_3] = 0$ and $d\text{N}_2\text{O}_5/dt = k_2[\text{NO}_2][\text{NO}_3] - k_{-2}[\text{N}_2\text{O}_5] - (f_{\text{het}} + f_{\text{homo}})[\text{N}_2\text{O}_5] = 0$. The approximate time to acquire stationary state thus depends on the production and loss rates of both NO$_3$ and N$_2$O$_5$.

Time dependent values of $d\text{NO}_3/dt$ and $d\text{N}_2\text{O}_5/dt$ were determined by numerical simulation in a manner similar to that described by Brown et al. (2003a). Input parameters to the simulations were the measured NO$_2$ and O$_3$ concentrations and temperature dependent kinetic expressions for reactions R1, R2 (together defining the production rates of NO$_3$ and N$_2$O$_5$) and variable first order loss terms for removal of NO$_3$ and N$_2$O$_5$. The first-order loss terms for NO$_3$ and N$_2$O$_5$ ($f_{\text{dir}}(\text{NO}_3)$, $f_{\text{het}}$, $f_{\text{homo}}$) were adjusted until the simulated NO$_3$ and N$_2$O$_5$ mixing ratios were similar to those measured. In conjunction with NO$_3$ and N$_2$O$_5$ lifetimes of the order of minutes, the relatively warm night-time temperatures and low NO$_2$ concentrations at the Kleiner Feldberg in May, meant that stationary state was achieved within 1–2 h after dusk. Given the distance to local emission regions (see above) and wind speeds of between 10 and 20 km/h this suggest that a steady state analysis was appropriate.

The slow increase in NO$_3$ lifetime early in the night could have been caused by a reduction in the mixing ratio of biogenic trace gases in the hours following dusk. Using rate coefficients of $7.0 \times 10^{-13}$ and $6.2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for reaction of NO$_3$ with isoprene and $\alpha$-pinene, respectively (IUPAC, 2009) and initially ignoring indirect loss processes, we calculate that a NO$_3$ lifetime of $\approx 100$ s would be associated with isoprene levels of 0.60 ppb or $\alpha$-pinene levels of $\approx 68$ ppt. Emissions of biogenic organics are temperature and light-intensity dependent (Fehsenfeld et al., 1992) and the levels mentioned above would appear reasonable for moderate, spring-time emissions of biogenic organics in a forested area.

As we did not take measurements of organic compounds during the campaign we have no data which confirm efficient removal of NO$_3$ by e.g. isoprene or $\alpha$-pinene.
There appear to be no published datasets on measurements of gas-phase biogenic trace gases at the Kleiner Feldberg, though some data taken with a proton transfer mass spectrometer over a 4 day period in June of 2005 confirmed the expected presence of isoprene and terpenes in this forested area (V. Sinha and J. Williams, personal communication, 2009). Furthermore, these datasets indicate that both isoprene and terpene concentrations decreased slowly after sundown, only returning to baseline levels in the early hours of the next morning. This is thus consistent with the observed slow increase in NO$_3$ lifetimes over the same period.

A further indication for the presence of biogenic volatile organic compounds (VOCs) is the observation of new particle formation at the Kleiner Feldberg; indeed April–May was the most intense nucleation period during 2008. New particle formation took place during the measurement period on the following days: 8th–13th and 15th of May (day-time events) as well as during the evening of the 7th and the 14th of May (night-time events). Temperatures were moderately high and the nocturnal boundary layer rather shallow to facilitate accumulation of emitted VOCs. From the 15th onward the relative humidity increased substantially causing drizzle or rain and prevented the occurrence of nucleation. During this time the vegetation experienced a reduced drought stress resulting (presumably) in lower emission rates. At the same time aerosol mass and surface area declined because of wash out from the atmosphere.

On the last two days of the campaign, the NO$_3$ lifetime did not show a slow increase to a max value, but had already reached $\approx$300–400 s by 23:00 h (Fig. 8). As shown in Fig. 3, the last two days were meteorologically distinct from the first 4 as the wind direction changed to southwest, bringing cloud cover, lower temperatures and later in the night, rain and fog. The longer lifetime of NO$_3$ early on these nights was presumably related to reduced biogenic emissions. The periodic strong reductions in lifetime on the night 15th–16th May was coincident with precipitation at the site, presumably resulting in loss of N$_2$O$_5$ on large droplets (not monitored as the aerosol cut off was $\approx$0.5µm) or deposition to moist surfaces. Further, indirect processes leading to a reduction in the NO$_3$ lifetime are the loss of N$_2$O$_5$ on aerosol surface and with H$_2$O vapour. By inverting
expression Eq. 3 we obtain:

\[ f_{ss}(\text{NO}_3) \approx f_{\text{dir}} + K_{eq}[\text{NO}_2](f_{\text{het}} + f_{\text{homo}}) \] (11)

The relative importance of direct (gas-phase) and indirect (gas-phase and heterogeneous) losses of NO₃ are displayed for the nights of 13th and 16th May in Fig. 9. The heterogeneous loss rate of N₂O₅ (\( f_{\text{het}} \)) was calculated from the measured aerosol surface area using expression E4 and scaled by \( K_2[\text{NO}_2] \) and is presented in Fig. 9 (red line). The value used for the uptake coefficient, \( \gamma \), was 0.01, which is within the very large range of values derived from field observations. For example, low values of \( 0.5-6 \times 10^{-3} \) have been reported by (Brown et al., 2009) in aircraft measurements over Texas, which are consistent with \( \approx 3 \times 10^{-3} \) reported by (Allan et al., 1999; Ambrose et al., 2007) in marine air masses but much lower than values of 0.02–0.03 (Aldener et al., 2006; Ambrose et al., 2007) also obtained in marine environments. The uptake coefficient used is also smaller by a factor \( \approx 3 \) than measured for loss of N₂O₅ to dilute H₂SO₄ aerosol in the laboratory (Hallquist et al., 2000), though further laboratory studies have shown that the presence of organics can reduce this number significantly (Folkers et al., 2003). Although no aerosol composition data is available, some indication for the type of aerosol encountered at the Taunus Observatory was obtained by observing loss of NO₃ on an aged Teflon filter. In this case, an increase in NO₃ mixing ratio was seen directly after a filter change but was not accompanied by an increase in N₂O₅. This implies that the aerosol gathered on the filter contained a large organic fraction providing a reactive surface for NO₃ but one that did not support efficient hydrolysis of N₂O₅. On the 13th of May, it is clear from Fig. 9 that heterogeneous loss of N₂O₅ would have contributed only insignificantly to NO₃ removal even if \( \gamma = 0.03 \) had been used in the calculation. A similar picture emerges for the other nights before the 15th when the wind direction was predominantly Easterly and daytime temperatures were highest. In this period, the calculated maximum NO₃ loss rates due to heterogeneous loss of N₂O₅ were between 1.5 and \( 6 \times 10^{-4} \) s⁻¹ at the end of the night when the NO₃ lifetime was longest. Even then, the heterogeneous loss of N₂O₅ contributed
between only 7 and 28%. When averaged over the whole night, this figure becomes insignificantly small.

The frequency of NO\textsubscript{3} loss from stationary state caused by the homogeneous reaction of N\textsubscript{2}O\textsubscript{5} with water vapour (\(f_{\text{homo}}K_2[\text{NO}_2]\)) was initially calculated using the rate coefficients (\(k_{7a}\) and \(k_{7b}\)) preferred by IUPAC (2009), with H\textsubscript{2}O vapour concentrations calculated from the RH and temperature/pressure measurements of the DWD. The loss of NO\textsubscript{3} via this indirect route contributes to its overall loss only later in the night when the overall reactivity of the air has decreased.

Note that the indirect losses of NO\textsubscript{3} via homogeneous and heterogeneous N\textsubscript{2}O\textsubscript{5} reactions are constrained by measurements of H\textsubscript{2}O vapour and aerosol surface area which do not show a significant trend during the night, thus ruling them out as source of the reduction in reactivity (factor of 10) observed after dusk. In order to reproduce the time dependence of the NO\textsubscript{3} turnover lifetime on the night 12th–13th May, \(f_{\text{dir}}(\text{NO}_3)\) was calculated for an initial total reactivity (at dusk) equal to about 200 ppt \(\alpha\)-pinene equivalents, which was reduced during the night to \(\approx\)10 ppt (at 03:00) in a quasi-exponential manner, thus increasing the lifetime from \(\approx\)50 s at 21:00 on the 13th of May to \(\approx\)1000 s at 03:00 the next morning (grey line, Fig. 9).

For the night 16–17th May a slightly different picture emerges. On this night the NO\textsubscript{3} turn-over lifetime was longer, a result of a decrease in the concentration of VOC and aerosol surface area following a rainy period. Under these conditions and with an increase in RH to close to 100% the reaction of N\textsubscript{2}O\textsubscript{5} with H\textsubscript{2}O gains importance and, at 02:00 on the 17th would account for the entire reactivity of the NO\textsubscript{3} / N\textsubscript{2}O\textsubscript{5} system, i.e. \(f_{\text{homo}}K_2[\text{NO}_2] \approx (\tau_{\text{ss}}(\text{NO}_3))^{-1}\) if the IUPAC values were used.

The NO\textsubscript{3} losses can be separated into direct and indirect routes by using the fact that the NO\textsubscript{3} turnover lifetime depends non-linearly on the NO\textsubscript{2} concentration if N\textsubscript{2}O\textsubscript{5} losses are significant. This is apparent from expression Eq. 3, which has been utilised previously to extract e.g. the N\textsubscript{2}O\textsubscript{5} hydrolysis contribution to NO\textsubscript{3} loss (Heintz et al., 1996; Geyer et al., 2001; Aldener et al., 2006; Brown et al., 2006, 2009). Plotting the inverse of the NO\textsubscript{3} life-time versus \(K_2[\text{NO}_2]\) (with [NO\textsubscript{2}] in units of molecule cm\textsuperscript{-3}) should give
a straight line with slope equal to the $N_2O_5$ loss rate constant, $f_{\text{indir}}(NO_3)$ and intercept equal to the NO$_3$ loss rate constant $f_{\text{dir}}(NO_3)$. This analysis requires selection of data in which $f_{\text{dir}}(NO_3)$ and $f_{\text{indir}}(NO_3)$ are relatively constant, but for which there is sufficient variation in NO$_2$ to separate the direct and indirect NO$_3$ loss terms. On most nights this analysis resulted in strongly curved plots due to the slowly changing lifetime of NO$_3$ due to reaction with biogenic organics (see above). By selection of a small portion of the data (01:00 to 03:00) on the night of the 16th–17th of May in which significant variation on NO$_2$ was observed, a linear relationship was obtained (Fig. 10) with a slope ($f_{\text{indir}}(NO_3)$) very close to zero ($5\pm5\times10^{-6}$ s$^{-1}$) and intercept of $f_{\text{dir}}(NO_3) = 1.6\times10^{-3}$ s$^{-1}$ (red line). Setting $N_2O_5$ loss to aerosol to zero ($f_{\text{het}} = 0$), we take the literature data for $k_{7a}$ and $k_{7b}$ and the water vapour concentration of $2.8\times10^{17}$ molecule cm$^{-3}$ to calculate a value of $f_{\text{homo}} = 2\times10^{-4}$ s$^{-1}$ for this period. As shown in Fig. 10 (black line), this value clearly overestimates the true contribution of indirect losses by at least a factor of 3–4. By separating the contributions to $f_{\text{homo}}$ from Reaction (R7a) and (R7b) we can show that the second term (quadratic in [H$_2$O]) dominated the homogeneous gas-phase loss of $N_2O_5$ during the whole campaign with the ratio $k_{7b}[H_2O]^2/k_{7a}[H_2O]$ equal to unity only at a low RH of $\approx 30\%$, but increasing to $\approx 2.5$ at RH = 100\%.

This analysis has thus far ignored loss of $N_2O_5$ (or NO$_3$) by dry deposition. Aldener et al. (2006) used a $N_2O_5$ deposition velocity ($V_{\text{dep}}$) of 1 cm s$^{-1}$ to calculate the contribution of dry deposition to the total loss of $N_2O_5$. This value was based on estimates for HNO$_3$ and is not necessarily accurate. Adopting the same value and assuming a boundary layer height of 100 m would result in a frequency for dry deposition of $N_2O_5$ of $1\times10^{-4}$ s$^{-1}$, which when multiplied by $k_2[NO_2]$ (usually close to 10) would result in a significant fraction of NO$_3$ loss throughout the campaign. There are however many uncertainties associated with this calculation as neither the true value of $V_{\text{dep}}$ nor the boundary layer height are known. In addition this calculation ignores the strong vertical stratification often seen in the nocturnal boundary layer (Brown et al., 2007). The true factor by which $k_7$ is overestimated is thus most probably larger than 3–4 as $N_2O_5$ loss by dry deposition would serve to increase it further. One caveat to this approach is
however the assumption that there is no correlation between NO$_2$ mixing ratios and the major sink process(es) for NO$_3$ and N$_2$O$_5$, which is difficult to prove. The result is however consistent with the conclusions of Brown et al. (2006, 2009), who used airborne measurements of NO$_3$ and N$_2$O$_5$ to indicate that $k_7$ may be up to a factor 10 smaller than derived from laboratory data.

The blue line in Fig. 10 is the slope expected for equivalent direct and indirect losses of NO$_3$ and indicates that, for this limited dataset, N$_2$O$_5$ destruction plays only a minor role in controlling the NO$_3$ lifetime. This conclusion is broadly consistent with other measurements at continental, forested sites in Germany, where NO$_3$ has been found to be removed mainly by reaction with monoterpenes emitted by coniferous trees (Geyer and Platt, 2002).

3.3 NO$_x$ partitioning and daytime versus night-time loss of NO$_x$

The conversion of NO$_2$ to NO$_3$ and N$_2$O$_5$ followed by reactive losses either with gas-phase species or with aerosols and other surfaces represents a conversion of gas-phase NO$_x$ traces gases to NO$_y$ in both gas and particle phases. Assuming that NO is absent, the fraction of NO$_x$, $F$(NO$_x$), which is present in reactive form at night can be simply expressed as:

$$F$(NO$_x$) = \frac{[NO_3] + 2[N_2O_5]}{[NO_3] + 2[N_2O_5] + [NO_2]} \tag{12}$$

The partitioning of NO$_x$ to NO$_3$ and N$_2$O$_5$ is favoured by large O$_3$ concentrations (which increase to NO$_2$ oxidation rate) and low losses of NO$_3$ and N$_2$O$_5$. Figure 11 displays the variation of $F$(NO$_x$) on the nights of 13th and 15th May. The amount of NO$_x$ partitioned as NO$_3$ and N$_2$O$_5$ is initially negligible as the NO$_3$ and N$_2$O$_5$ lifetimes are short. Only later do NO$_3$ and N$_2$O$_5$ reach appreciable concentrations, with $F$(NO$_x$) reaching a maximum value of $\approx$20% on the 13th and $\approx$15% on the 15th May. The slow build up to larger values of $F$(NO$_x$) is due to the small rate coefficient for NO$_2$ + O$_3$.
(≈2×10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \text{ K}) \text{ resulting in NO}_2 \text{ half lives in the order of hours at 70 ppb O}_3 \text{ and also due to a slow decline in reactivity of NO}_3 \text{ in the early part of the night. NO}_3 \text{ and N}_2\text{O}_5 \text{ remaining at the end of the night are rapidly converted photolytically/thermally back to NO}_2 \text{ at dawn, hence the rapid reduction in } F(\text{NO}_x) \text{ at circa 06:00 on the 14th. On this particular night the nocturnal mean value of } F(\text{NO}_x) \text{ was } \approx 9\%. The same value was obtained as average over all nights of the campaign on which there was no precipitation. The average value of } F(\text{NO}_x) \text{ was only } \approx 3\% \text{ on the night 15th–16th, presumably due to efficient loss of N}_2\text{O}_5 \text{ on aqueous surfaces. As the lifetimes of NO}_3 \text{ and N}_2\text{O}_5 \text{ were much shorter than the duration of the night, and only a small fraction of NO}_2 \text{ that has been converted to NO}_3 \text{ and N}_2\text{O}_5 \text{ is converted back to NO}_2 \text{ at dawn, we can assume that all NO}_2 \text{ which was oxidised by O}_3 \text{ at night represents an irreversible loss of NO}_x \text{ to either organic or inorganic nitrates. In this case, the loss rate of NO}_x \text{ (} L_{\text{NO}_x} \text{) is given by: }

\begin{equation}
L_{\text{NO}_x} \approx n \cdot k_1[\text{NO}_2][\text{O}_3]
\end{equation}

where the factor } n \text{ is 1 if NO}_3 \text{ is lost only directly (e.g. by reaction with VOC) and is 2 if NO}_3 \text{ is lost indirectly via N}_2\text{O}_5 \text{ formation and reaction as two NO}_2 \text{ are required to make each N}_2\text{O}_5 \text{ molecule. For the present campaign we have shown that NO}_3 \text{ is lost predominantly by direct routes, so that } n \text{ should be close to 1. Figure 12 shows the N}_2\text{O}_5 \text{ and NO}_2 \text{ mixing ratios over a two night period, for which average night-time values were 1.65 ppb NO}_2 \text{ with O}_3 \text{ close to 60 ppb. From Eq. (13), nocturnal loss of NO}_x \text{ proceeded at a rate of } \approx 250 \text{ ppt/h over these two nights. The daytime loss of NO}_x \text{ is dominated by reaction of NO}_2 \text{ with the OH radical }

\begin{equation}
\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3
\end{equation}

with the rate of loss of NO}_2 \text{ via this route approximately given by } k_8[\text{OH}][\text{NO}_2], \text{ which is also the production rate of HNO}_3. \text{ There appears to be only one set of measurements HNO}_3 \text{ mixing ratios at the Taunus Observatory, in which values of } \approx 0.1–1 \text{ ppb were reported in November of 1990 (Fuzzi et al., 1994).}
Using a value of $1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $k_8$ the average daytime NO$_2$ concentration of $\approx 3 \text{ ppb}$ for the 9th of May and assuming a daytime average OH concentration of $4 \times 10^6 \text{ molecule cm}^{-3}$, we calculate a loss rate of $\approx 400 \text{ ppt/hour}$. As no measurements of OH were made during the campaign, the value of $4 \times 10^6 \text{ molecule cm}^{-3}$ for the daytime average OH concentration was calculated using the parameterisation of (Ehhalt and Rohrer, 2000) with daily averaged values of $J_{O1D} (\approx 3 \times 10^{-5} \text{ s}^{-1})$ and $J_{NO_2}$ ($\approx 9 \times 10^{-3} \text{ s}^{-1}$) measured at the Feldberg at a similar time of year (June 1999) and under similar insolation (Handisides, 2001). The present measurements of relatively large O$_3$ mixing ratios and previous measurements of peroxy radical mixing ratios of several 10s of pptv in June in previous years at the site (Handisides, 2001) indicate an active photochemistry and imply that this OH concentration is reasonable. It is also consistent with daytime measurements of OH at another forested mountain site under very similar levels of insolation and with comparable levels of O$_3$ (Handisides et al., 2003).

The simple calculations above show that day- and night-time losses of NO$_x$ are similar. However, as the ratio of night-time to day-time losses depends on insolation at the site, night-time losses will be favoured still more in the colder months as O$_3$ photolysis and OH production rate drop significantly. The fact that the night-time boundary layer is shallower than in the daytime will however have the converse effect and favour daytime oxidation. We can conclude that night-time loss of NO$_x$ due to NO$_3$ (and N$_2$O$_5$) formation is at least comparable to daytime loss driven by OH at the Taunus Observatory, confirming speculation that nitrate driven acidity in cloud water at the Kleiner Feldberg could be caused either by HNO$_3$ or N$_2$O$_5$ uptake (Fuzzi et al., 1994).

Although no VOCs were measured during the campaign, the persistently high night-time mixing ratios of NO$_3$ indicate and important role for the oxidation of VOCs at the site. An average daytime OH concentrations of $\approx 4 \times 10^6 \text{ molecule cm}^{-3}$ and an average night-time mixing ratio of 10 pptv for NO$_3$ result in a concentration ratio that favours NO$_3$ by a factor of $\approx 60$. The ratios of rate coefficients ($k_{OH}/k_{NO_3}$) for reaction of OH and NO$_3$ with isoprene and several monoterpenes favour OH and may be calculated
from reviewed kinetic data (Atkinson and Arey, 2003) as: isoprene (147), α-pinene (8.5), limonene (13.4), sabinene (11.7). These numbers indicate that whereas NO$_3$ will contribute significantly to isoprene removal, it would dominate for the mono-terpenes listed above. The simple calculation does not take the diurnal changes in VOC emission rates mixing ratios into account and a more detailed understanding of the relative importance of daytime versus night-time removal of boundary layer NO$_x$ and the fate of reactive VOCs at this site would require diel measurements of both the major oxidants (OH and NO$_3$) and the VOCs.

4 Conclusions

A complete set of nocturnal nitrogen oxides, O$_3$ and aerosol surface area was measured for the first time at the Taunus Observatory. The measurements provided both a test of the new NO$_3$/N$_2$O$_5$ instrument and delivered valuable information concerning night-time oxidation at the site. Both NO$_3$ and N$_2$O$_5$ were present above the detection limits on all nights and the relative concentrations were in accord with the temperature, NO$_2$ and the equilibrium constant for N$_2$O$_5$ formation and thermal dissociation. The major sink of NO$_x$ was found to be direct loss of NO$_3$ by reaction with biogenic hydrocarbons and nocturnal chemistry at this site was shown to contribute significantly both to the conversion of NO$_x$ to NO$_y$ and likely to the oxidation of biogenic VOCs. A steady state analysis was used to estimate direct and indirect losses of NO$_3$ and N$_2$O$_5$ and revealed shortcomings in the laboratory derived kinetics of the reaction of N$_2$O$_5$ with water-vapour.

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References


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Nocturnal nitrogen oxides at a rural mountain-site

J. N. Crowley et al.


Fig. 1. Upper: Topographic map indicating the location of the Taunus Observatory at the summit of the Kleiner Feldberg (from PhD thesis of G. M. Handisides). Lower: Relation of site to local cites indicating predominant wind directions during the campaign.
Fig. 2. Two-channel NO₃/N₂O₅ Instrument. The sample inlet was a 1.4 m long Teflon coated glass tube (ID 104 mm). Gas was sampled from the centre of the tube to the NO₃/N₂O₅ and NO/NO₂/O₃ instruments. The NO₃ cavity was made of PFA tubing and fittings (thermal insulation not shown), the N₂O₅ + NO₃ cavity was made of Teflon (FEP) coated glass (heating elements and insulation not shown). NO = NO addition point for NO₃ titration. F = PFA filter folder with 2 µm PTFE filter. OI = optical isolator. BS = beam splitter (70% for NO₃ cavity, 30% for NO₃ + N₂O₅ channel). PMT = housing with photomultiplier and interference filter. M = Aluminium coated mirror. LD = Laser diode in temperature controlled housing. CLD = chemiluminescence instrument for NO, NO₂ and O₃.
Fig. 3. Trace gas and meteorological overview. Temperature, wind speed and relative humidity were taken measured by the German weather service. Global radiation and wind direction were measured by the Hessen environmental agency (HLUG) who also monitored O\textsubscript{3}. The HLUG O\textsubscript{3} values have been scaled by a factor 0.82 to bring them into line with the MPI measurements.
Fig. 4. Data from 12th–13th as exemplary night-time dataset. Great variability in the NO$_3$ and N$_2$O$_5$ mixing ratios is apparent. The approximate time of local sunrise and sunset may be obtained from the half-hourly measurements of global radiation at the site.
Fig. 5. Measured mixing ratios of NO\textsubscript{2}, (upper panel, red line) NO\textsubscript{3} (lower panel) and N\textsubscript{2}O\textsubscript{5} (centre). The calculated NO\textsubscript{2} mixing ratios (black line in upper panel with grey error bounds) used evaluated, temperature dependent values of $K_2$ (Sander et al., 2003).
Fig. 6. Determination of the equilibrium constant, $K_2$. The NO$_2$, N$_2$O$_5$ and NO$_3$ data used were gathered over a $\approx 3$ h period (01:00 to 03:00) on the 9th of May when the NO$_3$ level was above 7 ppt.
Fig. 7. Determination of the equilibrium constant, $K_2$, throughout the campaign plotted versus temperature. Data were selected so that NO$_3$ was always greater than 5 ppt. The red and blue solid lines are recommended values for $K_2$ from evaluations of laboratory data. The black line is taken from the analysis of (Osthoff et al., 2007), based on their field measurements. Different colours are data from different days. JPL2003 = (Sander et al., 2003), JPL2006 = (Sander et al., 2006), Osthoff2007 = (Osthoff et al., 2007).
Fig. 8. NO$_3$ turn-over lifetimes and production rates (red lines) for NO$_3$ on each night of the campaign.
Fig. 9. Measured NO$_3$ turnover loss frequencies (black datapoints) and calculated loss frequencies due to direct and indirect loss processes on two different nights. Grey line (upper panel only): Hypothetical (direct) loss of NO$_3$ due to reaction with VOC. Blue line: Indirect loss due to N$_2$O$_5$ uptake to aerosol ($r_{het}K_2$[NO$_2$]). Red line: Indirect loss due to reaction of N$_2$O$_5$ with water vapour ($r_{homo}K_2$[NO$_2$]).
Fig. 10. Separation of direct and indirect loss of NO$_3$ on the night 16th–17th of May. The red solid line is the fitted value indicating close to zero indirect loss of NO$_3$. The black line was obtained by setting heterogeneous N$_2$O$_5$ loss to zero and accounting only for reaction with water vapour. The blue line represents equivalency of the direct and indirect losses of NO$_3$ (intercept = slope = 1.6 x 10$^{-3}$ s$^{-1}$).
Fig. 11. Fraction of night-time NO\textsubscript{x} as NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} on two meteorologically distinct campaign nights. 13th–14th: warm preceding day and wind from the east. 15th–16th: Wind from the southeast accompanied by rain.
Fig. 12. Daytime versus night-time loss of NO$_x$. Night-time N$_2$O$_5$ (black lines) and day/night-time NO$_2$ (red line) on the 8th–10th of May.