Variable lifetimes and loss mechanisms for NO$_3$ and N$_2$O$_5$ during the DOMINO campaign: contrasts between marine, urban and continental air

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Abstract. Nighttime mixing ratios of boundary layer N$_2$O$_5$ were determined using cavity-ring-down spectroscopy during the DOMINO campaign in Southern Spain (Diel Oxidant Mechanisms In relation to Nitrogen Oxides, 21 November 2008–8 December 2008). N$_2$O$_5$ mixing ratios ranged from below the detection limit (∼5 ppt) to ∼500 ppt. A steady-state analysis constrained by measured mixing ratios of N$_2$O$_5$, NO$_3$ and O$_3$ was used to derive NO$_3$ lifetimes and compare them to calculated rates of loss via gas-phase and heterogeneous reactions of both NO$_3$ and N$_2$O$_5$. Three distinct types of air masses were encountered, which were largely marine (Atlantic), continental or urban-industrial in origin. NO$_3$ lifetimes were longest in the Atlantic sector (up to ∼30 min) but were very short (a few seconds) in polluted, air masses from the local city and petroleum-related industrial complex of Huelva. Air from the continental sector was an intermediate case. The high reactivity to NO$_3$ of the urban air mass was not accounted for by gas-phase and heterogeneous reactions, rates of which were constrained by measurements of NO, volatile organic species and aerosol surface area. In general, high NO$_2$ mixing ratios were associated with low NO$_3$ lifetimes, though heterogeneous processes (e.g. reaction of N$_2$O$_5$ on aerosol) were generally less important than direct gas-phase losses of NO$_3$. The presence of SO$_2$ at levels above ∼2 ppb in the urban air sector was always associated with very low N$_2$O$_5$ mixing ratios indicating either very short NO$_3$ lifetimes in the presence of combustion-related emissions or an important role for reduced sulphur species in urban, nighttime chemistry. High production rates coupled with low lifetimes of NO$_3$ imply an important contribution of nighttime chemistry to removal of both NO$_x$ and VOC.

1 Introduction

The photochemically driven, OH-initiated oxidation processes during the day are supplemented by (or, for several classes of volatile organic compounds (VOCs) such as terpenes or CH$_3$SCH$_3$, surpassed by) night-time reactions with the NO$_3$ radical (Wayne et al., 1991). The interaction of NO$_3$ with VOCs leads to the formation of organic peroxy radicals, and via secondary reactions to HO$_2$ and OH (Platt et al., 1990; Sommariva et al., 2009). NO$_3$ can thus initiate and propagate nocturnal radical chemistry linking HO$_2$ and NO$_x$ chemistry and significantly impacting on oxidation rates of several classes of atmospheric traces gases.

NO$_3$ is formed predominantly in the reaction of NO$_2$ with O$_3$ (Reaction R1) and is converted to N$_2$O$_5$ via further reaction with NO$_2$ (Reaction R2). The thermal decomposition of N$_2$O$_5$ links the concentrations of NO$_3$ and N$_2$O$_5$ via the equilibrium constant, $K_3$. Simultaneous measurements of NO$_3$ and N$_2$O$_5$ (Brown et al., 2003a; Crowley et al., 2010) confirm that (under most conditions) the timescales to acquire equilibrium are sufficiently short that the relative concentrations of NO$_3$ and N$_2$O$_5$ in the atmosphere are controlled only by the temperature and levels of NO$_2$.

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad (R1)$$
\[ \text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad (\text{R2}) \]
\[ \text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M} \quad (\text{R3}) \]

The impacts of \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\) on nighttime chemistry depend on their relative rates of loss via gas-phase and heterogeneous reactions. Whereas \(\text{NO}_3\) is lost mainly via gas-phase reactions with e.g. VOCs (see above), \(\text{N}_2\text{O}_5\) is removed predominantly by heterogeneous hydrolysis on aqueous aerosol, which can substantially modify the amount of reactive nitrogen available for daytime photochemistry. In the polluted boundary layer, this process influences the fate of \(\text{NO}_3\) emissions and their potential for photochemical ozone formation and also (via heterogeneous chemistry on sulfate particles) links \(\text{O}_3\) production rates to emissions of \(\text{SO}_2\) from e.g. power plants or shipping (Brown et al., 2006). It has recently been shown that heterogeneous reactions of \(\text{N}_2\text{O}_5\) with chloride containing particles can also represent a significant source of photo-labile chlorine (in the form of \(\text{ClNO}_2\) with chloride containing particles) links \(\text{O}_3\) production rates to emissions of \(\text{SO}_2\) from e.g. power plants or shipping (Brown et al., 2006).

The objectives of this study were to examine the roles and relative importance of gas phase and heterogeneous processing of \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\) in chemically distinct air masses: urban (strong anthropogenic influence), continental (mainly biogenic emissions) and maritime. In order to achieve these objectives the \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\) measurements were accompanied by instrumentation for trace gas and aerosol characterisation (see later).

### 1.1 \(\text{NO}_3\) lifetimes

The production rate of \(\text{NO}_3\) is given by \(k_1 [\text{NO}_2][\text{O}_3]\) (generally we write \(k_1\) as the rate coefficient for Reaction Ri) so that its stationary state turnover lifetime, \(\tau_{ss}(\text{NO}_3)\), can be calculated from observations of its concentration and those of \(\text{O}_3\) and \(\text{NO}_2\):

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

Whenever we use the term “\(\text{NO}_3\) lifetimes” in the manuscript, we refer to \(\tau_{ss}(\text{NO}_3)\).

\(\text{NO}_3\) can be removed directly from the air by e.g. reaction with organic trace gases (Wayne et al., 1991) or indirectly via removal of \(\text{N}_2\text{O}_5\) via e.g. heterogeneous loss to aqueous particles. As described previously (Geyer et al., 2001b; Aldener et al., 2006; Crowley et al., 2010) the contributions of direct and indirect losses of \(\text{NO}_3\) to its lifetime can, in principal, be evaluated if \(K_2\) (the equilibrium constant \(k_2/k_3\)) and \([\text{NO}_2]\) are known:

\[
\tau_{ss}(\text{NO}_3) \approx \frac{1}{f_{ss}(\text{NO}_3)} \quad (2)
\]

where \(f_{ss}(\text{NO}_3)\) is the overall loss frequency of \(\text{NO}_3\) from stationary state and is equal to

\[
\sum_i (k_i [X]_i) + 0.25\bar{c}\gamma(\text{NO}_3) A + f_{dd}(\text{NO}_3)
\]

\[
+ (0.25\bar{c}\gamma(\text{N}_2\text{O}_5) A + f_{dd}(\text{N}_2\text{O}_5) + f_{\text{H}_2\text{O}}K_2[\text{NO}_2])
\]

In this expression, \(k_i\) (\(\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\)) is the rate coefficient for reaction of \(\text{NO}_3\) with trace gas \(i\) at concentration \([X]_i\) (\(\text{molecule}\ \text{cm}^{-3}\)), \(A\) is the aerosol surface area density (\(\text{cm}^2\ \text{cm}^{-3}\)), \(\bar{c}\) (\(\text{cm}\ \text{s}^{-1}\)) is the mean molecular velocity of \(\text{NO}_3\) or \(\text{N}_2\text{O}_5\), \(\gamma(\text{NO}_3)\) and \(\gamma(\text{N}_2\text{O}_5)\) are the dimensionless uptake coefficients for irreversible reaction of \(\text{NO}_3\) or \(\text{N}_2\text{O}_5\) with aerosol, \(f_{dd}\) (\(\text{s}^{-1}\)) is the first-order rate constant for dry deposition of \(\text{NO}_3\) or \(\text{N}_2\text{O}_5\) and \(f_{\text{H}_2\text{O}}\) (\(\text{s}^{-1}\)) represents the homogeneous, gas-phase loss of \(\text{N}_2\text{O}_5\) via reaction with water vapour.

Recent measurements of long lifetimes of \(\text{N}_2\text{O}_5\) even in the presence of high relative humidity (Brown et al., 2009; Crowley et al., 2010) imply that \(f_{\text{H}_2\text{O}}\) is too small to be important under most conditions. The rate of uptake of a trace gas to airborne particles can be reduced by concentration gradients close to the particle surface, which requires modification of the simple expression for the heterogeneous loss rate, \(k_{\text{het}} = 0.25\bar{c}\gamma A\), as used in Eq. (2). The effective uptake coefficient (\(\gamma_{\text{effective}}\)) is approximated by (Fuchs and Sutugin, 1970):

\[
\frac{1}{\gamma_{\text{effective}}} = \frac{1}{\gamma} + 0.75 + 0.283 Kn
\]

\[
\frac{1}{Kn(Kn+1)} \quad (3)
\]

where \(Kn = \frac{3D_g}{r_{sw}^2}\), \(r_{sw}\) is the radius of the particle at the maximum of the surface area weighted size distribution, and \(D_g\) is the gas phase diffusion coefficient of \(\text{N}_2\text{O}_5\) or \(\text{NO}_3\) at the appropriate pressure and temperature. For \(\text{N}_2\text{O}_5\), \(D_g\) is 0.085 \(\text{cm}^2\ \text{s}^{-1}\) at atmospheric pressure and 298 K (Wagner et al., 2008). During the nights of the campaign, the dominant contribution to aerosol surface area was by particles with diameters of less than \(\sim 200\ \text{nm}\). In this case, only uptake coefficients close to unity require significant correction. For example, an uptake coefficient of \(\sim 0.1\) would be reduced by transport limitations to \(\sim 0.09\), whereas a \(\gamma\) of 1 would reduce to \(\sim 0.5\). A value of 0.5 is therefore the approximate maximum value of \(\gamma(\text{N}_2\text{O}_5)\) or \(\gamma(\text{NO}_3)\), which can be used to calculate \(\text{NO}_3\) lifetimes using Eq. (2). More realistic (lower) values of \(\gamma\), derived from laboratory and field experiments are discussed later. At low aerosol loading (or low values of \(\gamma\)) and negligible dry deposition the term (in Eq. 2) \((0.25\bar{c}\gamma(\text{N}_2\text{O}_5) A + f_{dd}(\text{N}_2\text{O}_5) + f_{\text{H}_2\text{O}}K_2[\text{NO}_2])\) becomes diminishingly small and \(\text{NO}_3\) lifetimes are largely independent of \(\text{NO}_2\) concentrations. On the other hand, if gas-phase losses of \(\text{NO}_3\) are slow, \(\text{N}_2\text{O}_5\) chemistry can be important and \(\text{NO}_3\) lifetimes will show a dependence on the inverse \(\text{NO}_2\) concentration (Heintz et al., 1996; Martinez et al., 2000; Geyer et al., 2001b; Brown et al., 2003a, b, 2009; Aldener et al., 2006).

Certain conditions must be fulfilled if Eq. (2) is used to examine \(\text{NO}_3\) lifetimes and draw conclusions regarding direct

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and indirect loss routes. Firstly, NO$_3$ production rates are governed by a slow reaction between NO$_2$ and O$_3$. Application of a stationary state analysis to NO$_3$ lifetimes is only suited to air-masses where the chemical lifetime of NO$_3$ (or N$_2$O$_5$) is sufficiently short that stationary state is achieved with the transport time from the emission region to the measurement site (Brown et al., 2003a).

Stationary state is formally achieved when the rate of change of NO$_3$ and N$_2$O$_5$ are zero, i.e. $d$NO$_3$/dt $= k_1$[NO$_2$] [O$_3$] + $k_2$[N$_2$O$_5$] - $k_3$[NO$_2$] [O$_3$] - $k_4$[NO$_3$] [NO$_3$] = 0 and $d$N$_2$O$_5$/dt $= k_2$[NO$_2$] [NO$_3$] - $k_3$ [N$_2$O$_5$] - $k_5$[N$_2$O$_5$] = 0, where $k_1$[NO$_3$] and $k_5$[N$_2$O$_5$] are summed first order loss rate constants for any reactions involving NO$_3$ and N$_2$O$_5$. The approximate time to achieve stationary state thus depends on the production and loss rates of both NO$_3$ and N$_2$O$_5$ and is longer at high NO$_2$ mixing ratio and low temperatures.

Time dependent values of $d$NO$_3$/dt and $d$N$_2$O$_5$/dt were determined for an unfavourable case (i.e. high NO$_2$ mixing ratio of 10 ppb) by numerical simulation in a manner similar to that described previously (Brown et al., 2003a). The low N$_2$O$_5$ and NO$_3$ concentrations observed (implying short lifetimes) meant that stationary state was achieved within 1–2 h after dusk and within the time of transport from the major source of NO$_x$ (e.g. Huelva).

Equation (2) has been used to derive the direct and indirect contributions to NO$_3$ loss rates (Brown et al., 2009; Crowley et al., 2010) via the dependence of the observed lifetime on NO$_2$ mixing ratios. This approach will however break down if the trace gases which react directly with NO$_3$ are correlated (e.g. have the same chemical source or spatial distribution of emissions) with NO$_2$. This is unlikely to apply to regions where NO$_3$ losses are dominated by e.g. reaction with biogenic volatile organic compounds (BVOC) in clean air masses, but might be the case where NO$_3$ reacts with traces gases resulting from combustion processes in which NO$_2$ is also generated. In a similar vein, if aerosol surface area also co-varies with NO$_2$, use of Eq. (2) to separate the contributions of homogeneous and heterogeneous loss rates of N$_2$O$_5$ to the NO$_3$ lifetime is not possible.

2 Site description

The DOMINO campaign (Diel Oxidant Mechanisms In relation to Nitrogen Oxides, (21 November 2008–8 December 2008) took place at the Atmospheric Sounding Station (Base de Arenosillo), 37°05′58″N, 6°44′17″W) located on the Atlantic coast of the southern Spanish region of Moguer (Fig. 1). Measurements were conducted in a forested area (mainly Stone pines, Pinus pinea ∼5–10 m in height) with proximity to both extensive pollution sources and the Atlantic Ocean (the Atlantic coast was ∼300 m distant and ∼20 m lower) so that the chemical composition of air masses arriving at the site was highly dependent on wind direction. On-site wind directions between 290 and 340 degrees indicated that air masses had recently passed over the expansive industrial centre and port of Huelva (henceforth referred to as the “Huelva” sector) which was located about 30 km away, or with typical night-time winds-speeds of 8–18 km h$^{-1}$ about 2–3 h upwind. Huelva houses one of Europe’s larger oil refineries and pollution from this sector includes emissions from related industrial/shipping activity. Air from the Huelva sector arriving at the measurement site at night was frequently and strongly malodorous. Air arriving from the 150–270 degrees sector passed over the Atlantic (sector “Atlantic”) and generally contained low levels of NO$_x$. NO$_2$ plumes were occasionally observed in this sector, which were usually accompanied by enhanced levels of SO$_2$ indicating emissions from passing ships.

Wind directions between 0 and 45 degrees (sector “continental”) were from mainland Spain and passed no large cities for several hours prior to arrival at the site. Air arriving from Sevilla (∼60 degrees), following Huelva, the next largest potential source of pollutants, was rarely encountered during the night. Overall, during the nights of the campaign, the air arrived predominantly from the Huelva (∼50%) or continental sectors (∼35%), with air from the Atlantic sector (∼15%) encountered less frequently. Air mass back-trajectories calculated using HYSPLIT with GDAS meteorology (Draxler and Rolph, 2011) confirmed the allocation

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1El Arenosillo is a platform of the Atmospheric Research and Instrumentation Branch of the Spanish National Institute for Aerospace Technology (INTA) dedicated to atmospheric measurements in the Southwest of Spain.
of source region sector according to local wind directions. Figure 1 displays selected back-trajectories for air arriving at midnight from the Huelva sector (1), the continental sector (2) and the Atlantic sector (3).

3 Methods

3.1 NO$_3$ and N$_2$O$_5$

NO$_3$ and N$_2$O$_5$ mixing ratios were measured using a two-channel, off axis cavity-ring-down system (OA-CRD), which has recently been described in detail (Schuster et al., 2009; Crowley et al., 2010) and also by long-path, differential optical absorption spectroscopy (LP-DOAS). In the CRD instrument, one channel monitors NO$_3$ directly, the other is used to monitor the sum of NO$_3$ and N$_2$O$_5$ via thermal dissociation of N$_2$O$_5$. The instrument was located in the upper container of a two-container stack and sampled air through a few meters of 1/4 or 1/2" PFA-tubing with the inlet sampling from a height of between 7 and 12 m above ground level (~1–5 m above the closest canopy).

The 1/2” inlet was operated with a large bypass flow to reduce the residence time. A 2 μm pore Teflon filter (replaced every hour) in a PFA filter holder was located at the end of the inlet outside the container. The losses of NO$_3$ and N$_2$O$_5$ to the filter (15 ± 3 % and <2 %, respectively) were characterised prior to and after the campaign. Loss rates in the Teflon coated (DuPont, FEP) glass cavities were also measured during the campaign. Operational pressures and flows resulted in residence times in the inlet lines and cavities of between 0.6 and 1 s. CRD noise-levels changed during the campaign and varied between ~3 and 7 pptv for N$_2$O$_5$ and between 2 and 5 pptv for NO$_3$ (both with 5 s integration per datapoint). The detection limit is partly defined by accuracy of the chemical zero (measured by adding NO as described in detail previously (Schuster et al., 2009) and was between 2 and 3 pptv for NO$_3$ and 5–7 pptv for N$_2$O$_5$ (both assuming zero losses in the inlet tubing). However, NO$_3$ was not observed directly during the campaign even when N$_2$O$_5$ levels of several hundred pptv were present. As NO$_2$ levels were not sufficiently high and temperatures (controlling K$_2$) not sufficiently low to reduce NO$_3$ to below the detection limit, this indicates deviation of the NO$_2$-NO$_3$-N$_2$O$_5$ chemistry from equilibrium. With night-time temperatures occasionally as high as 15 °C, equilibrium should be established within in a few minutes, suggesting that any processes that rapidly drain NO$_3$ from equilibrium must be very local otherwise N$_2$O$_5$ would also have been completely removed.

A potential cause of dis-equilibrium between NO$_2$, O$_3$ and N$_2$O$_5$ is the loss of NO$_3$ in the PFA inlet. This had not been anticipated as it was not encountered on a previous campaign at a rural location (Crowley et al., 2010) in which a similar sampling strategy (long PFA line with 1 s residence time) had been periodically deployed in place of the normally used, FEP-coated high-volume flow glass sampling line. Use of new inlet lines did not result in observation of NO$_3$, even temporarily. On several occasions during the campaign a calibration source of NO$_3$ was added to the inlet to measure its transmission and also that of the NO$_3$ cavity. NO$_3$ was generated by the thermal decomposition (~90 °C) of N$_2$O$_5$, itself made by mixing NO$_2$ and O$_3$ in a blackened, FEP-coated glass reaction vessel as described previously (Schuster et al., 2009). Prior to heating, the mixture typically contained approximately 200–400 pptv N$_2$O$_5$, 150 ppbv O$_3$ and 5 ppbv NO$_2$. The results were rather surprising as the initial transmission of the inlet tubing to NO$_3$ was very low (on occasions less than 20 %) even if it was relatively fresh. The transmission increased with exposure to the O$_3$. NO$_2$, NO$_3$ mixture to a value (circa 70–80 %) commensurate with known loss rates of NO$_3$ in PFA tubing. This condition sometimes took as long as an hour to achieve. At the same time, loss rates of NO$_3$ in the cold cavity were recorded as high as 1 s$^{-1}$, a factor 5 larger than observed in the laboratory, whereas loss in the hot cavity (i.e. the N$_2$O$_5$ + NO$_3$ channel) proceeded at the usual rate (~0.2 s$^{-1}$). These observations indicate that the PFA tubing rapidly became reactive to NO$_3$ when exposed to the air and this reactivity could be reduced by extended passivation with high NO$_3$/O$_3$ concentrations or by heating to 90 °C. Post-campaign tests of the inlets used also revealed high (initial) reactivity to NO$_3$.

Assuming that the loss of NO$_3$ occurred in our inlet, it took place on a timescale (1 s) which is considerably shorter than the thermal lifetime of N$_2$O$_5$ (minutes), so that the N$_2$O$_5$ mixing ratios would not have been significantly affected. In this case we can calculate NO$_3$ ambient mixing ratios from the measured N$_2$O$_5$ and NO$_2$ and the equilibrium constant, K$_2$ via (Eq. 4).

$$[\text{NO}_3] = \frac{[\text{N}_2\text{O}_5]}{K_2[\text{NO}_2]}$$

As the inlet tubing was protected with a Teflon filter we do not anticipate large losses of N$_2$O$_5$ due to coating of the wall with aerosol. The disadvantage with this indirect calculation of NO$_3$ is that it relies on high quality (accurate, low noise), and preferably high time resolution NO$_2$ measurements. Some uncertainty is also associated with K$_2$, though recent field measurements of NO$_2$, NO$_3$ and N$_2$O$_5$ suggest that this is not more than 20 % (Osthoff et al., 2007; Crowley et al., 2010). The uncertainty in NO$_3$ mixing ratios calculated this way is thus considerably larger than via direct measurements and are estimated as about 35 % if N$_2$O$_5 < 7$ ppt. At lower levels of N$_2$O$_5$ the uncertainty in N$_2$O$_5$ (~40 % at 5 ppt) dominates. Long-path differential optical absorption spectroscopy (LP-DOAS, see below) measurements of NO$_3$ taken at a similar height to the CRD inlet are however in good agreement with the CRD-NO$_3$ mixing ratios derived from N$_2$O$_5$ and NO$_2$. 

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The LP-DOAS instrument applies the set-up from Merten et al. (2011) with a configuration described in Pöhler et al. (2010). It uses a telescope of 1.5 m focal length a 100 or 200 µm fibre bundle a 75 W XBO xenon arc lamp (Osram) and for spectral analysis an Acton 300i spectrometer with Roper Scientific CCD camera (Spec-10:2KBUV). The instrument was located at 9 m above the ground about 800 m north of the main sampling point. It was operated with three sets of retro-reflectors mounted on a tower at 20, 35 and 70 m above the ground at a distance of 4.8 km to the east, resulting in a total optical path-length of 9.6 km. The data analysis of NO\textsubscript{3} was performed in the spectral range from 615.0 nm to 673.8 nm with a gap between 644.1 nm to 657.8 nm to avoid strong water absorption lines. The reference spectra used were: NO\textsubscript{3} (Yokelson et al., 1994), NO\textsubscript{2} (Vandaele et al., 1998), O\textsubscript{3} (Voigt et al., 2001), H\textsubscript{2}O (Hitran 2006 from Gordon et al., 2007) and additionally a recorded spectrum at noon to correct for most H\textsubscript{2}O absorption, a background spectrum and a 3rd order polynomial. The standard deviation \( \sigma \) of the measurements was estimated according to Stutz and Platt (1996) and resulted in an average uncertainty for the NO\textsubscript{3} mixing ratio of 1 ppt. In this work we use data at from the lowest retro reflector only in order to compare with the CRD measurements.

### 3.2 NO\textsubscript{2} and NO

NO and NO\textsubscript{2} measurements were made with a modified commercial chemiluminescence detector (CLD 790 SR) originally manufactured by ECO Physics (Duernten, Switzerland). The quantitative detection of NO\textsubscript{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). The detection limits for the NO and NO\textsubscript{2} measurements were 6 pptv and 8 ppt, respectively for an integration period of 1 s. The total uncertainties for the measurements of NO, NO\textsubscript{2} were determined both to be 10 %, based on the reproducibility of in-field background measurements, calibrations, the uncertainties of the standards and the conversion efficiency of the photolytic converter. The drift in instrument zero was less than \( \sim 2 \) ppt over the duration of one night. The same device was described in more detail recently (Crowley et al., 2010).

### 3.3 O\textsubscript{3}, SO\textsubscript{2} and H\textsubscript{2}O

O\textsubscript{3} and SO\textsubscript{2} (Airpointer, Recordum GmbH) and H\textsubscript{2}O (LICOR 840 gas analyser, LI-COR, Inc.) were measured using instrumentation onboard the MoLa mobile platform (Diesch et al., 2011). Limits of detection and precision were 0.5 ppb and 1 ppb for both SO\textsubscript{2} and O\textsubscript{3}, 0.4 ppb and 1 ppb for NO\textsubscript{X}. Whilst Airpointer measurements of NO and NO\textsubscript{2} mirrored the trends seen using the ECO Physics device described above, they were not sufficiently accurate (especially at low NO\textsubscript{X} levels) to perform NO\textsubscript{3} lifetime analyses.

### 3.4 Volatile organic compounds

A commercially available instrument (AERO Laser model AL 4021, Germany) was used for in-situ HCHO measurements. This instrument is based on the Hantzsch reagent method, following the design described in Kelly and Fortune (1994). The time resolution is 160 s. Detection limit and precision were estimated from the 1\( \sigma \)-reproducibility of in-situ zero and calibration gas measurements as 22 pptv and \( \pm 15 \) %, respectively. The total uncertainty is estimated to be 29 %. An on-line sampling Thermal Desorption-Gas Chromatograph-Mass Spectrometer (TD-GC-MS) measurement system was used for the in-situ observation of anthropogenic VOCs such as ethylbenzene, and all xylene isomers as well as biogenic species such as isoprene and monoterpenes (Song et al., 2011). C\textsubscript{1}–C\textsubscript{4} alkenes and alkanes were not measured.

### 3.5 Aerosol measurements

Particle size information was obtained using MoLa instruments (see above). A Fast Mobility Particle Sizer (FMPS 3091, TSI, Inc.), 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 µm. The chemical composition of the non-refractory aerosol in the sub-micron range was measured by means of a High-Resolution-Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Res., Inc.). The soot (black carbon) concentration in PM\textsubscript{1} was determined by a Multi Angle Absorption Photometer (MAAP, Thermo E.C.). The aerosol surface area (ASA) used for calculating rates of trace gas uptake was calculated only from the FMPS dataset as, for most nights (including those examined in detail later), this contributed \( \geq 80 \) % of the total aerosol surface area and (in contrast to super-micron particles) was of known composition.

### 3.6 Meteorological parameters

Wind direction and speed, temperature and pressure and relative humidity and rain intensity at approximate inlet height were provided by MoLa instrumentation (WXT 510 weather station, Vaisala). Temperatures and wind directions were also available at heights of 25, 50 and 100 m from a local meteorological tower operated by INTA.

Several cloudless nights gave rise to a strong temperature inversion, with temperatures at a height of 100 m up to 5–6 °C warmer than those measured at the inlet height (\( \sim 10 \) m). This inversion would have lead to a very stable nocturnal boundary layer with efficient accumulation of low altitude emissions from e.g. the Huelva industrial area.
4 Measurements and discussion

Measurements of \( \text{N}_2\text{O}_5 \) and \( \text{NO}_3 \) were made on all campaign nights with the exception of 28–29 November. \( \text{N}_2\text{O}_5 \) was observed on most nights, though it was never present above the detection limit throughout the night but rather appeared in bursts of a few hours duration, reflecting differences in production and loss rates with changes in air-mass origin and/or local emissions. The observed mixing ratios of \( \text{N}_2\text{O}_5 \) are plotted for each night of the campaign in Fig. 2. As described above, \( \text{NO}_3 \) could not be detected directly using CRD but its mixing ratio was calculated from those of \( \text{N}_2\text{O}_5 \) and \( \text{NO}_2 \) and the equilibrium constant, \( K_2 \). The \( \text{NO}_3 \) data are generally in good agreement with DOAS measurements considering the differences in location and heights of inlet (CRD) and optical path (LP-DOAS).

As shown in Reactions (R1–R2), the production rates of \( \text{NO}_2 \) and \( \text{N}_2\text{O}_5 \) are governed by the \( \text{NO}_2 \) and \( \text{O}_3 \) mixing ratios. During the DOMINO campaign, night-time mixing ratios of \( \text{NO}_2 \) were highly variable, fluctuating from local background levels of \( \sim 1 \text{ ppb} \) to more than \( 15 \text{ ppb} \). The highest levels of \( \text{NO}_2 \) were associated with air masses that had passed over the Huelva sector, often arriving in plumes with a duration of about 1–2 h. Sub-ppbv levels of \( \text{NO}_2 \) were usually associated with the Atlantic sector. Apart from infrequent \( \text{NO} \) spikes presumably from traffic using local roads, night-time levels of \( \text{NO} \) were low. They were however, occasionally non-zero and on some nights 5–10 pptv of \( \text{NO} \) was present for a prolonged duration. Given that the lifetime of \( \text{NO} \) in the presence of \( > 15 \text{ ppbv} \) \( \text{O}_3 \) is only a few minutes, the presence of \( \text{NO} \) implies a local source. Indeed, with an average night-time wind-speeds of just \( 2.8 \text{ m s}^{-1} \) this implies a source located within about 500 m of the inlet. Possible sources of \( \text{NO} \) are emissions from the surrounding woodland soil. Apart from occasional plumes from Huelva, non-zero levels of \( \text{NO} \) were not associated with any single wind-direction which argues against a local, continuous point emission source (i.e. instrument exhaust-line).

Night-time \( \text{O}_3 \) was strongly anti-correlated with \( \text{NO}_2 \) and thus also showed significant variability, with typical levels of 15–40 ppbv. Air masses passing over the Huelva and coastal region (and sometimes the open ocean) often contained \( \text{SO}_2 \), with maximum levels of \( \sim 40 \text{ ppbv} \) in plumes originating from the port or Huelva areas. The \( \text{SO}_2 \) plumes were always associated with high levels of \( \text{NO}_2 \) with a similar temporal profile, indicating a common process as source. This might have been the result of petrochemical industry activity as flaring at the petrochemical complex in Huelva was frequently visible at night. A further possible source of \( \text{SO}_2 \) was ship emissions, either at sea or entering the harbour at Huelva. Note that the strait of Gibraltar (\( \sim 160 \text{ km} \) distant) is one of the world’s busiest shipping lanes. \( \text{SO}_2 \) was not observed above the limit of detection from the continental sector. We note that the presence of both \( \text{SO}_2 \) and \( \text{NO}_2 \) in a plume nearly always meant low levels or non-detection of \( \text{N}_2\text{O}_5 \), despite high \( \text{NO}_3 \) production rates. We discuss this particular aspect of \( \text{NO}_3/\text{N}_2\text{O}_5 \) chemistry in more detail later when analysing individual days.

Particles measured at the site displayed number size distributions with mode diameters of between 40 and 80 nm with a generally dominant organic fraction but with a significant sulphate component with short term increases that correlated with \( \text{SO}_2 \) plumes. The ammonium to sulphate mole ratio was always less than unity during the campaign, indicating that the aerosol was acidic (ratio of 2 = neutral aerosol).

4.1 \( \text{NO}_3 \) lifetimes

Despite large \( \text{NO}_3 \) production rates \( \text{N}_2\text{O}_5 \) was only sporadically observed, indicating reactive air-masses and short \( \text{NO}_3 \) or \( \text{N}_2\text{O}_5 \) lifetimes. More than 50 % of the campaign data revealed \( \text{NO}_3 \) lifetimes of less than 1 min, with lifetimes longer than 15 min representing only 0.5 % of the measurements. \( \text{NO}_3 \) lifetimes were found to be strongly dependent on wind direction, with the largest values measured in air masses originating from the Atlantic sector and the shortest lifetimes when air arrived from Huelva, with continental air an intermediate case. This is illustrated in Fig. 3.

During the campaign, \( \text{NO}_3 \) lifetimes were seen to be reduced at high \( \text{NO}_2 \) mixing ratios. Frequently, this is taken to be indicative of indirect losses of \( \text{NO}_3 \) (i.e. \( \text{N}_2\text{O}_5 \) driven, heterogeneous reactions). However, the \( \text{NO}_2 \) mixing ratio was also correlated with the available surface area, so that separation of the \( \text{NO}_3 \) losses into direct and indirect reactions (see Eq. 2) is problematic.

Below, we analyse three nights of the campaign in some detail, attempting to identify and quantify the various direct and indirect processes controlling \( \text{NO}_3 \) lifetimes. Each night represents a different air mass origin, covering each of the Atlantic, Huelva and continental sectors.

4.1.1 6–7 December: clean air from the Atlantic sector

Local wind directions indicated that air masses encountered during the latter part of the night spanning the 6–7 December arrived from the Atlantic sector. Back trajectories (Fig. 1) confirmed that the air had spent at least 3 days over the Atlantic Ocean prior to arriving at the site.

Selected trace gas and aerosol measurements, meteorological data and calculated \( \text{NO}_3 \) lifetimes are plotted in Fig. 4. After 02:30, \( \text{O}_3 \) levels were between 25 and 35 ppb, with \( \text{NO}_2 \) close to 1 ppbv, resulting in comparatively low \( \text{NO}_3 \) production rates (\( \sim 2 \times 10^{-2} \text{ ppt s}^{-1} \)). On this night, \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) measurements started only at 01:45 on the 7th due to instrument tests. \( \text{N}_2\text{O}_5 \) was observed at levels up to \( \sim 50 \text{ pptv} \) with \( \text{NO}_3 \) lifetimes (calculated via Eq. 1) occasionally greater than 30 min. These represent the longest \( \text{NO}_3 \) lifetimes encountered during the campaign and are consistent with observations of extended \( \text{NO}_3 \) lifetimes in marine air at low \( \text{NO}_4 \) mixing ratios (Heintz et al., 1996; Carslaw et al.,...
Fig. 2. Campaign overview of measured N$_2$O$_5$, NO$_2$ and O$_3$ mixing ratios, aerosol surface area (ASA), temperature, relative humidity (RH) and calculated CRD-NO$_3$ mixing ratios (in red). The black NO$_3$ datapoints are LP-DOAS measurements. x-axis ticks are at midnight.

Prior to this time. Similarly, NO$_3$ lifetimes decreased more or less constantly from 04:30 until dawn. In both cases the short NO$_3$ lifetime was accompanied by non-zero NO mixing ratios and enhanced NO$_2$ levels. Prior to 02:30 somewhat reduced O$_3$ mixing ratios were observed along with elevated levels of SO$_2$ (2–3 ppbv) and a ∼20 pptv spike in the NO mixing ratio at 02:00, indicating some influence of local emissions. A rough estimate (ignoring dilution) of the age of the NO/NO$_2$ plume of ∼350 s could be estimated from the enhancement in the NO$_2$ mixing ratio (∼700 pptv), the NO and O$_3$ mixing ratios and rate constant for their mutual reaction. The observation of a decrease in a biogenic trace gas (pinene) from 10–20 pptv before 02:30 to 2–3 pptv after 02:30 supports a change in air-mass origin at this time. An increase in NO after 04:30 indicated weak local emissions. The cleanest, maritime air was thus sampled between ∼02:30 and 04:30 on this night.

Three rapid increases in the N$_2$O$_5$ mixing ratio (and τ NO$_3$) at 02:48, 03:20 and 04:06 are apparent in Fig. 4. These features correlate with small increases (less than 1 °C) in the temperature and indicate an influx of air from higher (warmer) layers within the nocturnal inversion, which were less impacted by ground level emissions of e.g. NO or other reactive trace gases. This is a strong indication of large gradients in NO$_3$ (and N$_2$O$_5$) at the site, which were corroborated by DOAS measurements of NO$_3$ at three different levels (Thieser et al., 2011).

Fig. 3. Wind-direction dependence of NO$_3$ lifetimes (nighttime only). ∼50% of the airmasses encountered at night came from the Huelva sector, and were associated with very short NO$_3$ lifetimes.

1997a, b; Allan et al., 2000). The CRD (calculated) and LP-DOAS derived NO$_3$ mixing ratios were in good agreement for most of the night. N$_2$O$_5$ was, however, not observed before ∼02:30 and its calculated lifetime was less than ∼100 s
In order to understand the factors which limit the NO$_3$ lifetimes during this night we first estimate the contribution of each constrained loss process for NO$_3$ and N$_2$O$_5$ to see if the summed loss (in the case of N$_2$O$_5$ scaled by $K_2[NO_2]$, see Eq. 2) is consistent with observations. Figure 5 reveals that the lifetime of NO$_3$ was dependent on NO$_2$ mixing ratios, with the largest lifetimes associated with low NO$_2$ mixing ratios. Such observations are frequently taken as evidence for}

**Loss of N$_2$O$_5$ to aerosols**

The uptake coefficient for hydrolysis of N$_2$O$_5$ on aqueous, sulphate containing, tropospheric aerosol has been measured using laboratory surrogate aerosol (Mozurkewich and Calvert, 1988; Hu and Abbatt, 1997; Kane et al., 2001; Folkers et al., 2003; Badger et al., 2006; Griffiths and Cox, 2009) and a value of $\gamma \sim 0.04$ at high relative humidity has been recommended (IUPAC, 2010). This is consistent with the largest values of $\gamma$ derived from calculations using field observations of NO$_3$ and N$_2$O$_5$ (Allan et al., 1999; Aldener et al., 2006; Ambrose et al., 2007; Bertram et al., 2009; Brown et al., 2009). Both laboratory and field work indicate that N$_2$O$_5$ uptake coefficients can be significantly lower in the presence of organic components or nitrate, although the presence of chloride can offset the nitrate effect (see e.g. Mentel et al., 1999; Anttila et al., 2006; Bertram and Thornton, 2009; Griffiths et al., 2009; Riemer et al., 2009). Riemer et al. (2009) showed that the uptake coefficient of N$_2$O$_5$ on a pure inorganic aerosol depended on the sulphate to nitrate ratio with maximum values of $\gamma(N_2O_5) = 0.02$ on pure sulphate, which reduced to $\sim 0.01$ when the sulphate and nitrate masses were equivalent. Bertram et al. (2009) measured N$_2$O$_5$ reactivity on ambient aerosol and found for one air sample a maximum value of $\gamma$ between 0.03 and 0.04 when the ratio of organic-to-sulphate particle mass was $\sim 2.5$. This decreased to 0.01 with an organic-to-sulphate ratio of 10. Bertram and Thornton (2009) also describe the particle water molarity dependence of $\gamma(N_2O_5)$ on the uptake of N$_2$O$_5$ to NH$_4$HSO$_4$ aerosol. Maximum values of $\gamma(N_2O_5) = 0.03$ were found when the H$_2$O molarity was 20 or greater, but which decreased rapidly below this threshold. Given that the organic mass fraction of the particles was frequently above 50 % before 04:30, lower values of $\gamma$ than 0.03 will apply irrespective of the nitrate content. Not only the organic mass fraction of the aerosol but also the oxidation state of the condensed organic species influences the rates of uptake of both N$_2$O$_5$ and NO$_3$, either indirectly via the water fraction of the aerosol (N$_2$O$_5$) or directly via the number of double bonds available for NO$_3$ to react with.

During the night 6–7 December the total aerosol surface area was low, consistent with relatively clean maritime air masses, with maximum values of about 90 µm$^2$ cm$^{-3}$ at the beginning of the NO$_3$/N$_2$O$_5$ measurements and decreasing to $\sim 30$ µm$^2$ cm$^{-3}$ at the end of the night.
The organic-to-sulphate ratio was ∼4 until 04:00 when it started decreasing to a value of ∼0.3 to 0.4 clearly indicating a change in air mass to a more marine one at this time. The sulphate to (sulphate + nitrate) ratio was between ∼0.6 and 0.9. The RH was above 90% all the time so that, late in the night, with high sulphate content and high RH, aqueous aerosol should support a large uptake coefficient, i.e. up to a maximum value of ∼0.04.

The total NO₃ loss rate, \( f_{ss}(\text{NO}_3) \), calculated using an uptake coefficient of 0.04 for the entire night is displayed in Fig. 6 where various contributors are compared. For most of the night, the low aerosol surface areas meant that N₂O₅ uptake to aerosol (R₉₂O₅ASA) accounted for only a few percent to \( f_{ss}(\text{NO}_3) \) with the exception of periods where the NO₃ lifetime was longest. For example, at 02:00–10% of the calculated total loss was due to heterogeneous processing of N₂O₅. When we consider that, especially during the early stages of the measurement, the aerosol had a dominant organic component a lower value than 0.04 for γ would be more realistic, which would further decrease the contribution of N₂O₅ loss. From 04:00 onwards, the contribution of N₂O₅ uptake to \( f_{ss}(\text{NO}_3) \) diminished as the NO₃ mixing ratio decreased (shifting the NO₃/N₂O₅ equilibrium towards NO₃). At ∼06:00 less than 5% of the measured loss frequency of NO₃ was due to N₂O₅ losses.

**Reaction of N₂O₅ with water vapour**

Laboratory experiments (Wahner et al., 1998) have provided evidence for a slow reaction between N₂O₅ and H₂O, which, under certain circumstances, (e.g., low aerosol loading) can contribute to the loss of N₂O₅.

\[
\text{N}_2\text{O}_5 + n\text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + (n - 1)\text{H}_2\text{O}
\]  

(R4)

The reaction was found to proceed with terms both linear and quadratic in [H₂O] so that the loss rate coefficient \( k_{\text{H}_2\text{O}} \) is described by \( k_{\text{H}_2\text{O}} = 2.5 \times 10^{-22} \text{[H}_2\text{O]} + 1.8 \times 10^{-39} \text{[H}_2\text{O}]^2 \text{s}^{-1} \). Measurements of long N₂O₅ lifetimes at high relatively humidity (Brown et al., 2009) strongly suggest that the true value may be a factor 10 lower. We therefore assess the impact of this reaction on NO₃ lifetimes using 0.1 \( k_{\text{H}_2\text{O}} \). This is displayed as Rwater of Fig. 6. At rates of \( <1 \times 10^{-4} \text{s}^{-1} \), reaction with H₂O has an insignificant impact on the overall loss rate of N₂O₅ (or NO₃) throughout the entire night.

**Dry deposition of N₂O₅**

Assuming neutral stratification and zero surface resistance (Geyer et al., 2001a) calculated an upper limit to the N₂O₅ loss frequency due to dry deposition within a 100 m high nocturnal boundary layer as \( 0.3 \times 10^{-4} \text{s}^{-1} \). When multiplied by \( K_2[\text{NO}_2] \), this results in a loss rate constant for NO₃ of \( <1 \times 10^{-4} \text{s}^{-1} \), contributing insignificantly to the NO₃ lifetime (Rdd N₂O₅ Fig. 6). Assuming a factor two lower (or higher) boundary layer would not alter this conclusion.

**Gas-phase reactions of NO₃**

Known reaction partners for NO₃, which were constrained by measurements were NO, α-pinene, isoprene and HCHO. The reactions of NO₃ with both NO and α-pinene have large rate coefficients \( k_5 = 2.6 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) whereas HCHO reacts much more slowly \( k_6 = 5.6 \times 10^{-16} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \). Isoprene is an intermediate case with \( k_7 = 7 \times 10^{-13} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) (Atkinson et al., 2004, 2006). At mixing ratios of less than 1 ppbv on this night HCHO did not contribute significantly to NO3 removal and is not further considered. Likewise, isoprene mixing ratios on this night were less than those of α-pinene and limonene and as isoprene reacts a factor ∼10 slower than α-pinene or limonene with NO₃, we do not need to consider Reaction (R7).

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

(R5)

\[
\text{NO}_3 + \alpha - \text{pinene} \rightarrow \text{products}
\]  

(R6)

\[
\text{NO}_3 + \text{isoprene} \rightarrow \text{products}
\]  

(R7)

\[
\text{NO}_3 + \text{limonene} \rightarrow \text{products}
\]  

(R8)

\[
\text{NO}_3 + \text{HCHO} \rightarrow \text{HNO}_3 + \text{HCO}
\]  

(R9)

The calculated, steady state, turnover loss rates of NO₃ for reaction with NO (RNO), α-pinene (Rpinene) and limonene (Rlimo) are illustrated in Fig. 6. Loss of NO₃ due to reaction...
with α-pinene and limonene was slow, reflecting the low concentrations and emission rates of biogenic trace gases during late autumn at this site (Song et al., 2011), but still significant in the early part of the night, where its contribution easily exceeds that of heterogeneous losses. The reaction with NO is unimportant until ~04:00 but thereafter becomes the dominant NO3 sink for the rest of the night and even at mixing ratios of just 5 pptv can account for the entire observed NO3 loss until ~06:00. After 06:00, the reaction of NO accounts for ~30% of the observed NO3 loss rate. Note that fine structure on the NO3 loss rate due to Reaction (R5) (RNO) is due to noise as the measurements were made close to the NO detection limit.

**Loss of NO3 to aerosols and via dry deposition**

Laboratory experiments have characterised the efficiency of uptake of NO3 to various environmental surfaces. Whereas the low solubility of NO3 in water leads to low uptake coefficients ($\gamma_{NO3} \leq 10^{-3}$) for interaction with aqueous droplets (Rudich et al., 1996), large values ($\gamma_{NO3} \sim 0.1$) have been found for uptake to low volatility, unsaturated organic liquids (Moise et al., 2002; Gross and Bertram, 2009; Gross et al., 2009), such as those present in secondary organic aerosol. Uptake of NO3 to urban aerosol (Tang et al., 2010) or organic aerosols (Gross et al., 2009) has been found to be orders of magnitude more efficient than N2O5 uptake to the same aerosol type. For the purpose of assessing the contribution of heterogeneous NO3 loss to aerosol we have used a value of $\gamma = 0.1$, which most probably represents an upper limit to the true value. Despite the use of this large value, the loss of NO3 to aerosol is not significant (RNO3ASA in Fig. 6) but nonetheless exceeds N2O5 loss rates via uptake to aerosol when N2O5 is low (i.e. when the NO3/N2O5 equilibrium is not strongly partitioned towards N2O5) as seen between 02:00 and 04:00. As for N2O5, dry deposition (RddNO3) is insignificant if a loss rate of $0.3 \times 10^{-4}$ s$^{-1}$ is adopted (Geyer et al., 2001a).

**Summary**

Some of the cleanest air-masses encountered at night in the campaign reached the measurement site on the night of 6–7 December and NO3 lifetimes were correspondingly long. A large fraction (and sometimes all) of the NO3 reactivity was accounted for with measured parameters as summarised in Fig. 6.

Although the results suggest that the aerosol loss of N2O5 contributed up to 20% to NO3 losses early in the night, recall that the $\gamma$ used was most likely too high for aerosol with a dominant organic fraction and thus may be considered an upper limit. Missing reactivity (i.e. measured NO3 lifetimes were shorter than calculated based on measured parameters) was apparent between circa 03:00 and 04:00 and also after 06:00. The deviation between measured and calculated NO3 lifetimes is similar in direction and magnitude to that observed previously in marine air masses (Sommariva et al., 2007).

Considering that this air mass had spent several days over the ocean, CH3SCH3 (not measured) is a likely contributor to NO3 reactivity. Strong evidence for CH3SCH3 in this air mass could be found in AMS measurements of significant methane-sulphonic acid concentrations on the morning of 7 December. Given a rate constant for reaction between NO3 and CH3SCH3 of $1.1 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson et al., 2004) the missing reactivity observed at ~06:00 (about 0.005 s$^{-1}$) would be provided by ~200 pptv of CH3SCH3.

As already mentioned, the plot of NO3 lifetime versus NO2 (Fig. 5) could be interpreted to indicate that indirect loss of NO3 (i.e. via N2O5 removal) is an important contributor to NO3 lifetimes. The discussion above indicates however, that the indirect losses are inefficient and a weak correlation between NO2 and NO explains the dependence of NO3 lifetimes on NO2. At high NO2 mixing ratios (e.g. 1–1.5 ppb) the calculated lifetimes are larger than measured. These data points were taken at the end of the night (after 06:00) and Fig. 6 also indicates missing reactivity during this period. In the absence of a significant change in wind direction, the plume like NO2 increases (about 0.5 ppb) during this part of the night may indicate local ship emissions and an increase in reactivity towards NO3 due to other trace gases co-emitted.

As a significant fraction of the NO3 reactivity is accounted for by measured NO (which must have a local source) the use of a steady-state analysis for the later part of this night is not entirely appropriate.

Low nighttime concentrations of NO have previously been reported to limit NO3 lifetimes in a relatively clean coastal environment, which may be impacted by local NO emissions, e.g. from soil (Sommariva et al., 2007).

**4.1.2 23–24 November: mixed air from the continental and Huelva sectors**

Measurements of N2O5 on this evening started at 20:00 UTC, about 2.5 h after sunset. The complete dataset, with meteorological information and other trace gas measurements is displayed in Fig. 7. Until midnight, the wind was mainly from the continental sector (close to 360 degrees) whereas after midnight it came mainly from the Huelva/Port sectors. Following a warm, cloud-free day, the night of the 23–24 November was characterised by low wind speeds and a strong temperature inversion (temperature at 50 m was ~7°C higher than at inlet height), implying a highly stratified nocturnal boundary layer. Back trajectories (Fig. 1) suggest that the air had travelled over the Atlantic before spending 1 day over central Spain with the last 6–12 h within the boundary layer.

NO2 levels showed large variability during the night with mixing ratios between 1 and 13 ppbv, whereas NO was...
always close to zero (<2 pptv) until about 04:30 when a few pptv were observed. Some plume like NO₂ features were accompanied by plumes of similar duration in SO₂ (up to ~3 ppbv), HCHO (up to ~1.5 ppbv) and increases in the overall aerosol surface area, implying common, likely combustion related sources. This is especially apparent in the plumes at midnight and 05:00. For each of the NO₂ plumes at ~20:00, 21:30 and 23:00 there is a significant increase in the N₂O₅ mixing ratio, caused by an increase in the NO₃ production rate. In contrast, N₂O₅ remains close to the detection limit for the entire NO₂ plume at midnight and reaches only low mixing ratios during the larger plumes at 05:00 and 06:30. Note that the NO₂ plume at ~23:00 (when SO₂ was close to zero) was accompanied by a positive gradient in the temperature, whereas the NO₂/SO₂ plume at midnight was accompanied by a negative temperature gradient. Similarly the NO₂/SO₂ plumes after 04:00 were accompanied by drops in temperature. The NO₂/SO₂ plumes were also accompanied by an increase in the aerosol surface area, caused by an increase in mainly the sulphate and nitrate content, but also the organic fraction of the aerosol.

Prior to midnight, NO₂ mixing ratios between ~1 and 6 ppbv and ozone levels of >25 ppbv resulted in large NO₃ production rates (up to ~0.12 pt s⁻¹) and the highest N₂O₅ mixing ratios in the entire campaign (~500 ppt) were measured. The high levels of NO₂ and moderately cold temperatures (283 K) meant that N₂O₅ was usually in greater than tenfold excess of the calculated NO₃ mixing ratio, and up to a factor of 50 greater at the peak of the NO₂ plumes. Prior to midnight, τₚₚₚ(NO₃) was fairly constant at about 75–150 s but was essentially zero for the period between midnight and 01:00 during the SO₂ plume. Log-book entries report significant levels of malodorous gases at the site. The dependence of the NO₃ lifetime on NO₂ and SO₂ mixing ratios and aerosol surface area (ASA) is summarised in Fig. 8. The shortest NO₃ lifetimes are clearly associated with large NO₂ concentrations (upper panel), likewise SO₂ mixing ratios above 1 ppbv are always associated with very short NO₃ lifetimes and there is also weak anti-correlation with aerosol surface area. The observed NO₂ and aerosol surface area dependencies would appear to indicate that heterogeneous loss of N₂O₅ is important. Similar to the treatment above for the Atlantic sector we therefore assess (via Eq. 2) gas-phase and heterogeneous loss mechanisms for NO₃ and N₂O₅ which were constrained by measurements and also identify potential (unmeasured) reactive trace gases.

**Heterogeneous loss of NO₃ and N₂O₅**

Compared to 7 December, the surface area available for interaction of aerosol with N₂O₅ or NO₃ was significantly larger on this night (factor of 2–3). The high levels of NO₂ observed result in large N₂O₅/NO₃ ratios, so that the heterogeneous losses would be expected to be more important for N₂O₅ than for NO₃. For this night the aerosol contained a very high organic component (up to 75% of the aerosol mass) with organic/sulphate ratios as high as 15 early in the night and never decreasing below about 3. The sulphate/(sulphate + nitrate) ratio was also quite low (0.3–0.7). As discussed above, γ(N₂O₅) on such particles would be expected to be less than 0.04. The uptake coefficient for NO₃ is poorly defined but potentially a factor of 10 larger (Tang et al., 2010). An absolute upper limit to the sum of direct and indirect NO₃ loss rates via heterogeneous uptake to aerosol was thus calculated using uptake coefficients of 0.04 for N₂O₅ and 0.5 for NO₃, the later representing diffusion limited uptake. This provides an estimate of the maximum contribution of heterogeneous reactions on aerosols to the NO₃ lifetime.

Figure 9 provides an overview of the relative importance of the constrained, direct and indirect loss processes for NO₃ on this night. Even though the uptake coefficients employed were upper limits, the calculated loss of N₂O₅ (RN₂O₅ASA) and NO₃ (RNO₃ASA) to aerosols does not account entirely for the observed NO₃ loss frequency (black dots) before ~23:30 on the 23rd. Despite the much larger uptake coefficient used for NO₃, its contribution to the total heterogeneous loss was similar to that of N₂O₅ as the NO₃−N₂O₅
partitioning was shifted towards $\text{N}_2\text{O}_5$ on this night with high $\text{NO}_2$ mixing ratios. During the first $\text{SO}_2$/NO$_2$ plume (centred at midnight) the NO$_3$ lifetime was drastically shortened and heterogeneous processes contribute an upper limit of $\sim 10\%$ to the overall measured loss frequency of NO$_3$ (R$\text{N}_2\text{O}_5$ASA + RNO$_3$ASA). Similarly, the summed effect of dry deposition of NO$_3$ and N$_2$O$_5$ (using the dry deposition rates listed above) can be disregarded as a major loss of either NO$_3$ or N$_2$O$_5$ (R$\text{dd}$).

Gas-Phase reactions of NO$_3$ and N$_2$O$_5$

Similar to 7 December, the homogeneous hydrolysis of N$_2$O$_5$ is not an important loss process in this air mass, contributing less than 1% to the NO$_3$ reactivity (Rwater of Fig. 9). Close to zero levels of NO during most of this night also rule out a significant impact (RNO). The sum of the direct NO$_3$ loss rates due to BVOC (the sum of $\alpha$-pinene, limonene and isoprene, Rbiogen) contributes significantly to NO$_3$ loss before 23:00, but only a few percent during the SO$_2$ plumes. Further measured trace gases which can react with NO$_3$ are HCHO and aromatics. At a mixing ratio of close to 1 ppbv and a rate coefficient close to $5 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson et al., 2006) HCHO can contribute a negligible $1 \times 10^{-5}$ s$^{-1}$ to the overall NO$_3$ loss rate. Similarly, with respective room temperature rate coefficients of $<3 \times 10^{-17}$, $7 \times 10^{-17}$, $\sim 4 \times 10^{-16}$ and $<6 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003), benzene ($\sim 80$ ppbv), toluene ($\sim 100$ ppbv), xylenes (sum of $p$, $m$ and $o$-xylene was $\sim 20$ ppbv) and ethylbenzene (8 ppbv) all react too slowly with NO$_3$ to contribute significantly.

Under certain circumstances, RO$_2$ (formed e.g. from NO$_3$ initiated oxidation of CH$_3$SCH$_3$ or ozonolysis of BVOC) has been shown to contribute to NO$_3$ loss (Sommariva et al., 2009). On this night, RO$_2$ mixing ratios of up to 80 pptv were observed between $\sim$midnight and 04:00 (Andrés-Hernández et al., 2011). In the absence of speciated RO$_2$ measurements we calculate the loss rate of NO$_3$ due to reaction with RO$_2$ assuming a rate coefficient of $2.3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ taken from evaluated kinetic data (Atkinson et al., 2006). This results in NO$_3$ loss rates of $\sim 5 \times 10^{-3}$ s$^{-1}$, which again is only a small fraction of the total loss rate ($\sim 4\%$ at midnight).

Clearly, the sum of constrained indirect and direct losses of NO$_3$ do not explain the short lifetimes observed during the SO$_2$ plumes. As heterogeneous processing cannot be enhanced in rate beyond that calculated using measured aerosol surface areas and upper limits for $\gamma$(NO$_3$) and $\gamma$(N$_2$O$_5$) we turn to potential gas-phase reactions, that were not constrained by measurements at the site.

Unknown or undetermined reactions/loss processes

The aerosol surface area and trace gases which were measured provided only a fraction of the observed reactivity after midnight on the 23rd–24th. A clue to the missing reactivity may be provided by the very short NO$_3$ lifetimes (or absence of N$_2$O$_5$) when SO$_2$ was present at levels above $\sim$1 ppbv (Figs. 7 and 8).

Whilst SO$_2$ itself does not react with NO$_3$, it may be co-emitted or co-located with emissions of more reactive traces gases. Two scenarios are considered below in which reduced
sulphur species or unsaturated VOCs are responsible for efficient NO\textsubscript{3} loss during periods of enhanced SO\textsubscript{2} on this night.

A log-book entry describes strongly malodorous air at the measurement site on this (and several other) nights. Malodorous, reduced sulphur compounds (RSC) are often associated with oil refining, pulp/paper mill and waste treatment activities (Nunes et al., 2005; Pal et al., 2009; Toda et al., 2010) and we note that not only a huge oil-refinery complex but also Spain’s largest pulp/paper mill is located in Huelva.

RSC with high reactivity to NO\textsubscript{3} are CH\textsubscript{3}SCH\textsubscript{3} (DMS), CH\textsubscript{3}SSCH\textsubscript{3} (DMDS) and CH\textsubscript{3}SH. NO\textsubscript{3} lifetimes are known to be strongly influenced by DMS emissions in marine air masses (Allan et al., 2000; Aldener et al., 2006; Sommariva et al., 2009) but a large contribution to NO\textsubscript{3} loss in urban air has also been reported (Shon and Kim, 2006).

The oxidation of RSC by NO\textsubscript{3} results in the formation of SO\textsubscript{2}, HCHO and RO\textsubscript{2} (Jensen et al., 1992) with (modelled) RO\textsubscript{2} levels often exceeding those observed during daylight (Sommariva et al., 2009). The rate coefficients for reaction of DMS, DMDS and CH\textsubscript{3}SH with NO\textsubscript{3} are all close to 1\times10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, so that a total mixing ratio of these RSC of 4 ppbv would provide an equivalent reactivity of 0.1 \text{ s}^{-1}. Whilst no measurements of RSC were available to support their potential role, we note that ppbv mixing ratios are not unrealistic as RSC emitted into a shallow, highly stratified boundary layer at night have no gas-phase loss mechanisms apart from reaction with NO\textsubscript{3}. Human odour thresholds for H\textsubscript{2}S, CH\textsubscript{3}SH, CH\textsubscript{3}SSCH\textsubscript{3} and CH\textsubscript{3}SSCH\textsubscript{3} are also in the ppbv regime (Kim et al., 2007; Pal et al., 2009).

In order to capture the NO\textsubscript{3} lifetime dependence on SO\textsubscript{2}, a reactive term, considering the presence of a trace gas at a constant fraction of the SO\textsubscript{2} mixing ratio and reacting with NO\textsubscript{3} with a rate constant of 1\times10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (i.e. like RSC) was added to Eq. (2). The result is the grey area (RSO\textsubscript{2}) of Fig. 9. The RSC to SO\textsubscript{2} ratio was adjusted (to ~2) to approximately capture the large NO\textsubscript{3} loss rates at midnight, bringing the measured and modelled steady state lifetime in rough agreement.

The co-incident increases in nighttime aerosol surface area and the sulphate component of the aerosol is difficult to account for in the RSC scenario unless a sufficient rate of oxidation of SO\textsubscript{2} (i.e. by reaction with OH) is available. Nighttime OH could conceivably be generated by reactions of RO\textsubscript{2} with NO\textsubscript{3} (Platt et al., 1990; Geyer et al., 2003). The increase in particle sulphate at the maximum of the 3 ppbv SO\textsubscript{2} plume was ~0.5 g m\textsuperscript{-3}, which would require oxidation via reaction with OH of 100 ppbv of SO\textsubscript{2} and efficient transfer of the H\textsubscript{2}SO\textsubscript{4} product to the particle phase. Assuming a total reaction time of 4 h (maximum transport time from Huelva), this would still require a constant nighttime OH concentration en route of ~2 \times 10^6 \text{ molecule cm}^{-3}.

Interactions between NO\textsubscript{3} and reduced sulphur thus provide an interesting but highly speculative explanation for some of the observations on this and other campaign nights, including short NO\textsubscript{3} lifetimes, high RO\textsubscript{2} levels and formation of HCHO and SO\textsubscript{2}, though we note that plume like increases in SO\textsubscript{2} were not always accompanied by increases in HCHO as illustrated for this night in Fig. 7.

In a second scenario, we consider the coincident arrival of the SO\textsubscript{2}, NO\textsubscript{2} and HCHO plumes to be due to their formation in a common combustion source, either related to shipping or oil-refinery activity. During this night the wind direction swept slowly from the continental sector to the Huelva sector with the plumes in NO\textsubscript{2} reflecting emissions from various point sources in the coastal-Huelva region. The short lifetimes of NO\textsubscript{3} after midnight reflect highly reactive air masses from Huelva, but not necessarily due to RSC. Hydrocarbon emissions related to the petrochemical industry, including unsaturated VOC such as 1,3-butadiene (Roberts et al., 2003) which are reactive towards NO\textsubscript{3} could then be responsible for the short NO\textsubscript{3} lifetimes. In this scenario, the source of the peroxy radicals observed on this night would be reaction of unsaturated hydrocarbons with either NO\textsubscript{3} or O\textsubscript{3}. In this context note that NO\textsubscript{3} reacts at least a factor 10 more slowly with unsaturated, petrochemical-related hydrocarbons (e.g. the rate coefficient for NO\textsubscript{3} with 1,3-butadiene is 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) than with RSC so that mixing ratios of several tens of ppbv of the alkene would be necessary to explain the short NO\textsubscript{3} lifetimes. In summary, the source of the peroxy radicals observed on this night would be reaction of unsaturated hydrocarbons with either NO\textsubscript{3} or O\textsubscript{3}. In this context note that NO\textsubscript{3} reacts at least a factor 10 more slowly with unsaturated, petrochemical-related hydrocarbons (e.g. the rate coefficient for NO\textsubscript{3} with 1,3-butadiene is 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) than with RSC so that mixing ratios of several tens of ppbv of the alkene would be necessary to explain the short NO\textsubscript{3} lifetimes. In summary, air from the Huelva sector and the port/coastal region close to Huelva was highly reactive towards NO\textsubscript{3} resulting in very short lifetimes which were controlled by gas-phase reactions and a diminished role for heterogeneous processes (either for NO\textsubscript{3} or N\textsubscript{2}O\textsubscript{5}). Whilst RSC and unsaturated VOC were proposed as potential reaction partners for NO\textsubscript{3} they were not constrained by measurements and for extended periods of the night (especially when NO\textsubscript{3} was observable) much of the reactivity is not accounted for.

### 4.1.3 26–27 November: air from the continental sector

On the night of 26–27 November, local wind directions indicated air masses originating from continental Spain which avoided large local cities and industrial centres such as Huelva or Seville. Back trajectories suggested that the air had spent the last two days over central Spain and northern France before reaching the site, gradually descending from ~3500 m to ground level over this period with only the last 4–6 h spent at altitudes of less than 500 m. Local wind speeds during the night were between 2.5 and 5 m s\textsuperscript{-1}.

On this night, NO\textsubscript{2} levels were generally under 2 ppbv except for a plume-like increase to ~4 ppbv at ~20:00 on the evening of the 26th (Fig. 10). As was frequently observed for the continental sector, NO\textsubscript{2} was correlated with black carbon but not with SO\textsubscript{2}, indicating that emission by road traffic was the most likely source. NO was close to the detection limit (2 ppt) during the whole night, except for some spikes due to very local (likely vehicular) emissions. The constancy of the NO mixing ratio through the night strongly suggests that the true value is zero and the 2 pptv is a residual from...
Fig. 10. Overview of measurements on the night of 26–27 November (air from the continental sector). For NO₃, the black datapoints are CRD measurements, the red squares (≈30 min resolution) are DOAS measurements.

zero correction. O₃ levels were constant at ≈25–30 ppbv. Levels of biogenic hydrocarbons (isoprene, pinene) were low (≈10 pptv) as on other nights of the campaign. Mixing ratios of aromatics were similar to the 23rd (less than 100 pptv). Aerosol surface areas were between 25 and 80 µm² cm⁻³ and were correlated with NO₂. The aerosol was acidic (NH₄⁺/SO₄²⁻ = 0.6) with a dominant organic fraction (the organic to sulphate ratio was ≈4 until 04:00 when it slowly decreased to 2).

NO₂ could be measured above the detection limit at almost all times during this night, with maximum mixing ratios of ≈100 pptv and steady-state NO₃-lifetimes up to 900 s. Intermediate to those observed for the Huelva and Atlantic sectors. The CRD and DOAS-derived NO₃ mixing ratios were in good agreement, especially after midnight. The observations are summarised in Fig. 10.

As in the discussion of the previous case studies, direct and indirect losses of NO₃ were assessed based on measured aerosol surface areas and trace gases. For this purpose, NO mixing ratios were assumed to be zero. The calculations are summarised in Fig. 11. Between midnight and 07:00, the presence of α-pinene and limonene at mixing ratios of 5–10 pptv results in loss rates of ≈4 × 10⁻³ s⁻¹. The calculated NO₃ loss rate in this period thus exceeds that measured suggesting that reactivity is entirely accounted for by reasonably well constrained gas-phase reactions. This allows us to estimate upper bounds for the rates of all other loss mechanisms, including uptake to aerosol on this night. The rate of direct loss of NO₃ to the organic component of the aerosol is of major uncertainty as the nature of the organic fraction (and thus availability of e.g. double bonds with which NO₃ can react) is unknown. A value of γ NO₃ = 0.1 contributes only insignificantly to the NO₃ lifetime whereas a value of 0.5 (diffusion limited uptake) would increase the discrepancy between observed and calculated lifetimes. A similar effect would be obtained by use of a large value (e.g. 0.1) for γ(N₂O₅). On this night, the organic to sulphate ratio was ≈2–4 and the sulphate to (sulphate+nitrates) ratio was fairly constant at 0.6, implying a more likely value of γ (N₂O₅) of ≈0.01 (Riemer et al., 2009), which is also consistent with our observations. In the first half of the night (up to ≈midnight) NO₃ lifetimes were much shorter and highly variable, with loss rates up to 0.05 s⁻¹ (lifetimes of just 200 s). We can rule out that this increase in the NO₃ loss frequency is due to a change in reactivity of the aerosol to either N₂O₅ or NO₃. Neither the aerosol composition (i.e. organic, nitrate and sulphate fractions and acidity) nor the relative humidity changed significantly during the night so a large change in γ (factor 10) is not anticipated. Also, the large variability in the loss frequency is not mirrored by changes in aerosol surface area, but is most likely associated with fluctuations in rates of vertical mixing within a highly stratified nocturnal boundary layer, with longer lived NO₃ present in higher
layers. Inspection of the temperature and \( \text{N}_2 \text{O}_3 \) trends during this night reveals significant correlation, with higher temperatures (i.e. air from higher altitudes) bringing more \( \text{NO}_3 \). Measurements of a strong vertical gradient in \( \text{N}_2 \text{O}_3 \) on this night (Thieser et al., 2011) confirm this interpretation.

### 4.2 Nocturnal loss of \( \text{NO}_x \) and VOCs

During DOMINO, the efficiency of nocturnal loss of \( \text{NO}_x \) to particulate phase or to long-lived reservoir species (e.g. \( \text{HNO}_3 \)) which may undergo deposition, will depend both on the absolute and relative rates of processing of \( \text{NO}_3 \) (in gas-phase reactions) and \( \text{N}_2 \text{O}_3 \) (in heterogeneous reactions). If direct loss processes of \( \text{NO}_3 \) are slow and \( \text{N}_2 \text{O}_3 \) uptake to particles is inefficient, the \( \text{NO}_3-\text{N}_2 \text{O}_3 \) equilibrium-pair represents only a temporary \( \text{NO}_3 \) reservoir. \( \text{N}_2 \text{O}_5 \) or \( \text{NO}_3 \) formed in the night will release \( \text{NO}_x \) at sunrise as \( \text{NO}_3 \) lifetimes are shortened by photolysis (to form both NO and \( \text{NO}_2 \)) and reaction with NO (to form \( \text{NO}_2 \)). \( \text{N}_2 \text{O}_3 \) decomposes thermally to \( \text{NO}_2 \) and \( \text{NO}_3 \), so that \( \text{NO}_x \) is recovered and available for \( \text{O}_3 \) production. In the present campaign, nighttime lifetimes of \( \text{NO}_3 \) were generally so short that efficient irreversible loss of \( \text{NO}_3 \) occurred. \( \text{NO}_3 \) lifetimes of just a few minutes imply that the rate of loss of boundary layer \( \text{NO}_x \) is approximately equal to the rate of \( \text{NO}_3 \) formation i.e.

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

where the factor \( n \) is 1 if \( \text{NO}_3 \) is lost only directly (e.g. by reaction with VOC) and is 2 if \( \text{NO}_3 \) is lost indirectly only via \( \text{N}_2 \text{O}_5 \) formation and reaction as two \( \text{NO}_2 \) are required to make each \( \text{N}_2 \text{O}_5 \) molecule. For the present campaign we have shown that, when produced at high rates, \( \text{NO}_3 \) is lost predominantly by direct routes, so that \( n \) should be close to

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1. Figure 12 displays the integrated \( \text{NO}_x \) losses via reaction of \( \text{NO}_2 \) with \( \text{O}_3 \) for the three case studies outlined above. These calculations indicate that over the course of a 12 h night, 0.8, 1.0 and 1.8 ppbv of \( \text{NO}_x \) were removed from the boundary layer on the 23–24th, 26–27th and 6–7th, respectively. This is equivalent to \( \sim 70\% \) of \( \text{NO}_2 \) as mean mixing ratios were 1.2, 2.7 and 1.3 ppbv on these nights. The average loss rates were in the range \( 1.9–4.2 \times 10^{-5} \) ppbv of \( \text{NO}_2 \) per second. Assuming that \( \text{NO}_3 \) is lost entirely by reaction with VOC (and not reaction with NO or by \( \text{NO}_3 \) or \( \text{N}_2 \text{O}_5 \) uptake to aerosol), this is also the loss rate of VOC over the same period. For comparison, a 12 h, daytime loss of \( \text{NO}_2 \) via reaction with OH of \( 2 \times 10^{-5} \text{ s}^{-1} \) would be obtained for average OH and \( \text{NO}_2 \) mixing ratios of 0.04 and 2000 ppt, respectively, though the greater daytime boundary layer depth would favour the OH mechanism.

### 5 Summary and conclusions

Measurements of \( \text{N}_2 \text{O}_5 \) and steady-state calculations of \( \text{NO}_3 \) lifetimes during the DOMINO campaign revealed stark differences according to the type of air mass encountered. The longest lifetimes (\( \sim 30\text{ min} \)) of \( \text{NO}_3 \) were encountered in air masses arriving from the Atlantic sector. Air from the Huelva urban (petrochemical and industrial) sector had high production rates of \( \text{NO}_3 \), but frequently concentrations close to the detection limit and lifetimes of only a few seconds. The high reactivity could only be partially accounted for by measured trace gases and aerosol surface areas. Lifetimes of \( \text{NO}_3 \) were always very short when \( \text{SO}_2 \) was observed at the site, either due to reactions of \( \text{NO}_3 \) with RSC or due to common or co-located emissions (e.g. combustion) sources of other reactive trace gases. The relationship between the \( \text{NO}_3 \) lifetime, \( \text{SO}_2 \), \( \text{NO}_2 \) and ASA over the course of the entire campaign
is illustrated in Fig. 13. Clearly, polluted air masses (NO$_2$ or SO$_2$ > 2 ppbv) do not support long NO$_3$ lifetimes.

NO$_3$ in air from the continental sector had lifetimes which were similar to other forested areas (e.g. Crowley et al., 2010), but which were occasionally significantly shortened, presumably due to the impact of anthropogenic emissions. In general these results show that NO$_3$ (or N$_2$O$_5$) mixing ratios in air masses from urban and industrial centres were controlled by gas-phase reactions of NO$_3$ and cannot be accurately estimated from production terms (e.g. NO$_2$ and O$_3$ mixing ratios) and measured BVOC and aerosol. However, the combination of high NO$_3$ production rates and short lifetimes frequently observed during the campaign implies large nocturnal processing rates for the VOCs mainly responsible for NO$_3$ loss, and thus a high production rate of organic peroxy radicals and secondary oxidation products, such as carbonyl compounds and organic nitrates/nitric acid.

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