



Interferences in photolytic NO₂ measurements: explanation for an apparent missing oxidant?

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Abstract. Measurement of NO₂ at low concentrations (tens of ppt) is non-trivial. A variety of techniques exist, with the conversion of NO₂ into NO followed by chemiluminescent detection of NO being prevalent. Historically this conversion has used a catalytic approach (molybdenum); however, this has been plagued with interferences. More recently, photolytic conversion based on UV-LED irradiation of a reaction cell has been used. Although this appears to be robust there have been a range of observations in low-NO_x environments which have measured higher NO₂ concentrations than might be expected from steady-state analysis of simultaneously measured NO, O₃, *j*NO₂, etc. A range of explanations exist in the literature, most of which focus on an unknown and unmeasured “compound X” that is able to convert NO to NO₂ selectively. Here we explore in the laboratory the interference on the photolytic NO₂ measurements from the thermal decomposition of peroxyacetyl nitrate (PAN) within the photolysis cell. We find that approximately 5 % of the PAN decomposes within the instrument, providing a potentially significant interference. We parameterize the decomposition in terms of the temperature of the light source, the ambient temperature, and a mixing timescale (~ 0.4 s for our instrument) and expand the parametric analysis to other atmospheric compounds that decompose readily to NO₂ (HO₂NO₂, N₂O₅, CH₃O₂NO₂, IONO₂, BrONO₂, higher PANs). We apply these parameters to the output of a global atmospheric model (GEOS-Chem) to investigate the global impact of this interference on (1) the NO₂ measurements and (2) the NO₂ : NO ratio, i.e. the Leighton relation-

ship. We find that there are significant interferences in cold regions with low NO_x concentrations such as the Antarctic, the remote Southern Hemisphere, and the upper troposphere. Although this interference is likely instrument-specific, the thermal decomposition to NO₂ within the instrument's photolysis cell could give an at least partial explanation for the anomalously high NO₂ that has been reported in remote regions. The interference can be minimized by better instrument characterization, coupled to instrumental designs which reduce the heating within the cell, thus simplifying interpretation of data from remote locations.

1 Introduction

Accurate quantification of atmospheric nitrogen oxide (NO_x, which is predominantly NO + NO₂ but includes small contributions from NO₃, N₂O₅, HONO, HO₂NO₂, etc.) concentrations is crucial for many aspects of tropospheric chemistry. NO_x plays a central role in the chemistry of the troposphere, mainly through its impact on ozone (O₃) and hydroxyl (OH) radical concentrations. O₃ is a greenhouse gas (Wang et al., 1995) that adversely impacts human health (Mauzerall et al., 2005; Skalska et al., 2010) and leads to ecosystem damage (Ainsworth et al., 2012; Ashmore, 2005; Hollaway et al., 2012). It is produced through the reaction of peroxy radicals (HO₂ and RO₂) with NO (Dalsøren and Isaksen, 2006; Lelieveld et al., 2004). The OH radical is the primary oxidizing agent in the atmosphere (Crutzen, 1979; Levy, 1972) as

it controls the concentration of other key atmospheric constituents such as methane (CH₄), carbon monoxide (CO), and volatile organic compounds (VOCs). It is both produced through the reaction of NO with HO₂ and is lost by its reaction with NO₂. NO₂ itself also poses a public health risk (Stieb et al., 2002). Thus, understanding the sources, sinks, and distribution of NO_x is of central importance to understanding the composition of the troposphere.

During the daytime there is fast cycling between NO and NO₂, due to the rapid photolysis of NO₂ and the reaction of NO and O₃ to form NO₂ (Kley et al., 1981).

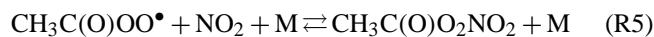


Placing NO₂ into steady state and assuming that these three reactions are the only chemistry occurring leads to the Leighton relationship, ϕ (Leighton, 1961), in Eq. (1).

$$1 = \frac{k_1 [\text{NO}][\text{O}_3]}{j_{\text{NO}_2} [\text{NO}_2]} = \phi \quad (1)$$

The quantities in the relationship are readily measured and deviations from unity have been interpreted to signify missing (i.e. non-ozone) oxidants of NO. These perturbations have been used to infer the existence of oxidants such as peroxy radicals, halogen oxides, and the nitrate radical in the atmosphere, which have subsequently been confirmed by direct measurement (Brown et al., 2005; Mannschreck et al., 2004; Trebs et al., 2012; Volz-Thomas et al., 2003).

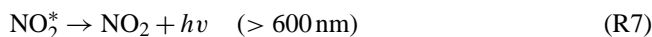
The concentration of NO_x varies from > 100 ppb (parts per billion) next to roads (Carslaw, 2005; Pandey et al., 2008) to low ppt (parts per trillion) in the remote atmosphere (Lee et al., 2009). Direct transport of NO_x from polluted to remote regions is not efficient, because NO_x is removed from the atmosphere on a timescale of around a day by the reaction of NO₂ with OH and the hydrolysis of N₂O₅ on aerosol surfaces (Brown et al., 2004; Dentener and Crutzen, 1993; Riemer et al., 2003). Instead, reservoir species such as peroxyacetyl nitrate are made in polluted regions (where concentrations in both NO_x and peroxyacetyl precursors such as acetaldehyde are elevated) and are subsequently transported to remote regions, where they thermally break down to release NO_x (Fischer et al., 2014; Moxim et al., 1996; Roberts et al., 2007).



The equilibrium between peroxyacetyl radicals, NO₂, and PAN (Reactions R4 and R5) is highly temperature-sensitive. Thus, the PAN lifetime changes from 30 min at 25 °C (Bridier et al., 1991) to 5.36 years at -26 °C (Kleindienst, 1994).

Measurements of NO_x species in the remote atmosphere have been made over the last 40 years. Multiple in situ techniques are available such as LIF (laser-induced fluorescence;

Matsumoto and Kajii, 2003), CRDS (cavity ring-down spectroscopy; Osthoff et al., 2006), and QCL (quantum cascade laser; Tuzson et al., 2013). However, probably the most extensively used approach has been based on the chemiluminescent reaction between NO and O₃. This exploits the reaction between NO and O₃ (Reaction R6), which generates an electronically excited NO₂^{*} (²B₁) molecule which decays to its ground state through the release of a photon (Reaction R7) (Clough and Thrush, 1967; Clyne et al., 1964).



This forms the basis of the chemiluminescence analysis of NO (Drummond et al., 1985; Fontijn et al., 1970; Kelly et al., 1980; Peterson and Honrath, 1999). The number of photons emitted by the decay of excited NO₂^{*} to NO₂ is proportional to the NO present before reaction with O₃ (Drummond et al., 1985). The photons emitted are detected by a cooled photomultiplier tube (PMT) with the sample under low pressure (to maximize the fluorescence lifetime of the NO₂^{*}) in order to yield a signal which is linearly proportional to the number density of NO in the sample gas (Fontijn et al., 1970). Quenching of the NO₂ excited state occurs due to a range of atmospheric compounds (N₂, Ar, CO, CO₂, CH₄, O₂, He, H₂, and H₂O) (Clough and Thrush, 1967; Drummond et al., 1985; Zabielski et al., 1984). Quenching is minimized by operating at high vacuum to reduce collision probability. However, quenching still occurs; thus, it is necessary to calibrate the detectors response (sensitivity) to a known concentration of NO regularly. Changing ambient humidity in the sample has a marked effect on drift in sensitivity and necessitates being corrected for, sample drying, or sample humidifying to mitigate.

With NO chemiluminescence analysers it is also possible to analyse NO₂ regarding whether it is first converted to NO, either catalytically (typically heated molybdenum) as in Reaction (R8) (Villena et al., 2012) or by converting NO₂ into NO photolytically (Ryerson et al., 2000), exploiting Reaction (R1).



To measure NO and NO₂, the sample flows through the NO₂ to NO converter (of either type) to the reaction chamber, where the NO + O₃ reaction occurs and the decay of NO₂^{*} to NO₂ allows the concentration of NO + NO₂ in the air to be measured. Then, the sample flow is switched to bypass the NO₂ to NO converter. Now, only NO present in the sample is detected in the chemiluminescence reaction. The NO signal is then subtracted from the NO + NO₂ (NO_x) signal, giving the NO₂ signal. Both techniques for converting NO₂ to NO can be subject to interference. Catalytic conversion has been well documented to have positive responses to NO_y species such as nitrous and nitric acid as well as organic nitrates (Dunlea et al., 2007; Grosjean and Harrison, 1985; Winer

et al., 1974). Photolytic conversion has been demonstrated to be affected by a negative interference from the photolysis products of VOCs reacting with NO within the photolysis cell (Villena et al., 2012) and has a possible positive interference from thermal decomposition of NO_y (McClenny et al., 2002).

Measurements of NO and NO₂ have been made in a range of low-NO_x locations using the chemiluminescence technique (Huntrieser et al., 2007; Lee et al., 2009; Peterson and Honrath, 1999; Zhang et al., 2008). Measurement of NO_x by the NO chemiluminescent technique in these locations can be challenging (Yang et al., 2004), often operating close to the limit of detection (LOD). Corrections may be necessary for oxidation of NO to NO₂ in the inlet by O₃ and, more problematically, by peroxy radicals produced by, for example, PAN decomposition within the inlet. This oxidation acts to perturb the observed Leighton relationship in two ways: by release of NO₂ and by oxidation of NO by peroxy radicals to NO₂. Where NO and NO₂ are measured by one channel by switching the UV elements on and off periodically, there may be a greater discrepancy in the Leighton ratio as NO is oxidized to NO₂ by peroxy radicals produced from the thermal decomposition of PAN within the still warm, but not illuminated, NO₂ converter. Small corrections for a NO offset are typically made by assuming it is equivalent to a stable night-time value in remote regions (Lee et al., 2009), whilst the NO₂ offset is usually deduced from sampling a source of zero air (which may be used for NO if a stable night-time value is not obtainable). Correction for changing NO₂ photolytic conversion efficiency due to O₃ in the photolysis cell (see Sect. 2.2, Eq. 2) might also be appropriate when O₃ varies greatly or calibration in ambient air is not possible, i.e. in zero air, which contains no O₃.

Yang et al. (2004) identified a statistical source of error when determining NO and NO₂ by chemiluminescence. Yang et al. (2004) demonstrate that uncertainties in averaging signals which fall below ~ 10 times the 1σ limit of detection result in large errors in the NO₂ : NO ratio, with extreme bias exhibited when signals fall below a signal-to-noise ratio ~ 5 . This work shows that using weighted geometric mean of PMT counts to determine NO and NO_x (and hence NO₂), rather than the unweighted or arithmetic mean, results in the least measurement bias. This error is in addition to any artifact signal biasing either NO or NO₂, as well as uncertainties in, for example, the NO₂ conversion efficiency.

Some measurements made in remote (low-NO_x) locations, such as Antarctica and over the open ocean have at times identified an unexplained imbalance in the Leighton relationship (Bauguitte et al., 2012; Frey et al., 2013, 2015; Hosaynali Beygi et al., 2011). Measured NO₂ concentrations are higher than would be expected from the observed NO, O₃, and j NO₂ along with reasonable concentrations of other oxidants (peroxy radicals, halogen oxides). Various explanations have been posited in order to overcome the apparent oxidation gap, typically relying on an unmeasured oxidant, or

pushing known chemistry into theoretical realms by theorizing high turnover of short-lived species (Cantrell et al., 2003; Frey et al., 2013, 2015; Hosaynali Beygi et al., 2011). An alternative explanation would be an unknown interference on the NO₂ measurement increasing its apparent concentration, if this interference has a similar diurnal concentration profile.

Here we explore the potential of PAN (as a probe for other NO_y species) to interfere with chemiluminescence NO₂ measurements. In Sect. 2 we provide details of the experimental studies undertaken. In Sect. 3 we describe the results of experiments introducing differing concentrations of PAN into NO₂ converter/chemiluminescence systems. In Sect. 4 we analyse the potential for errors with different NO_x systems to investigate the interference on the measurement of NO₂ from PAN. In Sect. 5 we evaluate the impact of this interference on NO₂ measurements and on the Leighton relationship through the use of a global model. Lastly, we provide conclusions in Sect. 6.

2 Experimental details

In Sect. 2.1 we describe the two chemiluminescence instruments used for the analysis. The NO₂ converters are described in Sect. 2.2. In Sect. 2.3 the LIF instrument used to provide a reference analysis is described. We describe our protocol for production of PAN by acetone photolysis in Sect. 2.4. We provide details of the zero-air generation in Sect. 2.5. Then in Sect. 2.6 we describe the experimental methodology of PAN interference tests and Sect. 2.7 describes residency time tests.

2.1 Instrumentation

Chemiluminescent measurements were performed using dual-channel Air Quality Design Inc. (Golden, Colorado, USA) instruments equipped with UV-LED-based photolytic NO₂ converters – commonly referred to as blue light converters (BLCs). Two similar instruments were employed: the “laboratory” NO_x analyser (Sect. 2.1.1), on which the majority of the experiments were performed, and the “aircraft” NO_x analyser (Sect. 2.1.2), on which only temperature-controlled BLC experiments were performed.

Both instruments feature independent mass-flow-controlled sample flows on each channel (NO and NO_x). The wetted surfaces of the instrument are constructed of 1/4 in. PFA tubing, with the exception of 316 stainless steel unions/MFC internals.

Both instruments are calibrated for NO by internal, automatic standard addition. Calibration for NO₂ converter efficiency is by internal automatic gas-phase titration of NO with O₃ to form NO₂ with the NO signal measured with the BLC lamps active and inactive as described by Lee et al. (2009). Artifacts in both NO and NO₂ are measured whilst sampling zero air.

2.1.1 Laboratory NO_x analyser

The laboratory NO_x analyser from Air Quality Design Inc. (AQD) is a custom dual-channel instrument designed for fast response and very low limit of detection (LOD) of 2.5 pptv averaged over 1 min. The dual-channel design means that there are effectively two separate NO chemiluminescence instruments working in parallel. Both channels have identical flow paths and share identical duplicate equipment: ozonizers, MFCs, PMTs, etc. Both channels share the same vacuum pump – an Edwards XDS 35i. One channel is equipped with a BLC immediately in front of the MFC flow control/low-pressure side of the system. It is possible to analyse NO with one channel and NO_x with the other to provide a constant, fast measurement (1 Hz) of NO and NO₂. Alternatively, a single channel can be used with the BLC in a switching mode so that it is active for only 40 % of the duty cycle to provide NO and NO₂ measurement – the other 60 % of the duty cycle is devoted to NO (40 %) and measuring zero (20 %). In this case the second channel might be used for NO_y by connection of a catalytic converter to the inlet as is the setup at the Cape Verde Atmospheric Observatory GAW station (Lee et al., 2009). In these experiments both modes were used in order to replicate different instrument designs: a switching mode with a 40 % duty cycle of the NO₂ converter and a total sample flow of 1 standard L min⁻¹, and a parallel mode with a 100 % duty cycle of the NO₂ converter with a total sample flow of 2 standard L min⁻¹. Chemiluminescent zero is determined for 30 s every 5 min. A chemiluminescent zero is acquired by increasing the NO + O₃ reaction time by diverting the sample flow to a pre-reactor, where greater than 99 % of NO is reacted. The pre-reactor is a PFA volume immediately prior to the detection cell through which usually only O₃ flows but which, during zero, both the sample gas and O₃ flow. In this way, photon counts arising from slower (~2 orders of magnitude) alkene + O₃ reactions are accounted for and subtracted from the NO signal.

The nominal sensitivity of the instrument is 3.5 and 4.0 counts s⁻¹ ppt⁻¹ (± 5 %) on channel 1 (NO) and channel 2 (NO and NO_x) respectively. The ± 5 % uncertainty arises from the error in the NO standard concentration, the error of the sample and standard mass flow controllers, and the reproducibility of the sensitivity determination. Sensitivity drift was mitigated by performing all experiments under an overflow of stable zero air; thus, no changes in, for example, humidity, which affects chemiluminescent quenching, occurred. The 1 min LOD (2σ) is ~ 2.5 pptv.

2.1.2 Aircraft NO_x analyser

The aircraft NO_x analyser, also from AQD, operates similarly to the lab NO_x analyser, with some alterations to make it suited to aircraft operation. These changes do not affect its use on the ground. It can therefore be considered analogous to the lab NO_x analyser with the exception of the BLC.

This is of a non-standard design that uses six more powerful UV diodes which require active Peltier/forced air cooling in order to maintain an operating temperature close to ambient. The special requirements for this NO₂ converter are primarily because of the high sample flow rates needed to measure NO_x fluxes on an airborne platform at reduced pressure. However, in this study the sample flow rate was a constant 1 standard L min⁻¹ per channel at ambient temperature and pressure.

The nominal sensitivity of the instrument is 8.3 and 11.6 counts s⁻¹ ppt⁻¹ (± 5 %) on channel 1 (NO) and channel 2 (NO_x) respectively. The 1 min LOD (2σ) is ~ 1.0 pptv.

2.2 NO₂ converters

Photolytic converters for the two chemiluminescent systems were supplied by AQD and manufactured according to their proprietary standards (Buhr, 2004, 2007). Other photolytic NO₂ systems have also been developed with variations in design, but operating similarly (Pollack et al., 2011; Sadanaga et al., 2010). Experiments with either NO₂ converter were carried out at ambient temperature and pressure: 20 °C, 1 atm.

Photolytic converters employ Reaction (R1) to convert NO₂ to NO over a narrow wavelength band, thus providing a more selective NO₂ measurement to that provided by molybdenum catalysts (Ridley et al., 1988; Ryerson et al., 2000). The conversion efficiency is determined by Eq. (2), where t is the residence time within the photolysis cell. Here $k[\text{Ox}]$ is the concentration and rate constant of any oxidant that reacts with NO to form NO₂ (Ryerson et al., 2000).

$$\text{CE} = \left[\frac{jt}{jt + k[\text{Ox}]t} \right] \left[1 - \exp(-jt - k[\text{Ox}]t) \right] \quad (2)$$

The rate constant of photolysis of NO₂ (j), and thus the rate of production of additional NO beyond that in the original sample, is given in Eq. (3).

$$j(T) = \int_{\lambda \text{ min}}^{\lambda \text{ max}} F(\lambda) \sigma(\lambda, T) \phi(\lambda, T) d\lambda \quad (3)$$

In Eq. (3) j is the rate constant (s⁻¹), F is the spectral photon flux (photons cm⁻² s⁻¹ nm⁻¹), σ is the absorption cross section of NO₂ (cm²), ϕ is the quantum yield (dimensionless) of NO₂ photodissociation, and T is the temperature (Sander et al., 2011). The j value of the converter is practically determined by the irradiant photolysis power of the UV-emitting elements and how efficiently the power is used.

2.2.1 Standard BLC

Standard BLCs consist of two ends housing the UV LEDs (1 W, 395 nm, UV Hex, Norlux Corp.) within a heat sink to which a cooling fan is attached. The ends are bolted to

a central section with rubber gaskets forming an airtight seal. Within the centre section a propriety Teflon-like material block is housed which serves as a highly UV-reflective (> 0.95) cavity through which the sample gas flows (Buhr, 2007). On two of the opposing sides of the centre section are 1/4 in. Swagelok fittings acting as an inlet and outlet for the sample gas.

The volume of this illuminated sample chamber is 16 mL, which, with a standard flow rate of 1 standard L min⁻¹, gives a sample residence time of 0.96 s. Additional lamp end units were also supplied by AQD.

The conversion efficiency of the standard BLC with a sample flow of 1 standard L min⁻¹ was between 22 and 42 % ($j = 0.2... 0.6 \text{ s}^{-1}$) depending on the combination of lamp units used, whilst the external temperature of the converter was typically 34 to 45 °C. All experiments were carried out with sample gas at ambient temperature and pressure: 20 °C, 1 atm.

2.2.2 High-powered BLC

The high-powered BLC of the aircraft instrument is designed to operate at a higher flow rate (1.5 standard L min⁻¹) and lower pressure (~ 300 Torr), and therefore lower residence time, to that of the standard BLC to allow fast time resolution measurements from an aircraft. For this reason a greater number (six) of more powerful UV LEDs (2 W, 395 nm, Nichia Corp.) are used in order that the conversion efficiency is acceptable under these conditions. The lamps are placed evenly along two sides of a cylindrical cavity of the same highly UV reflective Teflon with inlets at opposing ends. The high-powered BLC lamps are actively (Peltier) cooled to 47 °C, and without Peltier cooling reached 77 °C. It was therefore possible to control the internal temperature of the BLC by varying the power supplied to the Peltier elements via the temperature controller.

The volume of this illuminated sample chamber is 10 mL, which, with a standard flow rate of 1 standard L min⁻¹, gives a sample residence time of 0.60 s, resulting in a conversion efficiency of 93 % ($j = 6.5 \text{ s}^{-1}$).

2.3 TD-LIF analyser

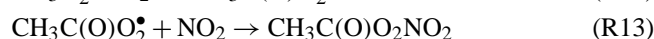
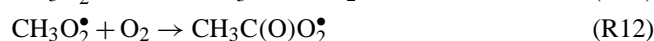
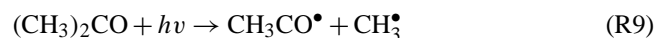
Laser-induced fluorescence (LIF) provides a direct NO₂ measurement, as opposed to chemiluminescence with conversion. A direct method of NO₂ determination to compare with the BLC NO₂ converters is desirable in order to properly know the source of any “artifact” NO₂ signal.

The thermal dissociation laser-induced fluorescence (TD-LIF) system is a custom instrument developed for aircraft and ground-based observations of NO₂, Σ PNs, Σ ANs, and HNO₃. A detailed description of the TD-LIF instrument can be found in Di Carlo et al. (2013), with a short description given here. The instrument uses LIF to detect NO₂ concentrations directly (Dari-Salisburgo et al., 2009; Mat-

sumoto and Kajii, 2003; Matsumoto et al., 2001; Thornton et al., 2000) and, coupled with a thermal dissociation inlet system, allows measurement of peroxy nitrates (Σ PNs), alkyl nitrates (Σ ANs), and HNO₃ after conversion into NO₂ (Day et al., 2002). The TD-LIF comprises four main parts: the laser source, the detection cell system, the inlet system, and the pumps. The laser source is a Nd:YAG double-pulse laser (Spectra-Physics, model Navigator I) that emits light at 532 nm with a power of 3.8 W, a repetition rate of 15 kHz, and 20 ns pulse width. The detection cell system comprises four identical cells, one for each compound class, to allow simultaneous measurements. Each cell is formed by a cube and two arms where the laser beam passes through the sample air flow in the centre of the cell. Perpendicular to both (laser beam and air flow) there is the detector that is a gated photomultiplier with lens and long-pass filters to optimize the fluorescence detection, minimizing the non-fluorescence light that reaches the detector (Di Carlo et al., 2013; Dari-Salisburgo et al., 2009). The pump system includes a Roots blower coupled to a rotary vane pump to maintain a flow of 6 L min⁻¹. The common inlet system is split into four channels: one at ambient temperature to measure NO₂, and the last three heated at 200, 400, and 550 °C to thermally dissociate Σ PNs, Σ ANs, and HNO₃ respectively into NO₂ (Di Carlo et al., 2013). To minimize quenching due to atmospheric molecules, and therefore increase the sensitivity of the TD-LIF, each cell is kept at low pressure (3–4 Torr). This increases the fluorescence lifetime and facilitates the time gating of the photomultiplier to further reduce the background (Dari-Salisburgo et al., 2009). The TD-LIF is routinely checked for background by an overflow of zero air in the detection cells and is calibrated by standard addition of a known amount of NO₂ from a cylinder (NIST traceable) diluted in zero air – the flow of both zero air and NO₂ being MFC-controlled. The time resolution of the measurements is 10 Hz and the detection limits are 9.8, 18.4, 28.1, and 49.7 pptv (1 s, $S/N = 2$) for NO₂, Σ PNs, Σ ANs, and HNO₃ cells respectively (Di Carlo et al., 2013).

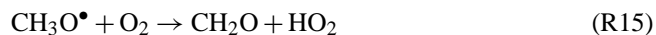
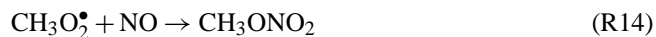
2.4 PAN preparation

In order to test the sensitivity of the instrument to peroxyacetyl nitrate (PAN) interferences, it was prepared by means of the photolysis of acetone and NO in air as described by (Meyrahn et al., 1987) and later by (Warneck and Zerbach, 1992; Flocke et al., 2005). Reactions (R9)–(R13) show the reaction sequence by which PAN is formed by acetone photolysis (Singh et al., 1995).



Here, NO₂ reacts stoichiometrically with the peroxyacetyl radical to form PAN. In practice, an excess of acetone is used to ensure that NO reacts completely. A dedicated “PAN generator”, as used by Whalley et al. (2004), was employed to produce a consistent source of > 95 % pure PAN (Flocke et al., 2005; Mills et al., 2007). The generator consists of flow control elements for the NO standard gas, the acetone flow, and the zero-air diluent flow; a thermostatted (30 °C) acetone permeation oven consisting of a reservoir of HPLC grade acetone (ACS grade, Acros) with a silicone permeation tube placed in the headspace through which zero air flows; and a Pyrex glass photolysis cell illuminated by UV light centred at 285 nm (Pen-Ray mercury lamp, UVP). The Pyrex functions to filter wavelengths below 290 nm within the photolysis cell, thus minimizing PAN photolysis (Mills et al., 2007).

A minor product also found in the photolysis of acetone is methyl nitrate, MeONO₂, which is typically approximately 1 % of the total yield (Mills et al., 2007). The proposed origin of the methyl nitrate (Williams et al., 2014) is shown in Reaction (R14) and formaldehyde, which is formed as a major by-product is shown in Reaction (R15) (Singh et al., 1995; Warneck and Zerbach, 1992).



Methyl nitrate is also found in the atmosphere through oceanic emission (Moore and Blough, 2002) and as a product of the thermal decomposition of PAN (Fischer and Nwankwoala, 1995; Roumelis and Glavas, 1992; Warneck and Zerbach, 1992).

All flow rates within the PAN generator were calibrated using a Gilian Gilibrator-2 air flow calibrator (Sensidyne). The PAN generator is capable of continuously producing 0.1–20.0 ppbv PAN. Linearity and mixing ratio of the PAN output was confirmed by a PAN-GC equipped with an ECD detector as described by Whalley et al. (2004), and also by complete reduction back to NO using a heated (325 °C) molybdenum catalyst (Thermo Environmental). The LIF instrument, described in Sect. 2.2.3, was used to quantify NO₂ produced directly in the PAN generator, which other authors (Flocke et al., 2005) have found to be the main impurity, with the results presented in Sect. 2.6 showing that ≤ 1 % NO₂ is emitted directly.

2.5 Zero air

Zero air was generated from dried (−40 T_d) compressed air by subsequent filtering through a cartridge of molecular sieve (13×, Sigma Aldrich) to ensure a consistent humidity throughout all experiments and was regenerated by heating to 250 °C for 24 h when necessary. A second filter cartridge placed after the molecular sieve was packed with Sofnofil (Molecular Products) and activated charcoal (Sigma Aldrich) in order to remove ozone, NO_x, and VOCs which may be

present in the compressed air. Zero air generated from the compressed air and filter cartridges system and zero air from an Eco Physics AG PAG 003 pure air generator (the industry standard) were both sampled by the NO chemiluminescence analyser. No difference in the counts of the NO analyser was observed between the two sources of zero air, both showing levels of NO below the LOD (< 2.5 pptv). Thus the NO content of both sources of zero air was considered to be insignificant and comparably low.

The NO₂ content of any zero air used is critical (more so than NO) in this study. In order to determine the NO₂ content of the zero-air sources, a direct measurement of NO₂ was required in order to avoid biasing the experimental procedure. The LIF instrument described in Sect. 2.2.3 was used to compare the zero-air sources (Table 1).

Zero air from both the PAG 003 and the filter stack was sampled by the NO₂ LIF analyser. Additionally, high-grade bottled zero air (BTCA 178, BOC speciality gases) was analysed for NO₂. Table 1 shows the photomultiplier counts per second whilst sampling 1.5 standard L min^{−1} of zero air. The dark counts of the PMT in the absence of laser light are typically less than 3 counts s^{−1}. The counts recorded are therefore the sum of any NO₂ fluorescence and scattered laser light. It is clear that the Sofnofil–carbon filter system has an advantage over both the PAG 003 and BTCA 178 zero-air sources in that a lower signal for NO₂ fluorescence was observed. Typical sensitivity of the LIF NO₂ channel was ~ 180 counts s^{−1} ppb^{−1}; thus, a 4–4.5 counts s^{−1} improvement in zero background equates to 22–25 ppt improvement in accuracy. Consequently, all dilution, zeroing, and PAN generation utilized the Sofnofil–carbon filter system.

2.6 Experimental procedure

The NO_x analysers were first calibrated for sensitivity/converter efficiency whilst sampling zero air by overflowing the inlet from the internal source prior to the experiment for at least 2 h. This is because the PAN from the generator is in zero air which has a very low dew point (−40 T_d) and the sensitivity of the NO_x analyser is reduced by high humidity in ambient sample gas. This means that switching the NO_x analyser from sampling ambient (humid) air to zero air causes the sensitivity to rise slowly and the humidity inside of the reaction cell to decrease. After establishing an NO flow (4.78 ppm NO in N₂, BOC speciality gases) of 0.5 mL min^{−1} into the PAN generator, the acetone flow was then adjusted to ~ 10 mL min^{−1} and the diluent flow of zero air adjusted to achieve the desired output mixing ratio. The internal zero air of the NO_x analyser was then shut off so that the NO_x analyser was sampling zero air from the PAN generator. Note that the total flow from the PAN generator always exceeded the sample requirements of the NO_x analyser with excess flow vented to the atmosphere. The system was then allowed to stabilize until a consistent NO value was recorded on the NO_x analyser. Next, the acetone photolysis lamp of the PAN

Table 1. Comparison of the NO₂ observed from measurement of three zero-air sources (Eco Physics AG PAG 003, BOC speciality gases BTCA 178, and Sofnofil–carbon–13× molecular sieve filters) by LIF. The average of ten 1 min averages is shown in pptv, normalized to the lowest reading, in raw PMT counts s⁻¹ as well as the standard deviation of those averages.

	PAG 003	BTCA 178	Sofnofil–carbon
Normalized concentration (pptv)	23.06	26.17	–
Signal (counts s ⁻¹)	88.10	88.66	83.95
Standard deviation	1.64	1.56	1.81

generator was switched on so that acetone was photolysed in the presence of NO to form PAN. Complete NO conversion to PAN was indicated by the fact that in all cases the NO signal measured by the NO_x analyser fell to ~ 0 ppbv after the acetone–NO mixture was illuminated by the photolysis lamp; > 99.5 % conversion was reported by Mills et al. (2007) with the same system. The diluent flow from the PAN generator was then varied to achieve PAN mixing ratios of between 0.2 and 1.3 ppbv. The corresponding NO₂ signal was recorded once stable. This procedure was repeated for various combinations of BLC lamps/assemblies and analyser operation modes.

In order to investigate any interference from unreacted acetone, the NO_x analyser was allowed to sample the output of the PAN generator with the photolysis lamp off, i.e. a flow of acetone and NO gas. No additional NO₂ signal relative to zero air was observed during these experiments at any mixing ratio of NO.

To investigate any interference from unreacted peroxy radicals left over from photolysis of excess acetone, produced in Reaction (R6), the NO_x analyser was allowed to sample acetone that had been photolysed within the PAN generator in the absence of NO. NO was then added downstream of the photolysis cell at the NO_x analyser inlet. In this way, any peroxy radicals exiting the PAN generator will cause a loss of NO and a production of NO₂ which can be quantified. No loss of NO or production of NO₂ was observed, indicating that peroxy radicals from acetone photolysis within the PAN generator do not have a long enough lifetime (self-reaction or surface loss) before entering the BLC to cause an interference or “PERCA-like” (calibrated peroxy radical chemical amplifier; Clemitshaw et al., 1997) chemistry within the BLC.

It should be noted that sampling acetone does cause a small increase in the chemiluminescent zero count (a few hundred counts on a signal of ~ 4000) of the NO_x analyser as acetone does react with ozone; this chemiluminescence interference is known (Dunlea et al., 2007) and is accounted for in the measurements by the chemiluminescent zero taken every 5 min described in Sect. 2.1.1.

To test whether the PAN generator produced any NO₂ directly (i.e. rather than as a consequence of decomposition of PAN to NO₂ within the BLC), a direct measurement of NO₂ was employed using the TD-LIF described in Sect. 2.2.3. The

measured signal relative to pure zero air was measured in the LIF NO₂ channel when sampling various mixing ratios of PAN from the generator as shown in Fig. 1. It is evident that the NO₂ signal observed while sampling PAN from the generator lies within the noise of the zero signal measurement. In this case each point represents a 10 min average, as does the zero measurement. With an averaging time of 10 min the theoretical limit of detection is estimated to be less than 0.1 pptv – taking a 10 Hz LOD of 9.8 pptv, and averaging 6000 points (i.e. 10 min), the precision improves by a factor of approximately $1/\sqrt{n}$, where n is the number of points averaged (Lee et al., 2009). It is therefore conservatively estimated that < 10 ppt NO₂ at 1000 ppt PAN (< 1 %) is produced by the PAN generator. This is less than previously estimated (Mills et al., 2007), albeit at higher PAN mixing ratios and lower residence times within the acetone photolysis cell with the same generator.

It was therefore determined that only PAN could be an interfering species in the BLC from the PAN generator. The small percentage of methyl nitrate which may be produced is discounted due to it being less thermally labile than PAN itself. Additionally, the percentage interference observed is significantly greater than any expected or reported methyl nitrate yield from PAN synthesis by acetone photolysis i.e. 1 % (Mills et al., 2007). In the following discussion we address the possibility of photolytic and thermal dissociation of PAN or methyl nitrate to NO₂ and subsequently NO within the photolytic convertor.

2.7 Residence time

The residence time of PAN in the 2.7 m PFA inlet linking the PAN generator to the NO_x analysers (shown in Table 2) was varied by varying the flow rate. This was achieved by altering the sample flows through the each of the NO_x analyser channels (which share a common inlet). Residence times were 2.10 and 1.05 s⁻¹ for one- and two-channel operation respectively.

3 Impact of PAN on NO₂ measurements

In this section we describe experiments investigating the impact of PAN on the two NO₂ instruments measurements. In Sect. 3.1 and 3.2 we explore the interference in the labora-

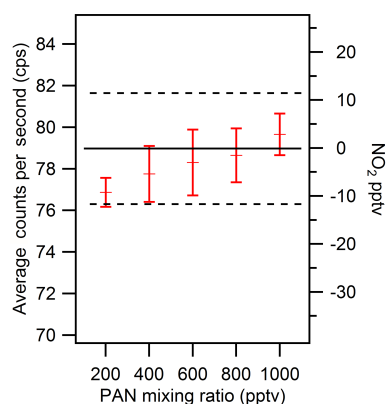


Figure 1. The average raw counts per second (left) and pptv (right) recorded by a LIF instrument when sampling various mixing ratios of PAN (in red) and zero air (black). The variance of the zero-air signal is also shown (dashed black). The average signal while sampling PAN falls within the noise of the zero signal.

Table 2. Effect of varying the residence time of PAN (1.0 ppb) within a 2.7 m PFA inlet on artifact NO₂ in switching mode.

	Inlet residence time (s ⁻¹)			
	0.84	1.05	1.40	2.10
NO ₂ (%)	5.4	5.4	5.2	5.3

tory instrument with a range of BLC convertors, eliminating any possibility for inlet effects in Sect. 3.3, and in Sect. 3.4 we explore the interference in the aircraft instrument which has an active cooling of the convertor. In Sect. 3.5 we investigate whether photolytic decomposition of PAN could lead to the interferences, and in Sect. 3.6 we investigate whether thermal decomposition could be the source.

3.1 Standard BLC and laboratory NO_x analyser in constant mode

PAN was introduced to the laboratory NO_x analyser, equipped with a BLC as described in Sect. 2.2.1, diluted in zero air through a range of mixing ratios. The resulting mixing ratio recorded by the analyser is presented in the following sections. Figure 2 shows that the artifact NO₂ signal is proportional to increasing PAN mixing ratios. An artificial signal corresponding to 8 to 25 % of the initial PAN mixing ratio was generated.

The percentage conversion of PAN to NO₂ is on average highest at the lowest converter efficiency and vice versa. Potential reasons for this effect are addressed in Sect. 3.6.

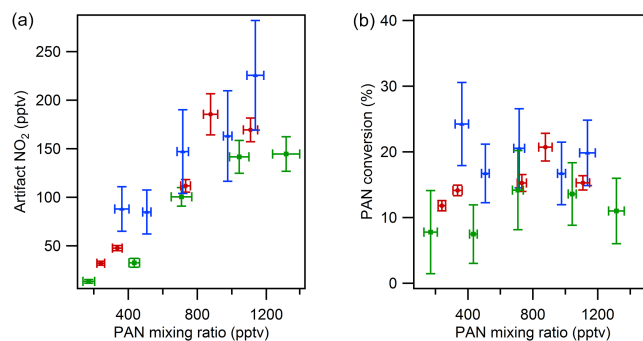


Figure 2. The measured NO₂ artifact signal (a) of the supplied PAN mixing ratio, and as a percentage (b), for three BLC units operating in constant mode separated by NO₂ conversion efficiency. Green: 41 %; red: 35 %; blue: 22 %.

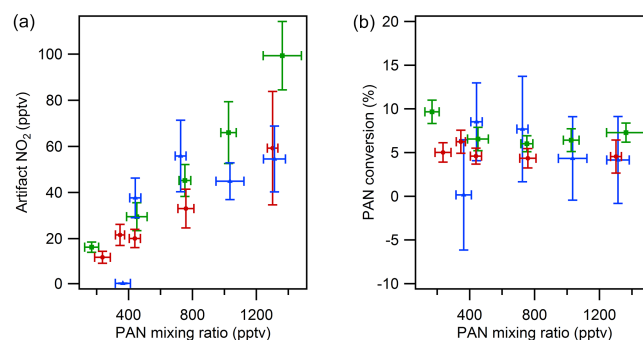


Figure 3. The measured NO₂ artifact signal as a function of the supplied PAN mixing ratio (a), and as a percentage (b), for three BLC units operating in switching mode separated by NO₂ conversion efficiency. Green: 41 %; red: 35 %; blue: 22 %.

3.2 Standard BLC and laboratory NO_x analyser in switching mode

Figure 3 shows the artifact NO₂ signal resulting from PAN using the same three BLC units operated in switching mode (40 % duty cycle). The percentage PAN conversion observed is lower in all cases than in the corresponding constant mode. This is likely due to the lower lamp temperature as a result of operating only 40 % of the time. The relationship between conversion efficiency and signal is not as clearly evident here as for constant mode operation (Fig. 2). It is possible that the greater variation in the measurement due to the lower amounts of NO₂ produced obscured any trend; however, it is clear that there is still a significant proportion of PAN measured as NO₂ – an average of 5.8 %.

3.3 Inlet residence time effects

It is not clear from either Fig. 2 or 3 whether the PAN decomposition occurs within the BLC exclusively or within the inlet of the system, as has been claimed previously (Fehsenfeld et al., 1987). Previous studies (Fehsenfeld et al., 1990;

Ridley et al., 1988; Sadanaga et al., 2010) have also reported a small PAN interference with photolytic converters, while some have found the contribution to the NO₂ signal from PAN to be negligible (Ryerson et al., 2000). Others (Val Martin et al., 2008) acknowledge the possibility for interference and estimate a small (2 to 4 pptv) positive bias. The photolytic converter designs in these studies vary greatly in their implementation and do not have the same ubiquity as BLCs used here, i.e. within the GAW network (Penkett et al., 2011).

Table 2 demonstrates that the residence time of PAN within the inlet does not affect the signal arising from PAN decomposition in our system. This rules out any significant contribution from PAN decomposition in the inlet to any artifact signal. The inlet in this case consists of ~ 2.7 m 1/4 in. PFA tubing shielded from light and held at 20 °C. In other applications – for example if the inlet is heated, contaminated, or has a very long residence time – it is quite possible that significant PAN decomposition occurs.

From these experiments it is evident that a significant NO₂ signal is observed when sampling PAN diluted in zero air. The signal seen corresponds to around 8 to 25 % of the PAN supplied, which represents a significant interference. The possibility of thermal decomposition within the inlet was ruled out.

3.4 High-powered and actively cooled photolytic NO₂ converter

Figure 4 shows the difference in NO₂ signal between the cooled and uncooled high-powered BLC described in Sect. 2.2.2. In all of the cooled cases the NO₂ measured was significantly lower than in the uncooled case; this accounts for any increased artifact (the signal recorded when sampling zero air) in the uncooled case. The conversion efficiency was 93 % for NO₂ → NO.

The effect of actively cooling the BLC lamps is significant, as apparent in the much lower NO₂ concentrations measured whilst sampling a range of PAN mixing ratios (Fig. 4). It is therefore evident that there is a significant effect of cooling the UV LEDs which acts to mitigate any signal arising from PAN.

3.5 Possible photolytic interferences of BLCs

There exists potential for photolytic interferences in photolytic converters, e.g. HONO, depending on their spectral overlap. Here we investigate this possibility with BLCs by taking the spectral output of a range of LED units against the absorption cross sections of various atmospheric compounds.

Spectral radiograms of the UV-LED elements of standard BLCs were obtained using an Ocean Optics QE65000 spectral radiometer coupled to a 2 π quartz collector. The spectrometer and collector optics were calibrated using an NIST traceable light source (OL FEL-A, Gooch and Housego) and ultra-linear power supply (OL 83A, Gooch and Housego).

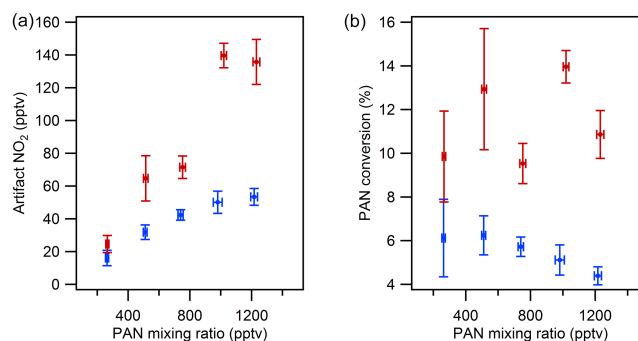


Figure 4. The measured NO₂ artifact signal as a function of the supplied PAN mixing ratio (a), and as a percentage (b), for the cooled (blue) and uncooled (red) high-powered BLC.

The light source is a 1000 W quartz–halogen tungsten coiled-coil filament lamp with spectral irradiance standard F-1128. The lamp was operated at 8 A DC (125 V), with the lamp–collector distance fixed at 50 cm. Calibration was carried out in a light-sealed chamber. Spectra of the BLC UV-LED lamps were taken within the same light-proof chamber with the same distance between the lamp and collector.

Figure 5 shows the spectral emission of six different BLC UV-LED units. These units ranged in age from new to nearing the end of their service life – i.e. the conversion efficiency of the whole BLC unit had fallen below acceptable limits. As the LED units age, the relative intensity of their outputs declines; this decrease in intensity can be due to dimming of the overall output or failure of individual array elements determined by visual inspection during operation. It should be pointed out, however, that the light intensity of the UV LEDs is not directly proportional to the NO₂ conversion efficiency of the complete whole BLC. Rather, the conversion efficiency is strongly dictated by the condition of the reflective Teflon-like cavity. For example, disabling one of the two lamps in a BLC does not reduce the conversion efficiency by half but by a much smaller percentage. Additionally, replacing the UV-LED elements of a converter whose conversion efficiency has dropped below 30 % with new lamps will not lead to a recovery of the conversion. Scrupulous cleaning of the reflective cavity with solvent and mild abrasion of the surface will, however, recover the conversion efficiency considerably. This is because Teflon-like block is a bulk reflector, that is, the UV penetrates up to ~ 1 cm into the material. It is this reflective property that makes most efficient use of the light and achieves high conversion efficiency at low residence times. Adsorption of any UV absorbing material on the surface reduces the reflectivity dramatically. Additionally, the Teflon block is somewhat porous and so contaminants may penetrate into the bulk (or at least below the surface). Solvent may remove most of the contaminants (though strong solvents can damage the block); however, those which have moved below the surface can only be removed by removing the contaminated layer of Teflon. The porosity also

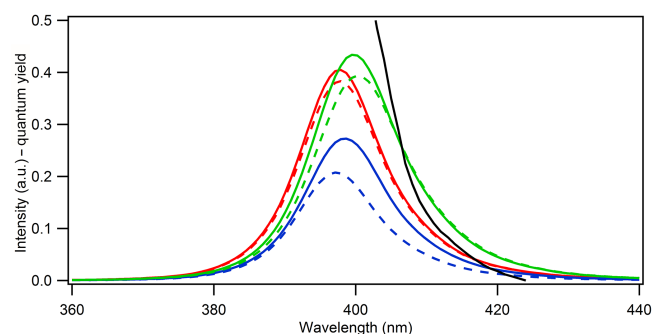


Figure 5. Spectral output vs. wavelength of two new, previously unused BLC lamps (no. 1, solid green; no. 2, dashed green), two used lamps (no. 3, solid red; no. 4, dashed red) still within acceptable conversion efficiency, and two which fall below acceptable limits (no. 5, solid blue; no. 6, dashed blue). The NO₂ quantum yield is shown in black.

gives rise to the artifact NO₂ signal as new material off-gases (as can other surfaces, e.g. LED lens). Sample gas may also diffuse into, and out of, the bulk very slowly giving a small memory effect as NO_x and NO_y exchange with the sample stream.

Figure 6 depicts the absorption cross sections of atmospheric nitrogen compounds (Sander et al., 2011) against the measured spectral output of UG5 UV-passing filter glass (Schott, 1997) used in lamp-type photolytic converter (PLC) optics (e.g. Eco Physics AG PLC 760), and the averaged measured spectral output of six individual BLC UV-LED arrays of varying running hours. Also shown is the NO₂ quantum yield (Gardner et al., 1987; Koepke et al., 2010). It can be discerned that the UV-LED output overlaps fully with the NO₂ absorption band and the NO₂ quantum yield and is therefore photon-efficient. It is also shown that there is minimal overlap with HONO and no overlap in the spectrum at all with PAN. It has been shown (Carbajo and Orr-Ewing, 2010; Talukdar et al., 1997) that there is no overlap with methyl, ethyl, or isopropyl nitrate – methyl nitrate being a minor impurity in PAN synthesis. There is only very minor overlap in the PLC optics spectrum with PAN, methyl ethyl, and isopropyl nitrate. PLC optics exhibit a great deal of overlap with HONO, which the UV LEDs do not. Both systems suffer some overlap with NO₃ radicals and BrONO₂, more so in the case of PLC optics than for UV LEDs. It is evident that PAN is unable to be photolysed in a BLC, nor in other types of photolytic converters, due to the narrow spectral output of UV not having overlap with the PAN absorption spectrum. Other species such as HONO, BrONO₂, and NO₃ radicals may constitute a photolytic interference.

3.6 Possible thermal interferences in BLCs

The thermal and electronic characteristics of the standard BLC lamps were found in bench tests and are summarized in Table 3. Each lamp was run constantly whilst recording

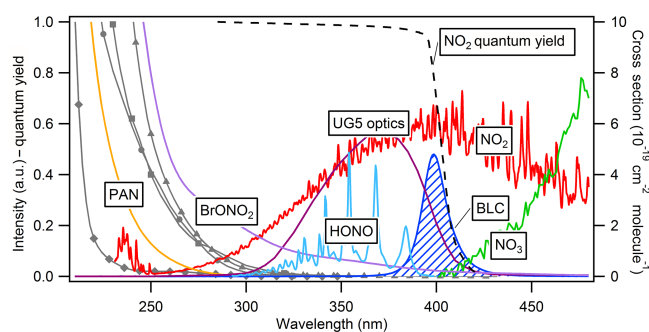


Figure 6. Absorption cross section (red) and quantum yield (dashed black) of NO₂, presented with the spectral output of UG5 optical filtering (purple) and an average of the six BLC lamps used in this study output (dark blue). Interfering species are shown – NO₃ radicals (green), HONO (light blue), and BrONO₂ (lilac) – which are overlapped significantly by the UG5 optics – completely in the case of HONO, whilst much less overlap is exhibited by the UV LEDs of the BLC. Also shown is PAN (gold), which is clearly not overlapped by either UG5 or BLC light sources. Additional non-interfering species – ClONO₂ (triangles), N₂O₅ (squares), HO₂NO₂ (circles), and HNO₃ (diamonds) – shown for reference.

Table 3. Peak surface temperature and current drawn by BLC lamps in a bench test at 20.0 °C showing converter efficiency, current, and surface temperature.

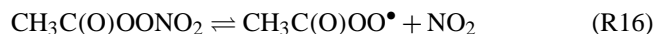
Lamp no.	Converter efficiency (%) ±1	BLC lamp surface temperature (°C) ±0.05	Current draw (A) ±0.0005
1	41	79.8	0.969
2		75.3	0.953
3	35	77.6	0.933
4		74.0	0.931
5	22	76.2	0.916
6		56.4	0.567

the surface temperature and power draw of the light-emitting element. The surface temperature was recorded once a stable maximum had been reached and maintained for at least 10 min – representative of using a BLC in constant mode. The ambient temperature during the experiments was 20 °C.

Table 3 describes the power draw and surface temperature of three BLC UV-LED lamp pairs measured during tests, along with their NO₂ → NO converter efficiencies when assembled as a complete BLC. The surface temperature of the individual lamps correlates positively with the power drawn by each lamp ($R^2 = 0.96$) and indeed with output intensity (Fig. 2), but with each lamp pair there is only weak correlation ($R^2 = 0.43$) between converter efficiency and temperature. It is worth noting that the power consumption is a combination of the light output, heat dissipation, and power to the cooling fan. It is clear, however, that the temperature ex-

perienced by the sample gas within the NO₂ converter is significantly above ambient. In fact, the entire NO₂ conversion cavity is heated by the lamps, leading to external temperatures of the converter of between 34 and 45 °C.

It is known that the major product from thermal decomposition of PAN is NO₂ (Reaction R16; Roumelis and Glavas, 1992; Tuazon et al., 1991). The NO₂ produced thermally within the converter may then be photolysed to NO and thus be measured as NO_x and attributed to atmospheric NO₂.



A model of the gas-phase thermal decomposition of PAN over a range of temperatures within the BLC with a residence time of 0.96 s is shown in Fig. 7. The model run was conducted in FACSIMILE kinetic modelling software (MCPA Software Ltd.) using rate constants from IUPAC evaluated kinetic data (Atkinson et al., 2006).

The model output indicates that measurable PAN decomposition to NO₂ occurs above ~ 50 °C. At the maximum LED surface temperature recorded (80 °C), the model predicts ~ 30 % decomposition of PAN to NO₂. However, as only the two UV-LED lamps are at such an elevated temperature, we can expect a temperature gradient/heating rate within the BLC so that the average temperature seen by the sample gas over the 0.96 s residence is somewhat lower. We assume that only gas-phase decomposition occurs, rather than any surface enhanced heterogeneous process; however, as the BLC has Teflon, stainless steel, rubber, conformal coating, etc. contacting the sample gas (some of which maybe heated to an extent), it is a possibility. Ryerson et al. (2000) found no measurable heterogeneous PAN decomposition on the quartz surface of their converter. It is expected that, in a switching mode with only 40 % duty cycle of the lamps, the LED surface temperature would be lower also. This is borne out when using the external surface temperature of the BLC as a proxy – the temperature was lower in switching mode than in constant mode for the same conversion efficiency. It is shown more clearly in the inset that an average temperature of 60 °C would cause a 4.6 % decomposition of PAN and account for the NO₂ measured during experiments with the standard BLCs. Therefore, together with the spectral measurements reported in Sect. 3.5, it seems highly unlikely that the source of the artifact signal is through direct photolysis of PAN, leaving thermal decomposition, modelled in Fig. 7, the remaining explanation.

In Sect. 3.1 the percentage conversion of PAN to NO₂ was found to be, on average, highest at the lowest converter efficiency and vice versa. The fact that the converter temperatures are very similar at different converter efficiencies (Table 3) suggests that the percentage of PAN thermally dissociated in each case is similar. An explanation for the inverse relationship between percentage conversion of PAN to NO and conversion efficiency (Fig. 2) lies in the way that the NO₂ concentration is derived, which is an inverse function of the assumed conversion efficiency as in Eq. (2), where converter

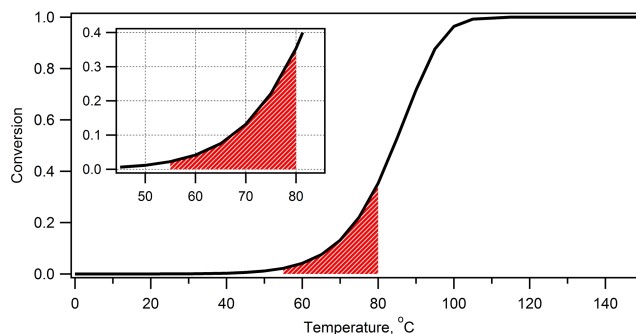


Figure 7. Model of thermal decomposition of PAN to NO₂ with a residence time of 0.96 s at temperatures between 0 and 150 °C. Inset is detail of 45 to 85 °C. The red shaded area corresponds to the temperature range of the UV LEDs of a BLC. Kinetic data from IUPAC (Atkinson et al., 2006).

efficiency is expressed fractionally. If in fact the conversion efficiency of PAN to NO in the converter was not related to the measured NO₂ to NO conversion efficiency but instead a constant value, then the apparent relationship between CE and percent conversion would disappear. This explanation is consistent with the fact that, when the average conversion percentage in Fig. 2 is normalized to conversion efficiency, the percentage for the three BLCs is remarkably similar (Table 4) to the average PAN decomposition of 4.6 % needed to produce the spurious signal observed.

Above a threshold temperature of 25 °C, the NO₂ formed in Reaction (R16) may be vibrationally excited (likely NO₂ (²A₁)) through the dissipation of internal energy from the parent PAN molecule (Mazely et al., 1995); this NO₂^{*} is then more readily photolysed to NO within the BLC than ground-state NO₂. The discussion above suggests that a similar proportion of the NO₂ evolved from thermal dissociation of PAN is converted to NO within the BLC, leading to the apparent inverse correlation between conversion efficiency and PAN “artifact”. Consequently, the lower NO₂ → NO conversion efficiency of a BLC, the greater the positive error in NO₂ when PAN is present.

4 Atmospheric implications

We have shown that a significant proportion of PAN can be decomposed under the normal operating conditions of a BLC equipped NO chemiluminescence instrument, leading to a spurious increase in measured NO₂ of 8 to 25 % of the PAN supplied. The UV-LED light source was found to reach a temperature of 56 to 80 °C in normal operation, with the surface temperature correlating positively with power draw and output intensity. The elevated temperature of the UV LEDs causes a positive bias in NO₂ by thermal decomposition of PAN.

Table 4. The average percentage conversion of PAN to NO₂ measured, and normalized to the converter efficiency of each BLC.

	Converter efficiency (%) ±1		
	41	35	22
Measured %	10.8	15.9	19.6
Normalized %	4.4	5.2	4.3

The positive bias in NO₂ measurements by NO chemiluminescence using BLCs has implications for remote background sites. Figure 8 shows the thermal decomposition profiles of many common NO_y species. Whereas only a small fraction of PAN is found to convert to NO₂ at the operating temperatures (~ 5 % at 60 °C) of the instrument, a number of more thermally labile compounds exist.

The degree of gas-phase thermal decomposition within the instrument will depend upon the thermal profile of the air ($T(t)$) as it passes through the instrument. This can be parameterized as a mixing timescale (τ s) for temperature from the ambient temperature (T_0) to that of the BLC (T_{BLC}) as in Eq. (4).

$$T(t) = T_0 + (T_{\text{BLC}} - T_0) \exp\left(-\frac{t}{\tau}\right) \quad (4)$$

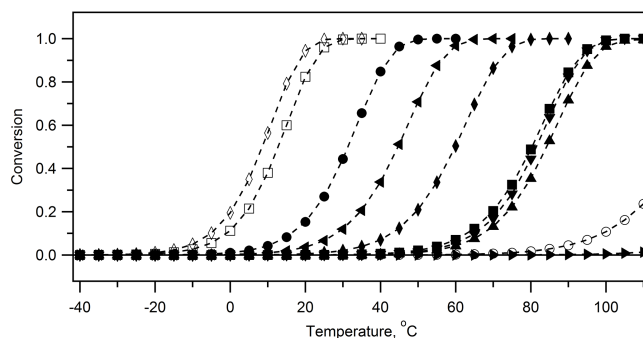
The rate at which thermal equilibrium is reached within the cell, τ , is calculated as 0.42 s from the observed PAN decomposition of 4.6 %, at 20 °C ambient temperature, a BLC temperature of 75 °C, and a 1 s residence time. This allows calculation of the potential interference from other thermally labile NO_y compounds.

Given a first-order loss of the PAN-like compound and a temperature profile within the instrument as described in Eq. (4), we have Eq. (5):

$$\frac{d[\text{PAN}]}{dt} = -k(T)[\text{PAN}] = -k(t)[\text{PAN}]. \quad (5)$$

Given the laboratory observations of the temperature dependence of the rate constant (typically $k(T) = A \exp(-B/T)$), and the parameterized temperature within the instrument ($T(t)$), the fraction of the compounds that will have decomposed can be found by numerical integration.

Figure 9 uses output from the GEOS-Chem model (version 9.2, <http://www.geos-chem.org>; Bey et al., 2001) run at 2° × 2.5° resolution, plus updates described in Sherwen et al. (2016), to provide an estimate of the interference on NO₂ from the decomposition of NO_y species within a BLC photolytic converter. The species used for this analysis are PAN, MPAN, PPN, IONO₂, BrONO₂, N₂O₅, CH₃O₂NO₂, and HO₂NO₂. Thermal decomposition information are taken from IUPAC evaluated kinetic data (Atkinson et al., 2004, 2006, 2007). Interferences are calculated for each month of a 1-year simulation and the maximum value shown. The

**Figure 8.** Thermal decomposition profiles of IONO₂, \blacklozenge ; BrONO₂, \circ ; ClONO₂, \blacktriangleright ; HO₂NO₂, \bullet ; N₂O₅, \blacktriangleleft ; C₂H₅O₂NO₂, \diamond ; CH₃C(O)CH₂O₂NO₂, \square ; MPAN, \blacksquare ; PAN, \blacktriangle ; and PPN, \blacktriangledown . Calculated from IUPAC recommended kinetic data (Atkinson et al., 2004, 2006, 2007) using FACSIMILE kinetic modelling software (MCPA Software Ltd.) based on 1 s residence time. Note that CH₃O₂NO₂ is not shown but has the same profile as CH₃C(O)CH₂O₂NO₂.

estimate assumes a BLC conversion efficiency of 100 % NO₂ → NO and thus does not include the extra signal from the photolysis of NO₂* → NO with converters where conversion is less than unity – in this case a multiplying factor exists.

Figure 9 shows that in extreme circumstances NO₂ may be over-reported by many hundreds of percent. These are in regions that typically have low NO_x concentrations and are cold (polar), or in the upper troposphere. Here, the concentration of compounds such as PAN and HO₂NO₂ are high relative to NO_x and it is not surprising that thermal decomposition can have an impact. Upper tropospheric overestimates of NO₂ concentrations could be as high as 150 pptv, which we find due to CH₃O₂NO₂ abundance, which has previously been identified as a possible interference in NO₂ measurement by LIF and chemiluminescence (Browne et al., 2011; Nault et al., 2015).

The NO₂ bias shown in Fig. 9 impacts the modelled Leighton ratio. In Fig. 10 the model is sampled every daylight hour for every surface grid box for the month of March. The calculation shown in red is the Leighton ratio calculated from the modelled concentrations of NO, NO₂, jNO₂, O₃, T, HO₂, RO₂, BrO, and IO. The model values are in general close to 1. In blue the same calculation is performed but including the interferences on the NO₂ channel. The instrumental decomposition of NO_y over a range of BLC lamp temperatures between 20 and 95 °C is shown (described by τ of 0.42 s and a residency time of 1 s). Here there are significant interferences.

As shown in Fig. 10 the Leighton ratio can be extremely perturbed from what would be predicted for NO₂ converters which operate above ambient temperature. This is especially true in low-NO_x environments.

Unusual Leighton relationships have been seen in a range of previous studies (Bauguitte et al., 2012; Cantrell et al.,

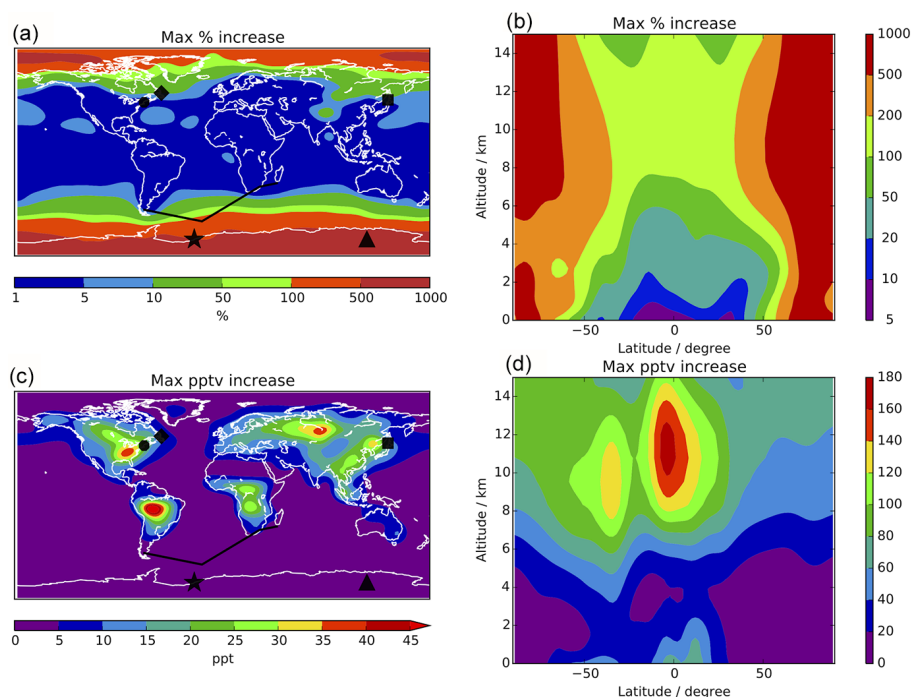


Figure 9. GEOS-Chem model output showing the monthly maximum percentage over-reporting of NO₂ determined by BLC/chemiluminescence (a) zonally and (b) by altitude in any month of a 1-year simulation. Panels (c) and (d) show the same in absolute pptv values. Surface values are the maximum over-reporting in any month; zonal values are the maximum over-reporting in any month and in any of the longitudinal grid boxes. The MD160 cruise track of Hosaynali-Beygi et al. (2011) is also shown in panels (a) and (c), as are the locations of the studies of Bauguitte et al. (2012), ★; Frey et al. (2013, 2015), ▲; Griffin et al. (2007), ●; Kanaya et al. (2007), ■; and Yang et al. (2004), ◆.

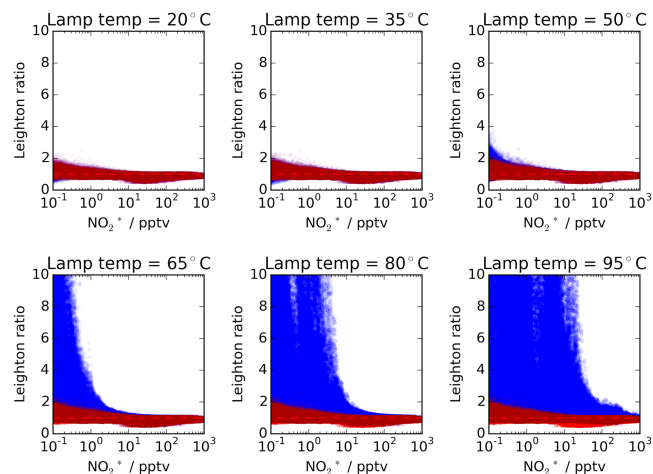


Figure 10. Leighton ratio calculated for each surface model grid-box for each daylight hour for March by the GEOS-Chem model as a function of the grid box NO₂ concentration. The instrument interference is characterized by a numerical solution of Eq. (5) with $\tau = 0.42$ s and a residence time of 1 s. Red shows the values calculated without the interference on the NO₂ concentration and blue indicates the values calculated with the interference. The interferences are calculated for different lamp temperatures, 20 to 95 °C.

1997, 2003; Frey et al., 2013, 2015; Griffin et al., 2007; Hosaynali Beygi et al., 2011; Kanaya et al., 2007; Yang et al., 2004), leading to either hypothesizing (a) an unknown, unmeasured, selective oxidant “compound X” or (b) theoretical mechanisms by which NO is converted to NO₂, which may be accounted for, in part, by a previously unaccounted for instrument bias our study has suggested. It is noteworthy that the studies of Bauguitte et al. (2012), Cantrell et al. (2003), Frey et al. (2013, 2015), Griffin et al. (2007), Hosaynali Beygi et al. (2011), Kanaya et al. (2007), and Yang et al. (2004) were all in locations where we predict a significant interference (indicated in Fig. 9), impacting on the observed Leighton relationship and complicating interpretation. However, whether specific NO₂ measurements have been influenced by a thermally labile NO_y bias will depend on the specific instrument conditions and geometries.

5 Conclusions

Measurements of NO₂ collected using some types of photolytic converter and chemiluminescence systems may be significantly biased in low-NO_x environments. Thermal decomposition of NO_y species within the NO₂ converter can produce spuriously high readings; this is especially true in

pristine environments and at high elevations, where the NO_y to NO_x ratio may be high. Over-reporting of NO₂ has been shown to lead to apparent gaps in oxidation chemistry which cannot be explained with any available measurements. Unexplained high NO₂:NO ratios in such regions have to the orization of an unknown “compound X” which selectively oxidizes NO to NO₂.

Our study suggests a need for characterization of individual NO_x instruments using the BLC/NO chemiluminescence technique (or similar) with respect to interference from thermally decomposing NO_y species. A convenient method for this would be with a pure PAN source, or any other readily available NO_y species.

In order to mitigate overestimation of the NO₂ mixing ratio by thermally dissociating PAN and other compounds, it is imperative to avoid heating of the sample above ambient. This can be achieved by separating the gas flow from contact with the UV-emitting elements, and by cooling the photolysis cell. Reducing the residence time of the sample gas within an instrument where it may not be possible to maintain ambient temperature of the sample is an alternative, i.e. where the ambient temperature is unfeasibly low. This can be achieved by operating at reduced inlet pressure, with the additional benefit of faster response time. It is desirable to have the highest possible NO₂ → NO conversion efficiency, i.e. unity, to minimize uncertainty in NO₂ and to remove any multiplying effect of more easily photolysable vibrationally excited NO₂. It would also seem prudent that the sample gas should contact only chemically inert, non-porous materials in order to mitigate any heterogeneous processes or memory effect – quartz being an ideal material for photolysis cells.

Data availability

We thank the NASA Jet Propulsion Laboratory for providing comprehensive absorption cross-section data for atmospheric compounds which can be found at <http://jpldataeval.jpl.nasa.gov>.

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