Night-time chemistry above London: measurements of NO₃ and N₂O₅ from the BT Tower

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Abstract. Broadband cavity enhanced absorption spectroscopy (BBCEAS) has been used to measure the sum of concentrations of NO₃ and N₂O₅ from the BT (telecommunications) Tower 160 m above street level in central London during the REPARTEE II campaign in October and November 2007. Substantial variability was observed in these night-time nitrogen compounds: peak NO₃+N₂O₅ mixing ratios reached 800 pptv, whereas the mean night-time NO₃+N₂O₅ was approximately 30 pptv. Additionally, [NO₃+N₂O₅] showed negative correlations with [NO] and [NO₂] and a positive correlation with [O₃]. Co-measurements of temperature and NO₂ from the BT Tower were used to calculate the equilibrium partitioning between NO₃ and N₂O₅ which was always found to strongly favour N₂O₅ (NO₃/N₂O₅=0.01 to 0.04). Two methods are used to calculate the lifetimes for NO₃ and N₂O₅, the results being compared and discussed in terms of the implications for the night-time oxidation of nitrogen oxides and the night-time sinks for NOₓ.

1 Introduction

The nitrate radical (NO₃) is amongst the most important oxidants in the nocturnal boundary layer (NBL). It is responsible for initiating the processing of a wide range of anthropogenic and biogenic emissions and in its reactivity to some VOCs can be considered the night-time analogue of the hydroxyl radical. Understanding the atmospheric cycle of NO₃ -its formation and loss pathways, spatial variability, and role in the regulation of NOₓ (=NO+NO₂) and budgets of volatile organic compounds (VOCs) (Atkinson, 2000), is of key importance to understanding processes impacting surface ozone formation and air quality.

1.1 Chemistry of NO₃ and N₂O₅

Figure 1 shows a simplified scheme of nocturnal nitrogen oxide chemistry. NO₂ is formed from NO (Reaction R1), which has a predominant traffic source. NO₂ and O₃ react to form NO₃, (Reaction R2). During night-time, N₂O₅ can be formed through reaction of NO₂ and NO₃ (Reaction R3) and decomposes with rate coefficient k₃.
Fig. 1. Simplified schematic of nocturnal NO$_3$ chemical processes.

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad k_1 \]  
\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad k_2 \]  
\[ \text{NO}_2 + \text{NO}_3 + \text{M} \leftrightarrow \text{N}_2\text{O}_5 + \text{M} \quad k_3 \text{ (forward)}, \quad k_{-3} \text{ (reverse)} \]

At night NO$_3$ and N$_2$O$_5$ exist in a temperature dependent equilibrium (Wangberg et al., 1997) which is established within minutes under typical atmospheric conditions (Brown, 2003). The major sinks for NO$_3$ are solar photolysis (Stark et al., 2007) which effectively suppresses NO$_3$ and N$_2$O$_5$ concentrations during daylight hours, and the extremely fast reaction with NO (Hammer et al., 1986).

In addition to gas phase sinks, the heterogeneous conversion of N$_2$O$_5$ to aqueous nitrate (Reaction R4) provides an effective pathway for removal of NO$_3$ from the atmosphere (Brown et al., 2004; Dentener and Crutzen, 1993).

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \quad k_{\text{het}} \]  

Despite recognition of the importance of this process, its global influence remains relatively poorly quantified, in large part due to the complexity of the dependence of N$_2$O$_5$ uptake on aerosol chemical composition and mixing state (Hallquist et al., 2000; Mentel et al., 1996). Recent investigations have found that night-time removal of NO$_3$ (=all oxides of nitrogen) via the above channels can be almost as effective at removing NO$_3$ from the atmosphere as the major daytime pathway proceeding via the reaction of OH with NO$_2$ (Brown et al., 2007a, b) (Reaction R5).

\[ \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad k_5 \]

1.2 Vertical extent of NO$_3$ and N$_2$O$_5$ structure

A number of factors lead to pronounced vertical structure of N$_2$O$_5$ and NO$_3$ in the NBL. NO sources are generally located at the ground surface and act to suppress both local NO$_3$ and O$_3$ concentrations through NO$_3$ reacting with NO and O$_3$ loss (Reaction R1) leading to slower NO$_3$ formation (Reaction R2). Upon ascent through the atmosphere, O$_3$ levels increase and there is gradual conversion of NO to NO$_2$ followed by NO$_3$ and N$_2$O$_5$. The absence of significant sinks for NO$_3$ and N$_2$O$_5$ aloft enables significant concentrations of these species to grow, leading to distinct positive vertical concentration gradients.

Meteorological conditions also play a role in establishing vertical gradients. The absence of convection from the surface at night tends to decrease turbulent mixing and leads to a highly stratified, stable layer forming in the first few hundred metres of the NBL (Wood et al., 2010). The upper region of the NBL is therefore separated from the surface and is less affected by the surface emissions that can act to destroy NO$_3$.

1.3 Measurements of NO$_3$ and N$_2$O$_5$

Following the first detection of NO$_3$ in the troposphere by DOAS (Platt et al., 1980) a wide range of surface-based field studies have sought to investigate the role of NO$_3$ in polluted and clean air environments (e.g. Allan et al., 2000; Geyer et al., 2001; Smith et al., 1995). These studies were generally focused on NO$_3$ only, as N$_2$O$_5$ does not absorb at visible wavelengths, rendering it undetectable using the DOAS technique. In order to overcome this limitation, a number of NO$_3$ instruments have recently been developed to infer N$_2$O$_5$ concentrations through the thermal manipulation of the equilibrium between NO$_3$ and N$_2$O$_5$. These experiments have generally used high-finesse cavity techniques (e.g. Brown et al., 2007a; Dube et al., 2006), ionization mass spectrometry (Slusher et al., 2004) or Laser Induced Fluorescence (LIF) in-situ detectors for the NO$_3$ produced from thermal dissociation of N$_2$O$_5$ (Matsumoto et al., 2005b; Wood et al., 2005). Mixing ratios of up to 800 pptv of N$_2$O$_5$ were recently observed in Tokyo, Japan, using one such technique (Matsumoto et al., 2005a).

As the importance of NO$_3$ and N$_2$O$_5$ aloft has become apparent, a number of studies have sought to make vertically resolved measurements of NO$_3$ and N$_2$O$_5$ and this remains a very active area of interest (Aliwell and Jones, 1998; Brown et al., 2007a; Fish et al., 1999; Geyer and Stutz, 2004; Jones et al., 2005; Stutz et al., 2004). Brown et al. have recently reported airborne (2007a), tower (2007b), and ground based measurements (e.g. 2003b) in the USA, with more limited measurements being made by other groups over European regions (Aliwell and Jones, 1998; McFiggans et al., 2010; Penkett et al., 2007; Povey et al., 1998). Of particular note, there remain very few measurements at altitudes of 50–300 m above ground level, where airborne measurements (Brown et al., 2005) have suggested peak concentrations may exist. Given the difficulties in performing measurements aloft in urban areas, fewer still data exist on NO$_3$ and N$_2$O$_5$ concentrations above densely populated areas.
To this end, this paper presents in-situ, high time resolution measurements of \([\text{NO}_3+\text{N}_2\text{O}_5]\) performed using LED-based broadband cavity enhanced absorption spectroscopy (LED-BBCEAS) over a month-long period at an altitude of 160 m over central London. These measurements formed part of the second phase of the Regent’s Park and Tower Experiments (REPARTEE-II). We present an overview of the measurement dataset, together with an analysis of the lifetimes of \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\) and the importance of these species to boundary layer chemistry and removal of \(\text{NO}_x\) in this region.

2 Experimental

2.1 The measurement site

The LED-BBCEAS instrument was deployed on level 35 of the British Telecommunications tower, 160 m above ground level in central London, United Kingdom (51.31:17° N 0:08:20° W) for 28 nights between 19 October 2007 and 15 November 2007. This tower site is relatively unusual in a cityscape in that it is taller, by a factor of approximately 9 (Barlow et al., 2009) than any other building within \(\sim 1\) km of it. This leads to minimal local turbulence effects and loss of reactive atmospheric species to surfaces in the sampling vicinity. The tower is located close to large pollution sources, for example, Marylebone Road which is one of the busiest dual carriageways in London is approximately 300 m away from the foot of the tower. In contrast, the tower is also close (~700 m) to Regent’s Park, where local air quality conditions are thought to be representative of urban background levels. Various chemical, particulate and meteorological measurements were made during REPARTEE-II at the BT tower, in Regent’s Park and on Marylebone Road, and the reader is directed to Harrison et al. (2010) for further information.

2.2 Measurement technique: LED-BBCEAS

Broadband cavity enhanced absorption spectroscopy (BBCEAS) employing light emitting diode (LED) sources was used to provide in-situ measurements of the sum of \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\) on the BT tower. The BBCEAS technique was introduced in 2003 by Fiedler et al. (2003) and has since been developed by a number of groups (Platt et al., 2009; Ruth et al., 2007; Washenfelder et al., 2008) including the current authors (Ball et al., 2004; Langridge et al., 2006, 2008a, b). A detailed description of the BBCEAS technique and the instrument used in this study is provided in Langridge et al. (2008a) and only a brief outline is provided here.

A BBCEAS measurement is conducted by exciting a high finesse optical cavity with a broadband continuous-wave light source. The intensity transmitted through the cavity rapidly establishes a steady state level, determined principally by the input optical power, the cavity mirror reflectivity and the absorption and scattering properties of the intracavity medium. By performing spectrally resolved measurements of the transmitted cavity intensity both in the absence \((I_0)\) and presence \((I)\) of the absorbing gas of interest, the sample absorption coefficient can be determined from Eq. (1) (Fiedler et al., 2003), where \(R(\lambda)\) is the wavelength dependent reflectivity of the mirrors used to form the cavity and \(d_{\text{eff}}\) is the effective distance between cavity mirrors, accounting for differences between the true mirror-to-mirror distance and the length over which the sample gas fills the cavity.

\[
\text{Abs}(\lambda) = \left( \frac{I_0(\lambda)}{I(\lambda)} - 1 \right) \frac{1 - R(\lambda)}{d_{\text{eff}}}
\]  

where \(R(\lambda)\) is the wavelength dependent reflectivity of the mirrors used to form the cavity and \(d_{\text{eff}}\) is the effective distance between cavity mirrors, accounting for differences between the true mirror-to-mirror distance and the length over which the sample gas fills the cavity.

BBCEAS provides a direct and highly sensitive means with which to determine unambiguously the concentration of an absorbing gas in-situ. High sensitivity arises as a direct result of confining the sample gas within a high finesse optical cavity, which essentially acts as an extremely effective multi-pass optical cell. By constructing the cavity with mirrors of appropriately high reflectivity (e.g. \(R > 99.95\%\)), optical path lengths of many kilometers can be achieved within a cell with a physical footprint of only approximately \(1\) m\(^2\). This leads to sensitivities that are routinely better than \(5 \times 10^{-9}\) cm\(^{-1}\) in 10 s (Langridge et al., 2008a). The ability of BBCEAS to determine absorber concentrations unambiguously, regardless of the presence of additional overlapping absorption features, results from the use of a broadband light source and wavelength resolved detection. Wavelength resolved spectra are captured upon every acquisition, allowing multivariate spectral fitting techniques, akin to those commonly used for differential optical absorption spectroscopy (DOAS) (Platt et al., 1980) to be used to separate contributions from molecular absorption/scattering and particulate scattering from the total extinction signal (Ball and Jones, 2009; Ball et al., 2004; Langridge et al., 2006).

One factor complicating the application of DOAS fitting principles to the analysis of BBCEAS spectra can be departure from Beer-Lambert absorption behaviour caused by strong narrow-band absorption structure, which remains unresolved by the BBCEAS measurement’s limited spectral resolution. This complication is important for the analysis of BBCEAS spectra of \(\text{NO}_3\) absorption around 662 nm (used in this work), which overlaps with strong water vapour absorption in the \(4\nu + \delta\) polyad. The treatment of such complications has been described in detail by Langridge et al. (e.g. 2008a) and was applied here to analyse all ambient spectra.
2.3 LED-BBCEAS instrument

In the current work the BBCEAS instrument was operated across a wavelength range spanning 631–670 nm. This region captured the strong absorption peak of NO$_3$ centered at 662 nm corresponding to its $B^2E' - X^2A_2$ electronic transition, together with a significant portion of overlapping water vapour absorption structure. The instrument setup was very similar to that detailed in Langridge et al. (2008a), although operated with a slightly longer cavity length of 118.5 cm. The most important developments in this work were the use of a heated inlet to quantitatively convert ambient N$_2$O$_5$ to NO$_3$ and a heated cell to maintain the equilibrium in favour of NO$_3$.

The inlet was constructed from PFA tubing (Adtech ltd.) which has been shown to cause less NO$_3$ wall loss than alternative materials such as PTFE (Dube et al., 2006). Four individual lengths of 0.25” OD, 0.125” ID PFA tubing, each 50 cm long, were wrapped in heating tape and common insulation to form the inlet. The sample cell was constructed using 2 cm ID PFA tubing, which was also wrapped in heating tape and insulated. The inlet was joined to the sample cell at a 90° angle via a small machined PFA block employing push-fit o-ring seals. Both the inlet and sample cell were maintained at a temperature of 100 °C. A rotary pump and mass-flow controllers were used to pull air through the system at a constant flow rate of 6.8 SLPM (standard litres per minute). Assuming plug flow, residence times were 0.1 s and 2.5 s in the inlet and cell respectively. The residence time in the inlet was shown to be sufficient for >95% dissociation of N$_2$O$_5$ to NO$_3$ over the range conditions experienced during this deployment.

The cavity was mounted on an optical rail standing 1.4 m from the floor level (Fig. 2). The inlet was pointed towards the south-west (220°) and extended approximately 20 cm beyond a set of railings that enclosed the tower balcony.

2.4 Instrument operation

Spectra were collected using an integration time of 15 s for the duration of the project. Background spectra ($I_0$ in Eq. 1) were obtained by flushing the cavity with dry nitrogen at the same flow rate as used for ambient sampling. Since ambient ($I$) measurements were carried out in air, a correction was applied to the derived absorption coefficient to account for the small difference in Rayleigh scattering between N$_2$ and air. Collection of $I_0$ spectra was not fully automated during this deployment and the frequency with which they were acquired was determined, in large part, by the availability of access to the BT tower building. The intervals between $I_0$ spectra ranged from as short as 30 min to periods of several days. A typical deterioration in reflectivity over a period of 48 h was from a peak $R$ (at $\lambda=660$ nm) of 0.9999 to 0.9995.

As shown in Eq. (1), the mirror reflectivity, $R(\lambda)$, is required to determine absolute absorber concentrations from BBCEAS measurements. This quantity can change over time, for example due to dirtying of the cavity mirrors or slight changes in optical alignment caused by temperature fluctuations or mechanical movement. $R(\lambda)$ was measured periodically using phase shift cavity ringdown spectroscopy, as described by Langridge et al. (2008a). The mirror reflectivity was measured following every cavity re-alignment, mirror clean, or daily – whichever occurred most frequently, barring periods when access to the instrument was not possible for operational reasons. Calibrations of mirror reflectivity required approximately 1 hour to complete and were thus carried out during daylight hours where possible. This minimised loss of data during the night, where [NO$_3$+N$_2$O$_5$] was most likely to be above the instrumental limit of detection (LOD).

Typically, the effective ringdown time ($\tau$) at 660 nm of the nitrogen-flushed cavity was 25 ± 1 µs, corresponding to a reflectivity $R(\lambda)$ of 0.9999 ± 0.0001. Figure 3 shows a set of typical spectra measured during the course of the campaign. Both the NO$_3$ absorption structure together with that due to water vapour are clearly visible. NO$_3$ mixing ratios were retrieved by differential fitting and for these examples ranged from 33 to 298 pptv.

The degradation of effective mirror reflectivity between successive phase-shift calibrations was considered. In order to quantify this degradation, the spectrally derived water concentration (see Fig. 3) was compared to water concentrations derived from relative humidity (RH) measurements made at the same level on the tower (Harrison et al., 2010). There are a number of caveats involved comparing BBCEAS-derived water concentrations with relative humidity: evaporation from aerosols can act to increase humidity; pressure needs to be accurately known in order to be able to convert RH to water concentration; and water vapour absorption spectroscopy exhibits non Beer-Lambert behaviour due to the highly structured spectral lines not being fully resolved.
(Langridge, 2008; Platt and Stutz, 2008). These combined uncertainties justify not using measured and derived water mixing ratios as a primary method of mirror reflectivity calibration, but since they remain largely unchanged throughout the campaign, enable a deterioration factor to be then applied to the effective mirror reflectivity, maintaining the correlation between BBCEAS-derived humidity and that from RH measurement. This deterioration factor was never more than 0.0004%, which corresponds to a transmission efficiency reduction from 0.9998 to 0.9994 over a period of 3 days.

2.5 Uncertainty

LED-BBCEAS measurements are subject to both statistical errors, caused by uncertainty in the retrieval of spectral parameters, and systematic errors. The magnitudes of these errors are discussed here.

Statistical errors: the uncertainty in NO$_3$ spectral retrievals was found by determining the error in the gradient of a linear fit (Higbie, 1978) of the spectrally isolated NO$_3$ absorption component versus the NO$_3$ absorption cross section (Orphal et al., 2003). This method provides a good estimate for the measurement’s LOD (Langridge, 2008). The magnitude of this uncertainty was around 2 pptv for NO$_3$+N$_2$O$_5$ for the vast majority of the campaign, but did rise for some periods to levels around 8 pptv, as shown in Fig. 4. Errors caused by changes in atmospheric pressure and uncertainties in the absorption cross section all contribute to this LOD. These increased LODs showed some correlation with periods of high aerosol extinction, which acted to limit the effective optical path length within the cavity and thus lead to poorer measurement signal-to-noise ratios, and on other occasions appeared to correlate with drifts in LED temperature which are known to affect its emission spectrum (Lee et al., 2010).

Systematic errors: the major uncertainty in the current measurements resulted from losses of reactive species to the walls of the inlet and sample cell. N$_2$O$_5$ wall losses are generally small, but those of NO$_3$ are significantly larger (Fuchs et al., 2008). Although ambient NO$_3$ generally accounted for a small part of the overall NO$_3$+N$_2$O$_5$ fraction in these studies, since almost all N$_2$O$_5$ is converted to NO$_3$ in the inlet of the instrument, it is important to consider the NO$_3$ transmission efficiency through the full system. Model calculations based on those by Bitter et al. (2005) and Fuchs et al. (2008) were used to deduce the instrument’s transmission efficiency (TE) for NO$_3$+N$_2$O$_5$, taking into account the slightly different dimensions, flow rate and sample dilution in our inlet and cell. The first order wall loss coefficient for NO$_3$ on PFA reported by Dubé et al. of 0.2 ± 0.05 s$^{-1}$ was used and that for the machined Teflon portion was assumed to be the same as this area accounts for less than 1% of the total surface area of the cell and inlet so any differences were deemed negligible. The total net TE was found to be 68 ± 8% but it is noted that differences in geometry between this system and that of Dubé et al. (2006) could introduce additional unquantifiable error.

2.6 Co-measurements

NO$_x$ measurements were carried out using a commercial NO$_x$ analyser (Thermo TE42C-TL), employing a heated Mo catalyst for conversion of NO$_2$ to NO, with a temporal resolution of 1 min. A UV absorption O$_3$ monitor (2B-Tech Dual Beam) was also deployed (temporal resolution of 5 min), both at level T35 of the tower. Two measurements of turbulence in the vertical direction were used in this work: one from the 195 m level (mid-point of a 30 m vertical bin) of the suite of pulsed Doppler lidar (HALO Photonics, (Barlow et al., 2010); and one from an ultrasonic anemometer [(S.A.) (R3-50, Gill Instruments, UK) (Barlow et al., 2010; Wood et al., 2010)] situated at a height of 190 m on the top of the BT tower. A thorough discussion of vertical turbulence measurements during REPARTEE-II is detailed in Barlow et al. (2010) Furthermore, a measure of aerosol surface area ($S_a$) was derived using tandem (merged) Scanning Mobility Particle Sizer (SMPS) and Aerodynamic Particle Sizer (APS) measurements from level T35 of the tower (e.g. Dall’Osto et al., 2009; Shen et al., 2002). The reader is directed to the summary paper for this campaign for further information (Harrison et al., 2010).
Table 1. Statistics for night-time measurements of [NO$_3$+N$_2$O$_5$]/pptv. Night-time as defined by sunrise/sunset times. N: dataset size; 75% and 95% refers to 75th and 95th percentile; All data <LOD replaced with the median of the variable detection limit of around 2pptv and zero. Air masses grouped as indicated by a general inspection of 5-day back trajectories (Rolph, 2003) and coded by predominant origin as: P: Polar, EC: easterly continental; A: Altantic, NC: northern continental.

| Night               | N   | Min | 25% | Median | Mean | 75% | 95% | Max | Air mass |
|---------------------|-----|-----|-----|--------|------|-----|-----|-----|----------|
| 19 Oct–20 Oct       | 4368| <LOD| <LOD| 4      | 12   | 15  | 44  | 161 | P        |
| 20 Oct–21 Oct       | 4214| <LOD| <LOD| 3      | 9    | 57  | 47  | 337 | 789 P    |
| 21 Oct–22 Oct       | 4093| <LOD| <LOD| 3      | <LOD | 11  | 85  |     | NC       |
| 22 Oct–23 Oct       | 6872| <LOD| <LOD| 11     | 23   | 29  | 93  | 390 | EC       |
| 23 Oct–24 Oct       | 1946| <LOD| <LOD| 4      | 9    | 12  | 15  | 38  | 95 EC    |
| 24 Oct–25 Oct       | 2687| <LOD| <LOD| <LOD   | <LOD | <LOD| <LOD| 55  | EC       |
| 25 Oct–26 Oct       | 4280| <LOD| <LOD| <LOD   | <LOD | <LOD| <LOD| 183 | EC       |
| 29 Oct–30 Oct       | 207 | <LOD| 19  | 29     | 47   | 68  | 124 | 135 | A        |
| 30 Oct–31 Oct       | 4540| <LOD| 8   | 120    | 166  | 298 | 437 | 633 | A        |
| 31 Oct–1 Nov        | 4307| <LOD| <LOD| <LOD   | 4    | 4   | 20  | 117 | A        |
| 1 Nov–2 Nov         | 3977| <LOD| 4   | 37     | 60   | 99  | 183 | 283 | A        |
| 2 Nov–3 Nov         | 1206| <LOD| <LOD| <LOD   | 8    | 4   | 45  | 208 | A        |
| 5 Nov–6 Nov         | 4633| <LOD| 32  | 52     | 49   | 65  | 90  | 132 | P        |
| 6 Nov–7 Nov         | 5131| <LOD| <LOD| 12     | 31   | 45  | 123 | 237 | A        |
| 7 Nov–8 Nov         | 4552| <LOD| 9   | 25     | 32   | 46  | 92  | 182 | A        |
| 9 Nov–10 Nov        | 5155| <LOD| 22  | 43     | 48   | 70  | 106 | 197 | A        |
| 10 Nov–11 Nov       | 5207| <LOD| 14  | 25     | 28   | 40  | 59  | 119 | A        |
| 12 Nov–13 Nov       | 4881| <LOD| <LOD| 13     | 96   | 123 | 448 | 796 | P        |
| 13 Nov–14 Nov       | 5260| <LOD| 32  | 56     | 72   | 109 | 170 | 238 | P        |
| 14 Nov–15 Nov       | 4924| <LOD| 27  | 58     | 64   | 92  | 149 | 201 | NC       |
| All night-time data  | 82453| <LOD| <LOD| 16     | 44   | 52  | 180 | 796 |          |

3 Results

LED-BBCEAS measurements commenced on 19 October 2007 at 10:00 and concluded at 09:00 on 15 November 2007 (all times UTC). The full 15 s temporal resolution dataset is shown in Fig. 4. Some spectra have been discarded due to significant misalignment of the cavity or very large increase in the retrieved LOD (a LOD value is reported for all times where analysis has been carried out but only data where NO$_3$+N$_2$O$_5$ > LOD is shown in Fig. 4). Table 1 provides a statistical analysis of the dataset for night-periods when sufficient measurements were made. As expected, a significant diurnal trend is depicted as NO$_3$ is photolysed rapidly during the day and only rose above the LOD after, or within 30 min prior to sunset. A nocturnal (sunset to sunrise) mean NO$_3$+N$_2$O$_5$ mixing ratio over the whole campaign of 40 pptv was observed, with the highest nocturnal mean of 160 pptv on the night of 30–31 October 2007.

There is high variability in the temporal structure and magnitude of the observed night-time enhancements of NO$_3$ and N$_2$O$_5$ during this campaign. Although there were no concurrent ground-level NO$_3$ or N$_2$O$_5$ measurements, mixing ratios of NO$_3$+N$_2$O$_5$ measured at ground level tend to be of the order of 10 pptv (McFiggans et al., 2010), supporting the notion of a significant vertical gradient in the NBL of these species. It is generally observed in this dataset (see Figs. 5 and 7) that any plume or injection of NO into the surrounding air corresponded to a very rapid extinction of NO$_3$ and N$_2$O$_5$, suggesting that NO$_3$ and N$_2$O$_5$ mixing ratios are highly dependent on their source strength and therefore the titration of NO against O$_3$ and the very rapid reaction of NO$_3$ with NO to form NO$_2$. This is demonstrated by the very strong negative correlation of NO$_3$ with NO at night (Fig. 8). This is discussed further by examination of a case study period in Sect. 3.1.

3.1 Case study period: 30 October–1 November 2007

Figure 5 shows a detailed time series covering different chemical regimes of interest of NO$_3$+N$_2$O$_5$, O$_3$, (top panel) and NO, NO$_2$ (middle panel). The lower panel of Fig. 5 depicts two measurements of the variance of the vertical wind speed, $\sigma_w^2$ (m$^2$ s$^{-2}$) which is a measure of vertical turbulence and hence, an indicator of the stability of the boundary layer. Under stable conditions, vertical turbulence will be reduced, whereas under unstable conditions turbulence is higher, such as during the daytime when warming of the surface causes convection.
The first night depicted (30–31 October) illustrates a strong anti correlation of NO$_3$+N$_2$O$_5$ with NO and a positive correlation with O$_3$. However, this correlation breaks down at approximately 04:30 on 31 October, when O$_3$ mixing ratios remain moderately high (approximately 10 ppb), but there is a sudden apparent extinction of NO$_3$+N$_2$O$_5$ sinks. Of additional interest are the periods when the instrument was performing well but NO$_3$ and N$_2$O$_5$ levels were near or below this LOD. On some occasions, this appears to be due to a reduced NO$_3$ source as NO has titrated all available O$_3$ (for example sunset until 22:00 on 31 October). On other occasions, (for example ~02:00 to ~06:00 on 1 November), O$_3$ and NO$_2$ are both present, and therefore the NO$_3$ source remains high, yet very low mixing ratios of NO$_3$+N$_2$O$_5$ are observed. In this period, the higher turbulence observed may contribute to lower NO$_3$+N$_2$O$_5$ through reduced mixing time for N$_2$O$_5$ to form, or an increase in the rate of heterogeneous loss processes indicated by larger aerosol surface area. It is noted that the increase in turbulence is accompanied by an uplift in NO and therefore an increase in NO at the tower height. However, in this instance this is not accompanied by a significant decrease in O$_3$ and is not thought to therefore directly affect NO$_3$ production. The small increase in $\sigma_w^2$ prior to sunrise (approximately indicated by the 2nd blue square from the left in the top panel of Fig. 5), supports the hypothesis that under conditions of low turbulence, mixing ratios of NO$_3$+N$_2$O$_5$ are likely to be greater as there is less potential for deposition.

### 3.2 Partitioning of the NO$_3$ and N$_2$O$_5$ equilibrium

Where NO$_2$ and temperature data were available, the measured NO$_3$+N$_2$O$_5$ was partitioned into calculated ambient NO$_3$ and N$_2$O$_5$ concentrations assuming equilibrium conditions. The equilibrium partitioning of NO$_3$ and N$_2$O$_5$ can be calculated from the known (temperature dependent) equilibrium constant for Reaction (R3), provided, as is the case here, [NO$_2$] (where a chemical species in square brackets is the number density concentration of that species) and temperature are known.

\[
\frac{[NO_3]}{[N_2O_5]} = \frac{1}{K_{eq}(T)[NO_2]} \quad (2)
\]
The justification for assuming that N$_2$O$_5$ is in equilibrium with NO$_3$ and NO$_2$, tested by calculating the time for a chemical system to relax to equilibrium ($\tau_{eq}$), (e.g. Crowley et al., 2010).

$$\tau_{eq} = \frac{1}{k_{R3}[NO_2] + k_{-R3}}$$

$\tau_{eq}$ was derived for the measurements described here, using the forward and reverse rate coefficients for Reaction (R3) from Sander et al. (2003) calculated for the range of encountered temperatures, pressure of 1 atm, together with measured NO$_2$ concentrations, to give a mean time to reach equilibrium of 2.34 ± 1.66 s. The time to reach equilibrium was never more than 1 min, justifying the use of Eq. (2), as the median time for street-level emissions to reach tower height was calculated to be approximately 50 min (Barlow et al., 2010).

The mean equilibrium constant, $K_{eq}(T)$ (Sander, 2003), derived for the ambient temperature conditions of this campaign was $3.2 \pm 1.24 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ (Maximum: $K_{eq}$ (285 K): $8.72 \times 10^{-10}$ cm$^3$ molecule$^{-1}$, Minimum: $K_{eq}$ (277 K): $1.79 \times 10^{-10}$ cm$^3$ molecule$^{-1}$), giving a mean N$_2$O$_5$/NO$_3$ ratio over the campaign of 80. High NO$_2$ levels shift the equilibrium in Reaction (R3) so that almost all is N$_2$O$_5$, the maximum NO$_3$ observed at 31 October 2007 at 03:01 being 15 ± 0.3 pptv with corresponding N$_2$O$_5$ at this point being around 499 ± 1.63 pptv, (NO$_2$=4.3 ppbv, O$_3$ ~7–8 ppbv).

The NO$_2$ mixing ratios for REPARTEE-II were moderately high compared with other urban measurements (e.g. Platt et al., 1980) nocturnal mean ~20 ppbv (see Fig. 7), although not unusual for a central London site. The emissions profile and ambient temperatures of around 3–10°C in UK Autumn, lead to a high dominance of N$_2$O$_5$ in Reaction (R3). Therefore, where NO$_2$ data is unavailable and thus the equilibrium partitioning of NO$_3$ and N$_2$O$_5$ cannot be determined, it is reasonable to make the assumption that [NO$_3$+N$_2$O$_5$]=[$N_2O_5$]. The NO$_x$ analyser is likely to retrieve some fraction of NO$_3$ and N$_2$O$_5$ as NO$_2$, but as value of [NO$_3$+N$_2$O$_5$]/[NO$_x$] was found to be less than 1% for the duration of the campaign no correction was applied. Interferences from other NO$_x$ uncluding HONO and HNO$_3$ were considered, leading to a maximum interference of 16% assuming NO$_x$ and NO$_2$ maxima coincide. Since the effect of NO$_2$ on the calculation of the partitioning between NO$_3$ and N$_2$O$_5$ is small at the temperatures experienced during REPARTEE-II, this is only likely to be significant for the very low NO$_2$ periods (<5 ppbv). Figure 7 shows that such periods do not ever coincide with periods of high NO$_3$ or N$_2$O$_5$ and for the temperature and NO$_2$ conditions experienced during REPARTEE-II, a change of NO$_2$ of the order of 5–15% would have little effect on the already very small (~2%) N$_2$O$_5$ conversion to NO$_3$.

A useful parameter to identify, when dealing with a suite of NO$_x$ measurements, is the fraction of NO$_x$ that is stored in the nocturnal equilibrium between NO$_3$ and N$_2$O$_5$, or $F$(NO$_x$), (Reaction R3) as shown by Brown et al. (2004) and McLaren et al. (2004). Smaller values of $F$(NO$_x$) can be indicative of shorter N$_2$O$_5$ or NO$_3$ lifetimes; shorter lifetimes suggest rapid sinks for N$_2$O$_5$.

$$F(NO_x) = \frac{[NO_3]+2[N_2O_5]}{[NO_2]+[NO_3]+2[N_2O_5]}$$

A median value of $F$(NO$_x$) for REPARTEE-II night-times is around 0.05 with a mean of only 1% (Fig. 10). This is somewhat lower than previous studies in moderately polluted MBL and aloft (~0.05–0.2) (Brown et al., 2004; McLaren et al., 2010). Elevated mixing ratios of NO$_2$ also act to decrease $F$(NO$_x$) as measured here.

### 3.3 Correlations with ancillary data

No apparent correlation of [NO$_3$+N$_2$O$_5$] with wind direction was observed (Fig. 6), nor with air mass history from 5-day back trajectory calculations (Rolph, 2003), (Table 1) consistent with the measurement site being unbiased in terms of direction of local emissions of NO$_x$. No bias towards the BBCEAS instrument inlet direction (220°) was observed. Indeed, the probability distribution of wind directionality in Fig. 6 depicts that this was a common directional wind sector during REPARTEE-II, but only mixing ratios of <100 pptv for NO$_3$+N$_2$O$_5$ were measured at these times.

Figure 7 shows a summary of BBCEAS-derived components of the campaign dataset, along with some useful ancillary parameters for comparison. The maximum retrieved partitioned mixing ratios for the campaign in 1 h averages were 500 pptv for N$_2$O$_5$ and 10 pptv for NO$_3$. A negative correlation of night-time NO$_3$+N$_2$O$_5$ with NO (strong) and NO$_2$ (weak) and a positive correlation with O$_3$ are depicted...
Fig. 7. A summarised time series of measurements during REPARTEE-II. (a) LED-BBCEAS retrieved NO$_2$+N$_2$O$_5$ (red points), 1 h moving mean (black line). (b) Mixing ratios of NO, NO$_2$ and O$_3$; (c) mixing ratios of NO$_3$ and N$_2$O$_5$ as inferred from measurements in panels (a) and (b). Panel (c) Depicts the standard deviation of the vertical velocity variance ($\sigma^2_w$), a measure of turbulence in the vertical direction, as indicated by nearby lidar measurements (see text) at its nearest vertical level of 195m, and by the ultrasonic anemometer (S.A.) above the tower. Panel (e) shows nitrous acid (HONO), nitric acid (HNO$_3$) and nitrate aerosol (NO$_3^-$) mixing ratios for comparison. Hatched areas depict no measurement.

in Fig. 8. Panel (b) shows a direct consequence of the reaction of NO$_3$ with NO. The negative correlation with NO$_2$ is likely to be a result of an increased NO source for NO$_2$ production coinciding with a decrease in NO$_3$, as high periods of NO will act to decrease NO$_3$ and increase NO$_2$.

Turbulence measurements were used to indicate the meteorological regimes encountered in the NBL. The lidar is expected to slightly underestimate the vertical velocity variance compared to the sonic anemometer (Barlow et al., 2010) under more stable conditions due to the differing sampling
rate (4 s compared to 20 Hz respectively), this divergence is more apparent in Fig. 7. Figure 9 shows that \([\text{NO}_3+\text{N}_2\text{O}_5]\) is proportional to the inverse of both the mean night-time and maximum night-time \(\sigma^2_w\). This supports the theory that night-time \([\text{NO}_3+\text{N}_2\text{O}_5]\) enhancements occur when conditions are stable, turbulence is suppressed, and the BT tower measurements are somewhat decoupled from emissions from the surface.

### 3.4 Calculated lifetimes of \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\)

The lifetimes of \(\text{NO}_3\), \((\tau(\text{NO}_3))\) and \(\text{N}_2\text{O}_5\), \((\tau(\text{N}_2\text{O}_5))\) are useful for determining the magnitude of sources and sinks of \(\text{NO}_3\) in a particular regime. The lifetimes derived using Eqs. (5) and (6) rely on the assumption of a steady state for the production and loss of \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\) and have been used in many previous studies to derived useful parameters regarding night-time \(\text{NO}_3\).

\[
\tau(\text{NO}_3) = \frac{[\text{NO}_3]}{k_2[O_3][\text{NO}_2]} \tag{5}
\]

\[
\tau(\text{N}_2\text{O}_5) = \frac{[\text{N}_2\text{O}_5]}{k_2[O_3][\text{NO}_2]} \tag{6}
\]

It has been shown (Brown et al., 2003a) that for conditions such as those during REPARTEE-II, where moderate to high \(\text{NO}_2\) (mean night-time \(\text{NO}_2 \sim 20\) ppbv) and low temperatures are experienced, although \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\) are very likely to be in equilibrium (see Sect. 3.2), the time for \(\text{NO}_3\) and/or \(\text{N}_2\text{O}_5\) concentrations to reach a steady state with equal production and loss terms is likely to be several hours. This assumption was tested using a simple box model (not shown) and indeed, the derivatives of the \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\) mixing ratios were found to confirm that a steady state is unlikely to be established over the period of one night. In addition, a measurement over a small volume such as that sampled by LED-BBCEAS diverges from steady state through transport and turbulence, as well as chemical effects. Therefore, a steady state approximation was considered unlikely to be appropriate for much of this study. It was therefore deemed prudent to compare calculations of both a steady state lifetime and a lifetime for \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\) taking into account the likely absence of a steady state \((\tau^*)\) as per Eq. (7) (McLaren et al., 2010).

\[
\tau^*(\text{N}_2\text{O}_5 \text{ or } \text{NO}_3) = \frac{[\text{N}_2\text{O}_5 \text{ or } \text{NO}_3]}{k_2[O_3][\text{NO}_2](\frac{d[\text{NO}_3]}{dt}) - \frac{d[\text{N}_2\text{O}_5]}{dt})} \tag{7}
\]

The differential of \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\) with respect to time was calculated using a 3 point average of the 15 s BBCEAS data. The result of this calculation was found to be insensitive to using larger moving averages as the measured mixing ratios were highly variable on many temporal scales. It is noted that both lifetime analyses neglect any influence of transport effects. Both determinations of \(\tau_{ss}\) via Eqs. (5) and (6); and \(\tau^*\) using Eq. (7) (for both \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\)) have been performed here, and in contrast to the only previous reported example of this comparison (McLaren et al., 2010), a significant difference in the results of the two methods of lifetime calculation is reported here, with the latter resulting in highly variable lifetimes, with a mean value lower by approximately 75% of its steady state counterpart. This can be seen by the diurnal trends in Fig. 10. Of particular note is that the mean lies above the 95th percentile for much of the \(\tau^*\) (non-steady state) for both \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\) lifetimes, particularly in the second half of the night, showing the highly variable nature of \(\tau^*\). This indicates that transport effects are likely to be a dominant factor influencing \(\text{NO}_3\) and \(\text{N}_2\text{O}_5\) mixing ratios at this site.
Fig. 10. Hourly average diurnal trend plots and their statistical ranges for (a) NO$_3$+N$_2$O$_5$ mixing ratios; (b) $F$(NO$_3$); (c) $\tau_{ss}$*(NO$_3$)min and (d) non steady-state $\tau^*$(NO$_3$)/s; (e) $\tau_{ss}$*(N$_2$O$_5$)/min; (f) non steady-state $\tau^*$(N$_2$O$_5$)/s; for derivations of these values, see text. The large variability in both datasets is shown, as the mean being greater than the 95th percentile for much the non-steady-state treatment data. A shorter and more highly variable lifetime is determined by the non-steady state analysis.

3.5 Aerosol uptake of N$_2$O$_5$

The inability to assume a steady state under the [NO$_2$] and typical UK autumnal temperature conditions of REPARTEE-II renders the determination of the N$_2$O$_5$ uptake coefficient, $\gamma$(N$_2$O$_5$), difficult as many widely used determinations of $k_{het}$ require the assumption of a steady state between NO$_3$ and N$_2$O$_5$. The rate of uptake for Reaction (R4), $k_{het}$, was derived from Eq. (8) (Riemer et al., 2003):

$$k_{het} = \frac{1}{4}c_{N_2O_5}S_A\gamma(N_2O_5)$$  
(8)

Here, $c_{N_2O_5}$ is the mean molecular velocity of N$_2$O$_5$ and $S_A$ is the integrated surface area for all particles of <1 µm diameter, (see Sect. 2.6) which takes into account the diffusion limitations to particles (Bertram and Thornton, 2009). $S_A$ ranged from 200–1000 µm$^2$ cm$^{-2}$. The uptake coefficient, $\gamma(N_2O_5)$, was derived from a parameterisation detailed in Riemer et al. (2003) as a function of relative humidity (RH) and the ratio of mass fractions of sulphate and nitrate in aerosols (Nemitz et al., 2010a). Both the mass fraction and $S_A$ (Fig. 11) were highly variable during the campaign. Figure 11 shows a time series of calculated $k_{het}$ (Fig. 11), along with measured $S_A$ and calculated $\gamma(N_2O_5)$. Mean $k_{het}$ from these measurements was 0.17 ± 0.08 min$^{-1}$.

The short lifetimes of N$_2$O$_5$ depicted suggest its rapid conversion to HNO$_3$ via Reaction (R4). Reaction of N$_2$O$_5$ with H$_2$O on aerosol surfaces is considered to be the principal night-time pathway for HNO$_3$ formation, although there is likely to be some contribution from the reaction of NO$_3$ with anthropogenic VOCs (such as alkenes). Assuming that each NO$_3$ radical goes onto form N$_2$O$_5$ and then hydrolyses to two HNO$_3$ molecules, the total night-integrated contribution to HNO$_3$ ([HNO$_3$]$_{total}$) from Reaction (R4) can be calculated via two methods (Wood et al., 2005).

$$[\text{HNO}_3]_{total} = 2 \int \frac{[N_2O_5]}{\tau_{ss}(N_2O_5)} dt \approx 2 \int k_2[NO_2][O_3] dt$$  
(9)

The total integrated mixing ratio of HNO$_3$ was calculated for each night (sunset to sunrise) by both methods for complete nights where required ancillary datasets exist, (see Table 2) and was found to range from 2.4–11.3 ppbv via calculation using BBCEAS-inferred N$_2$O$_5$ mixing ratios and 6.6–13.5 ppbv using NO$_2$ and O$_3$ mixing ratios as measured during the campaign with the latter approach giving an average of 2 ppbv per night greater than the former. These differences serve to illustrate the shortcomings of a steady-state approximation in this instance. This difference could be due to the large calculated error in the transmission efficiency of the BBCEAS inlet potentially leading to underestimations in
Table 2. Total calculated night-time [HNO₃], using [N₂O₅] and \( \tau_{ss}(N₂O₅) \), (2nd column); and using \( k₂ \), [NO₂] and [O₃], (3rd column) of Eq. (9) for nights where a continuous dataset for all parameters were used.

| Night              | [HNO₃] \_\_ \_ /ppbv | [HNO₃] \_\_ \_ /ppbv |
|--------------------|-----------------------|-----------------------|
| 30 Oct–31 Oct      | 7.0±1.5               | 8.6±0.26              |
| 31 Oct–1 Nov       | 2.4±0.50              | 7.0±0.2               |
| 1 Nov–2 Nov        | 9.1±1.9               | 10.5±0.3              |
| 5 Nov–6 Nov        | 9.2±1.9               | 9.8±0.3               |
| 6 Nov–7 Nov        | 4.5±1.0               | 6.6±0.2               |
| 7 Nov–8 Nov        | 11.3±2.4              | 13.5±0.4              |

[N₂O₅], but is most likely due to the approximations made in assuming a steady state for calculation of \( \tau_{ss}(N₂O₅) \) (see Fig. 10), or losses other than to HNO₃ may be present, such as those involving NO₃ reactions. Aerosol surface areas, shown in Fig. 11 depict that these are not too small to be rate limiting. It should also be considered that reaction of HNO₃ with ammonia or sea salt would yield a significant aerosol lifetime, and \( 8.6 \pm 0.26 \) ppbv using NO₂ and O₃ mixing ratios which accounts for approximately 22 \( \mu \)gm⁻¹ HNO₃ as an integrated total for this night. As the mean HNO₃ mixing ratio measurements was approximately 0.17 ppbv during this night (Nemitz et al., 2010), calculated [HNO₃]₁₀ₐ₅ represents a very small fraction of the total step-function integration of the measured mean mixing ratio, of the order of 0.001%. HNO₃ is more likely to be formed once the air mass has travelled further from emissions sources than at this site, as longer transport and reaction times may be required for this to become a more dominant HNO₃ formation pathway.

4 Summary and conclusions

In this paper we have demonstrated the instrumental technique of LED-BBCEAS in a sustained deployment in a month-long field campaign. To our knowledge, these are the first measurements of NO₃ and N₂O₅ above a developed megacity, and give an in-situ insight into the complexity of urban nocturnal boundary layer chemistry in such a region. The instrument demonstrated the ability to measure make continuous sensitive measurements over periods long enough to perform quantitative diurnal trend analyses and produced an urban dataset useful for those wishing to test chemistry models on urban areas. A large variation in night-time concentrations was observed, with some high N₂O₅ (<800 ppbv) concentrations measured. N₂O₅ appears to be very reactive and calculated lifetimes were short (of the order of minutes). In addition to nights where large enhancements are observed, there were nights when the BBCEAS instrument was performing well and concentrations of N₂O₅ were below the LOD of around 2 pptv. These nights are of additional interest as they suggest an extremely large sink to source ratio, which appears to be unaccounted for by observed aerosol components. The complexity of the data rendered typical steady state analysis difficult and demonstrate the challenge of interpreting in-situ observations of short-lifetime species in a highly heterogeneous environment. The equilibrium between NO₃ and N₂O₅ was calculated from NO₂ and ambient temperature to be weighted heavily in favour of N₂O₅ and the maximum mixing ratio of NO₃ was 10 pptv averaged over 1 h. A positive correlation between the magnitude of [NO₃+N₂O₅] and [O₃] was observed along with a strong negative correlation with [NO] but it does not appear to be a simple function. A combination of chemical and physical sources and sinks appear to be important in determining [NO₃] and [N₂O₅], a theory supported by the negative correlation with a proxy for night-time turbulence. The short NO₃ and N₂O₅ lifetimes and high NO₂ conditions result in a low value of \( F(NO₃) \). However, this does not necessarily mean night-time nitrate chemistry is negligible, rather that the sinks for N₂O₅ may be very rapid, leading to a potential source of nitrate in aerosols. Departures from the NO₃ N₂O₅ equilibrium do not appear to be significant, though the high NO₂ and low temperatures slow the system’s approach to a steady-state. A comparison between steady state and non-steady state analyses of the lifetimes of N₂O₅ and NO₃ was performed and it was found that the system was unlikely to be in steady state, rendering steady state analysis of heterogeneous loss of N₂O₅ difficult. Estimates of the heterogeneous uptake of N₂O₅ suggest a small contribution of around 8 ppbv per night of HNO₃ via this route and suggest that potential alternate pathways for significant losses of NO₃ or N₂O₅ exist, perhaps through aerosol formation. These results demonstrate the complexity of small scale NBL...
chemical processes and how they may contribute to NO\textsubscript{y} loss budgets.

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