

Authors response

We would like to thank both referees for taking the time to review our work. Our responses to their points are detailed point-by-point below. Following that is a marked-up version of the manuscript showing the deletions and insertions based upon the reviewers comments. Additionally, but not marked figures 1,2,3,4 have changed to the working of their axis captions, figure 6 has been annotated at the request of referee 1, whilst figure 9 has a new colour scheme and locations of studies marked on it at the request of referee #1, figure 10 has been changed to include extra temperature scenarios at the request of reviewer #1.

Anonymous Referee #1

- The experiments were conducted with a photochemical PAN source and not with a synthetic standard. The output of photochemical PAN source contains many impurities such as HCHO and acetone. Further, the output of this source was coupled to the various instruments via short PFA Teflon tubing operated at high flow rates and short residence times, such that the instruments were likely exposed to high levels of (residual) peroxyradicals, potentially generating "PERCA" and other effects. In my opinion, the results presented in this manuscript should be confirmed with a synthetic PAN standard (whose output can be purified using a preparatory scale GC, if necessary).

The authors took great pains to ensure that the measurements were not affected by peroxy radicals (as nitric oxide was deliberately absent) and NO₂ produced from the PAN source and have already specifically addressed these concerns in the manuscript. Producing a pure PAN source (eg. from nitration of peracetic acid in tridecane) is non-trivial, requiring special equipment to deal with a potentially explosive reaction, and still requiring purification and verification of the source

We have suggested (in our conclusions), that investigators wishing to accurately determine leighton ratios could characterise their instruments for e.g. PAN decomposition, and that the optimal method for doing this would be with a pure PAN source.

We have endeavoured to be more clear in our explanations of the nature of the PAN interference, as detailed below.

- The authors should also consider thermal dissociation of PAN in an inlet not only produces NO₂, but also the PA radical, which can oxidize NO to NO₂ making the interference potentially even worse when ambient air is sampled (especially when determination of Leighton ratios is a goal).

Agreed. We have added text in the introduction which addresses the reviewers point, whilst addressing another of the reviewers suggestions about highlighting the difficulties of making low-level measurements.

- It's unclear from the manuscript how much of the existing literature on data sets could possibly be affected, apart from the GAW network (Penkett et al 2011) and the Hosaynali Beygi et al. (2011) study, which are mentioned. How widely has the BLC NO₂ technique been implemented?

This is not easy to find from the literature, instrument descriptions often lacking in any detail. The ACTRIS network of European monitoring sites (<http://www.actris.eu/>) use BLC NO₂ almost

exclusively. This study should however make BLC NO₂ users aware of the issue and assess whether it is consequential to their findings. Additionally, recent papers (Nault et al., 2015; Travis et al., 2016) have acknowledged the same issue with other techniques.

- On pp 28723 line 22 - pg 28724 line 28 the authors reinterpret the data by Hosaynali Beygi et al. (2011) and essentially conclude that the data and conclusions of the earlier study were incorrect. Since reinterpretation of earlier data that argued for missing NO oxidant(s) appears to be a major motivation for this study, this aspect should be featured more prominently and clearly in both the abstract and in the introduction. I was not involved with the Hosaynali Beygi et al. (2011) study and would very much be interested in hearing what the authors of that paper have to say. Though it is feasible that Reed et al. are, in fact, correct with their assertions, I do not believe that they provide sufficient evidence to make their case. Hosaynali Beygi et al. did, in fact, provide in their paper a thorough error analysis and stated that "We also calculated that in order for PAN to produce 7 pptv of additional NO₂, via thermal decomposition very high concentrations of PAN would be needed, i.e. at least several hundred pptv, which was not observed during the campaign." It seems a bit presumptuous of Reed et al. to now second-guess this statement and to question the other group's data on the basis of the performance of their own instruments. Hosaynali Beygi et al. stated clearly that there was not enough PAN in the Southern Atlantic ocean at the time of their cruise to cause significant interference. Further, key details as to how the instruments were operated, such as the internal operating temperature of the BLC converter, during the MD160 cruise are not known and may not have been the same as in the instruments used by Reed et al. I recommend that Reed et al. reword this paragraph and instead urge other users of BLC NO₂ instruments to test their instrument with PAN and characterize this interference, if found, and publish retractions or corrections to their papers, if necessary.

The reviewer is correct that Hosaynali Beygi estimates the contribution of PAN to ambient NO₂ to be minimal, as we ourselves have acknowledged in lines 8-17 p28724, due to the cool ambient temperatures in the atmosphere. However, the temperature within the instrument is the important factor, we argue, and is not what was addressed by Hosaynali Beygi. It is true that we do not know for certain the internal temperature of their BLC, but we do know that the BLC was operated in constant mode (information contained in Hosaynali Beygis' PhD thesis along with other interesting points; <http://ubm.opus.hbz-nrw.de/volltexte/2010/2242/pdf/doc.pdf>), and having several of the same units, from the same manufacturer, with the same residence time, we believe our system to be comparable. Air Quality Design is the successor to Sonoma Technology/Droplet measurement technologies, producing NO₂ converters to the same design. Hosaynali Beygi calculates that there is not enough PAN to produce the "extra" NO₂ observed at ambient temperatures, but not at the elevated temperatures within the BLCs.

However, we agree with the reviewer that it is inappropriate to re-interpret or second guess other authors' previous analysis. Instead we have removed this section and instead merely indicated (in fig. 9) the location of the Hosaynali Beygi study, as well as locations of other studies which have found discrepancies in the Leighton relationship (Bauguitte et al., 2012; Cantrell et al., 2003; Frey et al., 2013, 2015; Kanaya et al., 2007; Yang et al., 2004) noting that they were carried out in regions where we would predict an interference.

In our conclusions we have implored investigators who wish to determine Leighton relationships to characterise their instruments with a pure PAN source, or a source of any other readily available NO_y species.

Abstract: "Measurement of NO₂ at low concentrations" - please be quantitative and state what mixing ratio you would consider to be low (e.g., < 10 pptv).

We have now defined low as in the "10s of pptv". Technically low NO_x is an ozone destruction regime; however that is not what we refer to here.

pg 28701 line 8 - perhaps a better term is "greenhouse gas" in lieu of "climate gas".

Agreed, the manuscript has been changed to reflect this.

pg 28702 lines 5-7 "... signify missing (i.e. non ozone) oxidants of NO. These perturbations have been used to infer the existence of [other] oxidants..." I am assuming the authors refer to Hosaynali et al.'s work here (which should have been cited at this point) but I nevertheless suggest rephrasing this sentence. Peroxyradicals oxides, and the nitrate radical do exist (really) and have been quantified and shown to perturb the Leighton ratio on numerous occasions (in polluted environments and in the Arctic). I'd also suggest citing a larger volume of literature, for example, A. Volz-Thomas et al., Inorganic trace gases and peroxy radicals during BERLIOZ at Pabstthum: An investigation of the photostationary state of NO_x and O₃. *J. Geophys. Res.* 108, 8248 (2003); A. Geyer et al., Direct observations of daytime NO₃: Implications for urban boundary layer chemistry. *J. Geophys. Res.* 108, 4368 (2003); S. S. Brown et al., Aircraft observations of daytime NO₃ and N₂O₅ and their implications for tropospheric chemistry. *Journal Of Photochemistry And Photobiology A-Chemistry* 176, 270-278 (2005); K. Mannschreck, S. Gilge, C. Plass-Duelmer, W. Fricke, H. Berresheim, Assessment of the applicability of NO-NO₂-O₃ photostationary state to long-term measurements at the Hohenpeissenberg GAW Station, Germany. *Atmos. Chem. Phys.* 4, 1265-1277 (2004); J. Matsumoto et al., Examination on photostationary state of NO_x in the urban atmosphere in Japan. *Atmos. Environm.* 40, 3230-3239 (2006); I. Trebs et al., Impact of the Manaus urban plume on trace gas mixing ratios near the surface in the Amazon Basin: Implications for the NO-NO₂-O₃ photostationary state and peroxy radical levels. *J. Geophys. Res.* 117, D05307 (2012).

We agree with the reviewer. We were alluding to, but should have been more specific in mentioning, PA radicals, Halogen oxides etc. We did not intend to refer to Hosaynali Beygis paper.

We have amended the manuscript to be specific about the species which do perturb the actual Leighton ratio with the suggested papers cited (Brown et al., 2005; Mannschreck et al., 2004; Trebs et al., 2012; Volz-Thomas et al., 2003).

lines 14-15 "... which are high in both" please rephrase (suggestion: "where concentrations of ... are elevated").

Agreed, the appropriate change has been made to the text.

line 16 "thermally breakdown to release the NO_x". Much of the NO_x (I believe most) is released by photolysis and reaction with oxidants such as OH, in addition to thermal breakdown.

In the troposphere, thermal decomposition of PAN is the dominant loss process, photolysis and oxidation being relatively slow and minor contributors.

We have added supporting references to that effect (Fischer et al., 2013; Moxim et al., 1996; Roberts et al., 2007).

lines 23-25. Please define the acronym LIF and add the word "spectroscopy" after "ringdown" and "quantum cascade laser"

The requested changes have been made

pg 28703 lines 11-12 "to yield a signal which is linearly proportional to the number density of NO in the sample gas". It might be worthwhile to mention here that there are artifacts - e.g., quenching of the excited state by N₂, O₂ and water vapor. Please expand the text here and cite appropriate references.

Discussion of chemiluminescent quenching by water vapour etc. has been added (Clough and Thrush, 1967; Zabielski et al., 1984).

pg 28703, line 23. "...NO₂ signal". There are known interferences for this technique, some of which are discussed further down in the manuscript. Please expand here and cite appropriate papers, for example W. A. McClenny, E. J. Williams, R. C. Cohen, J. Stutz, Preparing to Measure the Effects of the NO_x SIP Call - Methods for Ambient Air Monitoring of NO, NO₂, NO_y, and Individual NO_z Species. J. Air Waste Manag. Assoc. 52, 542-562 (2002).

A short discussion of the long-known-about positive interferences in catalytic NO₂ converters (Dunlea et al., 2007; Grosjean and Harrison, 1985; Winer et al., 1974), and more recently, negative interferences in photolytic NO₂ converter systems has been added here (Villena et al., 2012). The reviewers suggested reference is included also (McClenny et al., 2002).

Page 28703, line 24. Please strike the word "successfully" - it's redundant as one has made a measurement, or not.

Done

line 26-27. It might be worth mentioning that these measurements are extremely challenging: instruments are typically close to the limits of detection, and data corrections (such as offset corrections and losses or production of NO to NO₂ within the instrument's inlet lines) may be substantial.

A short discussion of the difficulties in measurements in low NO_x environments including nighttime off-set, artifact, and other corrections has been added here.

pg 28704 line 8-10. "An alternative explanation would be an unknown interference on the NO₂ measurement increasing its apparent concentration." True, but this would require the interference and the alternate explanation (the missing oxidant) having the same diurnal concentration profiles. Perhaps add a qualifying statement here such as "... if this interference has a similar diurnal concentration profile".

We have added the qualifying statement at the reviewers' request.

pg 28708 line 21 "reach" should be "reached".

Corrected

pg 28705 "Artefacts in both NO and NO₂ are measured whilst sampling zero air." Did the authors mean to say "background levels"?

None zero off-set values (positive or negative) may be present in both NO and NO₂ signals. By sampling zero air (the same that all experiments were carried out under) any systematic off-set can be corrected for as not to bias the data.

line 18 "very low limit of detection". Please be quantitative here (I found the answer in the next paragraph). You may want to summarize this information along with the specs of the other NO_x instruments such as instrument inlet residence times in a table.

We have added this information at the first reference to it.

How do you define LOD (2 sigma or 3 sigma)?

2 sigma. Information added.

pg 28706, line 8. "3.5 and 4.0 cps/ppm". Please state the uncertainties for all sensitivities and comment on drifts (even if absent).

Uncertainty arises from the uncertainty of the NO standard, the mass flow controllers and the reproducibility of sensitivity determination. Sensitivity drifts due to changing e.g. water vapour are mitigated by all experiments and calibration occurring in stable (T_d) zero air.

The uncertainties and their sources have been added for sensitivity, and drift discussed.

pg 28710, lines 12-14. "(R9)–(R11) describe the mechanism by which PAN is formed from acetone" Typically, a mechanism lists all elementary reaction steps leading from the reactants to the products. (R9-11) leave out a few bits, such as the reaction of the acyl radical with oxygen to give the acylperoxy radical, reaction of methyl radical with oxygen to methyl peroxy radical, and the oxidation of NO to NO₂ by methyl peroxy radical to methoxy radical, which incidentally is the major source of the latter (and not R14 as suggested further below). Please correct. You may also want to change the word "mechanism" to "reaction sequence".

We have corrected the sequence (Singh et al., 1995) and changed the wording as requested by the reviewer

pg 28710 lines 20-21. It is stated that CH₃ONO₂ is formed as a side-product in 1% yield. Please state the yield of desired product, PAN, first (which is more important information).

Agreed, the description of the PAN generator and the yield of PAN produced (Flocke et al., 2005; Mills et al., 2007) has been moved above the description of methyl nitrate formation.

line 21-22. Methyl nitrate is, more likely, produced from reaction of CH₃O₂ with NO, and not from reaction 16 as CH₃O reacts quickly with O₂ to form formaldehyde and HO₂ - see J. E. Williams, G. Le Bras, A. Kukui, H. Ziereis, C. A. M. Brenninkmeijer, The impact of the chemical production of methyl nitrate from the NO + CH₃O₂ reaction on the global distributions of alkyl nitrates, nitrogen oxides and tropospheric ozone: a global modelling study. Atmos. Chem. Phys. 14, 2363-2382 (2014).

This is the scheme proposed originally by Warneck and Zerbach, (1992), however reaction has been corrected with the information from the referees suggested citation (Williams et al., 2014).

pg 28710, line 26. "that the formation of nitro-methane and HONO is also possible" A lot of things are possible in principle. Can you be quantitative here? I doubt that much nitromethane is generated, but would expect HNO₃ and NO₂ to be in greater abundance than the products mentioned.

Unfortunately, we cannot measure HNO₃ or nitro methane independently; however they are unable to interfere thermally or photolytically (indeed HCHO too which photolyses at <360 nm). We have measured the NO₂ directly and found it to be less than 1% so expect HNO₃ and nitro methane to be negligible. HONO interference in these particular converters is also negligible.

We have removed reference to these reactions/products as we can only speculate at their abundance and are irrelevant for this study.

pg 28711 line 15. R15 puzzles me. Isn't oxygen (air) added to this source? It would make short process of any CH₃ generated. line 24. Please comment on how much NO₂ is emitted from this source as thermal decomposition of PAN is non-negligible even at room temperature. I looked for this information but couldn't find section 2.4.1. (it is given much later on).

R15 is changed, and in the amended scheme the CH₃ + O₂ reaction is shown in R10.

We apologize for the mistake in section number; it should have read "section 2.6". We have amended the text with the relevant NO₂ production information and directed the reader to the correct experimental section.

pg 28712 line 20. Please be consistent and use only of "counts per second", "cps", "counts s⁻¹" (line 22)

We have altered all instances in the text to be consistent to "counts s⁻¹".

Table 1 gives concentrations in cps which is somewhat useless. State concentrations or mixing ratios instead.

The reviewer makes a good point. We have adapted the text and the table to show the signals as mixing ratios also. For this we have assumed that, although all three sources of zero air purport to be zero, the lowest signal is the only true zero and reported the two others relative to it. The LIF has a non-zero zero due to scattering of laser light and dark current counts from the PMTs, thus zero is always relative to an external source. Ideally, a tuneable laser would go off the NO₂ line to obtain a true zero, however this instrument used in this study has a constant wavelength laser.

pg 28713 "excess flow vented to the atmosphere." I'd be careful venting the excess source output as this type of source generates quite a bit of HCHO, a suspected carcinogen.

Noted

pg 28714 line "... and is accounted for in the measurements." But when the pen-ray lamp is turned on, the acetone concentration would be lower, no? Is that difference accounted for?

Yes, the chemiluminescent zero (the signal arising from slower alkene + O₃ reactions) was determined every 5 minutes on both instruments as a matter of course. The instrument description (section 2.1) has been amended to reflect this. Also, acetone is in relative excess to NO, the percentage change is minimal.

line 22-23. "It is therefore conservatively estimated that less than 1 ppt NO₂ at 1000 ppt PAN (0.1 %) is produced by the PAN generator" Such low NO₂:PAN ratios are surprising and puzzling. It is stated earlier that the PAN generator was operated at 30C; at this temperature, the equilibrium constant for NO₂+PA → PAN is ~1×10⁻⁸ cm³ molecule⁻¹. At 1000 pptv of PAN and assuming 1:1 stoichiometry of PA and NO₂, one would expect a PAN:NO₂ ratio of 1000:61, which drops to 1000:28 at 20C. If the observed ratio is higher, it implies that there is excess PA radical generated and likely also emitted by the source as this radical is surprisingly long-lived, in particular when PFA tubing at high flow rate are used. This excess of PA radical will undoubtedly lead to artifacts. I thus disagree with what is stated on line 26 ("It was therefore determined that only PAN could be an interfering species in the BLC from the PAN generator"), as the source obviously emits an excess of PA radical (and also HCHO and other peroxyradicals such as HO₂, and HONO). The PA radical concentration will likely exhibit an exponential gradient downstream of the PAN source (as it reacts with itself, or on the tubing walls), which will mean that the ratio of PAN:NO₂ is a moving target in these experiments, and (worse yet) different for each of the instruments depending on flow rate, residence time, inlet material, etc.

There are a few points here that we will address in turn.

Firstly, we apologize for the mistake on our part in stating that we estimate NO₂ to be less than 1 ppt at 1000 ppt PAN (line 22-23 p28714). This should read 10 ppt at 1000 ppt PAN (as a conservative measurement). This is now clear from figure 1 thanks to the reviewers suggestion regarding that figure.

Secondly, the PAN generator was operated at ambient temperature; only the acetone permeation source is thermostated at 30C. The description has been amended to make this clear (section 2.4)

Thirdly, regarding the interference of peroxy radicals left over from PAN synthesis. The PAN generator necessarily operates with an excess of PA radicals (as we state) to achieve the high yield of PAN product. In all experiments the same line was used (as stated), and furthermore we performed experiments varying the residence time of PAN in the inlet line (sect. 3.3) showing that longer or shorter residence times did not affect the signal observed. We have reworded the description in this section slightly to clarify the aims of the experiment.

Immediately above in lines 1-11 p28714 we address and performed experiments designed to quantify any effect of PA radicals outside of the PAN generator and found no effect/oxidation of NO to NO₂. Never-the-less experiments were carried out in the absence of NO, thus even if PA radicals

were present in the BLC they would constitute a counter-balance to PAN decomposition. Remembering that we actually can only measure NO and must convert NO₂ to quantify it, and having found NO₂ from the PAN source to be negligible, any NO₂ signal we see is the result of photolysed NO₂ from PAN decomposition which has not been oxidised back to NO₂ by eg. PA radicals before it reaches the detector of the instrument.

We do concede that the original description was not entirely clear so have reworded various parts of it accordingly.

pg 28715 line 6 "The residence time of PAN in the 2.7m PFA inlet linking the PAN generator to the NO_x analyser was varied by varying the flow rate." Please let the reader know at this point what the residence times typically were - for example, by referring to the table that is presented later on.

The text has been amended referring to the table and with the typical residence times.

Line 10 " In this section we discuss experiments " At this point, the results of the experiments haven't been presented yet; it's better to present the results first before discussing them.

"Discuss" corrected to "describe".

pg 28715 lines 21-22. "Figure 2 shows that the NO₂ signal is proportional to increasing PAN mixing ratios. The measured mixing ratios of NO₂ were 8–25% of the initial PAN mixing ratio. " This statement is confusing as it is not immediately clear what is meant by "NO₂ signal", which sounds as if the source emits 8-25% of NO₂. Please clarify the text (suggestion: "an artificial signal corresponding to 8-25% of the initial PAN mixing ratio was generated")

Agreed, we have clarified the point that the NO₂ signal is in fact a positive interference (artifact) arising from PAN.

pg 28718 lines 7-16 "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 a very important observation. Can you speculate as to what chemistry on the surface causes this?

The Teflon-like block is a bulk reflector, that is, the UV penetrates up to ~ 1cm 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 is quite porous and so 'dirt' 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 layer inhabit. The porosity also gives rise to the artifact which the reviewer may have observed. This is because gas diffuses into the bulk - let's say in a polluted environment – and when moved to a 'pristine' background site takes many months to reach

equilibrium with the ambient NO₂/NO_y. This is evident when sampling zero air. This is however a different discussion entirely.

A brief discussion of above has been amended to the manuscript, in part at the request of reviewer#2.

pg 28719, lines 4-9. "The thermal and electronic characteristics of the standard BLC lamps were ascertained in bench tests and are summarized in Table 3. Each lamp was run constantly on the bench whilst recording 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. " The lamp and ambient temperatures are not really relevant here - the temperature inside the gas cell is. Why not simply inserting a thermocouple probe into the converter to monitor the gas temperature when the instruments are operated? In practice, the gas flow might provide some (or a lot of) cooling.

Precisely, cooling of the lamp/cell by the incoming sample gas equates to heating of the sample gas above its ambient temperature. The energy dissipation of the lamp is the same with or without cooling by the sample. Therefore it is relevant to know how much energy as heat is generated by the lamps. Placing a thermocouple within the cell was considered but would damage/destroy what is quite an expensive piece of equipment without gaining much additional information.

pg 28721 line 4 "may be excited". Can you identify the state the NO₂ is excited to? NO₂* is a bit vague.

There are very few studies of the electronic properties of organic nitrates such as PAN. One such study of nitro methane exists (Arenas et al., 2003). NO₂(²A₁) state however seems most likely (Clough and Thrush, 1967). This has been amended to the text.

line 15 " to reach a temperature of 56 to 80C" I doubt the surface temperature of the lamp is the same as what the sample gas experiences.

Indeed, we address his point and account for cooling, what we call mixing timescale (τ), in our model. We also account for the temperature of the incoming gas and the temperature differential.

pg 28724 line 19 " ancillary " should be ancillary

Changed

line 21 "measurments"):

Changed

Figure 1 - Please add a second axis on the right hand side indicating the (relative) mixing ratios that 70, 72, ... 84 cps correspond to.

The requested change has been made to the figure and its caption.

Figure 9 - please add a qualifying statement to the caption "... over-reporting of NO₂ if this [state model] instrument were used" Please use a color scheme that provides better contrast and increase

the font size of the counter lines. You may want to indicate the location of the Hosaynali Beygi et al. (2011) study.

We presume the reviewer is referring to contour lines rather than counter lines which we have removed in lieu of a colour scheme with greater contrast. We have included the ship track of the MD160 cruise in the figure also and locations of other studies finding similar discrepancies in the Leighton ratio using comparable instruments.

Figures 2 and 3 - please strike the word "absolute" from the captions.

The requested change has been made to the figure

What does CE stand for? Is it the same as the "PAN conversion %" on the right hand side?

CE refers to the NO₂ conversion efficiencies of each BLC determined during calibration. The figure captions have been updated to make this clear.

Figure 2 - it would be instructive here to show "true NO₂" by the LIF instrument and change the axis title from "measured NO₂" to "NO₂ artifact" for clarity

The axis title has had the requested change made. The 'true NO₂' would be somewhere between 0-10 ppt (from lowest to highest PAN mixing ratios) i.e. which is shown in the amended figure 1. We believe "true NO₂" is therefore not particularly useful to show.

Figure 8 - this graph would benefit from some color. Please identify the cell temperature (e.g., as an underlay) to highlight the region of interest. Caption: IUPAC occasionally changes its recommended kinetic data. Please give an indication of what version was accessed.

Reference to IUPAC (Atkinson et al., 2006) has been added, and the figure has been annotated to show the BLC temperature window of interest with the figure caption altered accordingly.

Figure 10. Are 90C 105C realistic scenarios? Please remove these cases and 2 other instead - room temperature (20C), and 40C.

90 and 105 C are unfortunately quite realistic in BLCs of lamp surface temperatures, and in fact the newest generations are hotter. The Nichia LEDs used in older BLCs from Sonoma Tech and Droplet Measurement technologies are very thermally inefficient thermally. Later Air quality Design BLCs using the Norlux lamps, as used here, are more efficient per watt thermally. Newer higher power BLCs with NO₂ conversion efficiencies >90% operate at 120C after peaking over 200C when first powered on.

We have amended instead new scenarios which are 20, 35, 50, 65, 80, 95C.

References

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Anonymous Referee #2

It does not seem they've considered the possible interferences posed by methyl pernitrate ($\text{CH}_3\text{O}_2\text{NO}_2$), as discussed by Browne et al., *ACP*, 11, 4209–4219, doi:10.5194/acp-11-4209-2011, 2011. It would be worth including in the discussion as it touches on measurements in the UTLS.

The authors have indeed considered methyl pernitrate as a source of interference mentioning it several times; in the abstract pp 28700 line 18, pp 28722 line 19, and in figure 8.

However we have now made it clear that methyl pernitrate is the dominant source of error in the upper troposphere citing the reviewers suggested paper (Browne et al., 2013) and (Nault et al., 2015).

The authors may wish to call attention to another cause of spurious deviations from expected NO₂:NO ratios based on photolytic NO₂ measurements at low ambient mixing ratios, described in Appendix A of Yang et al., *JGR*, 109, D02312, doi:10.1029/2003JD003983, 2004.

We would like to thank the reviewer for drawing to our attention to what is a very comprehensive and detailed description of the inherent bias in statistical techniques and averaging used to calculate NO₂ from NO_x.

We have added a discussion and the appropriate citation of Yang et al. findings.

One difficulty of this kind of paper comes in generalizing from their instrument to all other instruments. A note is made in the abstract that "Although this interference is likely instrument specific. . ." but at times the text seems to imply they believe this may be more a general problem. The paper makes a strong case that the commercial "Blue Light Converters" (BLCs) they tested do exhibit this problem generally, but also cite a report that used a very different setup with a mercury arc lamp where PAN conversion was tested directly and found to be negligible. The

commercial BLCs used in the present report have UV-irradiated, sample-wetted surface materials (stainless steel, PTFE Teflon, LED chips etc.) that are not present in all other designs. Perhaps reconsidering the degree to which they generalize conclusions from the BLCs to other designs – or better, if they could, recommending materials that do not lead to their observed interferences? - would be warranted.

Indeed, it is the contacting of sample gas with the UV emitting elements which are necessarily hot which is the source of bias – which is absent in different set-ups such as with a mercury arc lamp; The reviewer is likely referring to the work of Ryerson et al., (2000) who found negligible PAN interference – surface mediated or otherwise.

We have, in our conclusions, made it clear that any system that heats a sample gas above ambient has the potential for interference and that the BLC method of contacting the sample with sometimes very hot LEDs is not optimal for accurate NO₂ determination. We recommend separating the UV emitter from the sample gas by e.g. quartz glass which has excellent UV transmission. In addition, but a separate subject, quartz being non-porous and very inert minimises any zero artifact or memory effect.

The paper could make a clearer distinction between gas-phase thermal decomposition of PAN, which is a straightforward calculation, and the possibility of surface-mediated decomposition of PAN on irradiated and heated surfaces.

It was beyond our capabilities to, with any certainty, discriminate between gas phase and surface mediated decomposition (again, as with Ryerson et al., (2000)) in such a complex system. We have performed various thermal decomposition experiments with NO_y species and found the material to be important. Below in Fig. 1 is the measured NO_x from the decomposition of n-Propyl Nitrate (chosen because of exhibiting little decomposition with the BLC).

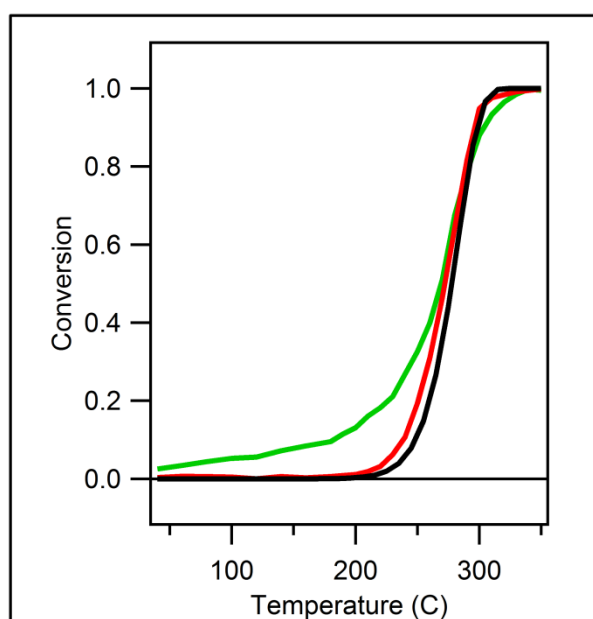


Figure 1. The purely gas phase model of n-Propyl Nitrate decomposition with 1 s residence time with data from IUPAC (Atkinson et al., 2006) is shown in black , the decomposition profile of the same

passed through a completely quartz/quartz packed furnace in red, and in green passed through a 316 stainless steel/quartz packed furnace.

Clearly the pure quartz performs much better than steel, even at low temperatures, at replicating the model, which is unsurprising given the transition metals present in stainless steel, such as molybdenum – a NO₂ reduction catalyst in its own right. Obviously the BLC has anodized aluminium; Teflon; conformal coating; epoxy resin; steel; and rubber contacting the sample gas at moderate but not excessive temperatures possibility for surface enhanced/heterogeneous decomposition exists. However we have no quantitative measure of this.

We have highlighted the possibility and distinction of heterogeneous processes in the discussion, suggesting quartz to be an ideal alternative material for a converter due to being inert and UV transparent.

This will make a solid contribution to ACP once these relatively minor issues are addressed.

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

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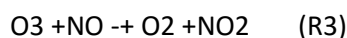
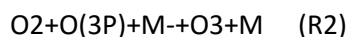
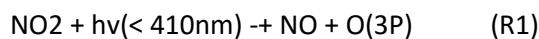
Abstract

Measurement of NO₂ at low concentrations ([10s 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, jNO₂ 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 relationship. 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, ~~it appears that~~ the thermal decomposition ~~of~~ NO₂ within the instrument's photolysis cell ~~may~~[could](#) give an [at least partial](#) explanation for the anomalously high NO₂ that has been reported in remote regions, ~~and would reconcile measured and modelled NO₂ to NO ratios without having to invoke novel chemistry.~~ [The interference can be minimized by](#) better instrument characterization, coupled to instrumental designs which reduce the heating within the cell ~~seem likely to minimize the interference in the future~~, thus simplifying interpretation of data from remote locations.

1 Introduction

Accurate quantification of atmospheric nitrogen ~~oxide~~[oxides](#) (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 [climategreenhouse](#) gas (Wang et al., 1995), 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 II, 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 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, c (Leighton, 1961), in Eq. (1).

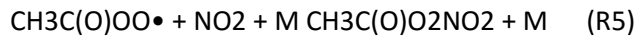
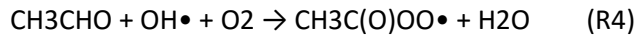
$$k_1 [\text{NO}][\text{O}_3]$$

$$j[\text{NO}_2]$$

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, ~~or~~ halogen ~~oxides~~[oxides](#), and the [nitrate radical](#) in the atmosphere [which have subsequently been confirmed by direct measurement \(Brown et al., 2005, Mannschreck et al., 2004, Trebs et al., 2012; Volz-Thomas et al., 2003\)](#) ~~(Bauguitte Cantrell; Frey et al., 2015)~~.

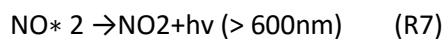
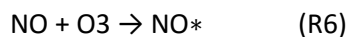
The concentration of NO varies from > 100 ppb (parts per billion) next to roads (Carslaw, 2005; Pandey et al., 2008) to low ppt (parts per trillion) in the remote atmosphere (Lee et al., 2009). Direct transport of NO from polluted to remote regions is not efficient, because NO_x is removed from the atmosphere 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 peroxy-acetyl nitrate are made in polluted regions (~~which are~~ [highwhere concentrations](#) in both NO and peroxy-acetyl precursors such as acetaldehyde [are](#)

[elevated](#)) and are subsequently transported to remote regions where they thermally breakdown to release ~~the~~ NO_x ([Fisher et al., 2014](#); [Moxim et al., 1996](#); [Roberts et al., 2007](#)).



The equilibrium between peroxy-acetyl radicals, NO_2 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 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 O_3 . This exploits the reaction between NO and O_3 (Reaction R6) which generates a [vibrationally electronically excited \$\text{NO}_2^*\$](#) ([2B1](#)) molecule which decays [into](#) 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 NO^* to NO_2 is proportional to the NO present before reaction with O_3 ([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 NO^*), 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 \$\text{NO}_2^*\$ excited state occurs due to a range of atmospheric compounds \(\$\text{N}_2\$, Ar, CO, \$\text{CO}_2\$, \$\text{CH}_4\$, \$\text{O}_2\$, He, \$\text{H}_2\$, and \$\text{H}_2\text{O}\$ \) \(\[Clough and Thrush, 1967\]\(#\); \[Drummond et al., 1985\]\(#\); \[Zabielski et al., 1984\]\(#\)\). Quenching is minimised 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 correcting for, sample drying, or sample humidifying to mitigate.](#)

With NO chemiluminescence analysers it is also possible to analyse NO_2 if it is first converted to NO, either catalytically (typically heated molybdenum) as in Reaction (R8) ([Villena et al., 2012](#)), or by converting NO_2 into NO photolytically ([Ryerson et al., 2000](#)), exploiting Reaction (R1).



To measure NO and NO_2 , the sample flows through the NO_2 to NO converter (of either type) to the reaction chamber where the $\text{NO} + \text{O}_3$ reaction occurs and the decay of NO^* to NO_2 allows the concentration of NO + NO_2 in the air to be measured. Then, the sample flow is switched to bypass the NO_2 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 + NO_2 (NO_x)~~ signal giving the ~~NO $_2$~~ signal. [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 **successfully** 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). However, 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 e.g. 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 oxidised 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 nighttime 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 nighttime 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. demonstrate that uncertainties in averaging signals which fall below ~ 10 times the 1 σ limit of detection result in large errors in NO₂ : NO ratio, with extreme bias exhibited when signals fall below a signal to noise ratio ~ 5. This work show that using weighted geometric mean of PMT counts to determine NO and NOT (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, and uncertainties in the NO₂ conversion efficiency etc.

Some measurements made in remote (low NO_x) locations, such as Antarctica and ~~in~~ over the open ocean have at times identified an unexplained imbalance in the Leighton relationship (Bauguitte et al., 2012; Cantrell et al., 1997; Frey et al., 2013, 2015; Hosaynali Beygi et al., 2011). Measured NO₂ concentrations are higher than would be expected from the observed NO, O₃, jNO₂ 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 ~~a~~ **mystery** an unmeasured oxidant, or pushing known chemistry into theoretical realms by theorizing high turnover of short-lived species ~~which may only have been measured in trace quantities~~ (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 ~~some~~ 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 and 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 ~~and~~ 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 ~~residence~~ [Sect. 2.7 describes residency](#) time tests ~~in Sect. 2.7~~.

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 inch 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). ~~Artefacts~~ [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~~ [of 2.5 pptv averaged over 1 minute](#). 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 NOT 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 to mea–suring 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 set-up 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 40% duty cycle of the NO₂ converter and a total sample flow of 1 standard L min⁻¹, and a parallel mode with 100% duty cycle of the NO₂ converter with a total sample flow of 2 standard L min⁻¹. [Photochemical zero is determined for 30 seconds every 5 minutes. A photochemical 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 Teflon volume immediately prior to the detection cell though 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 ~~eps~~counts s⁻¹ ppt⁻¹ ($\pm 5\%$) on channel 1 (NO) and channel 2 (NO and NO₂) respectively. [The \$\pm 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 e.g. 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 ~~but which~~. [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 ~~which~~. [This](#) is of a non-standard design ~~in that it~~ uses six more powerful UV-diodes which require active Peltier/forced air-cooling ~~controlled by a PID~~ 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 ~~eps~~counts s⁻¹ ppt⁻¹ ($\pm 5\%$) 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 Air Quality Design and manufactured according to their proprietary standards (Buhr, 2004, 2007). Systems have also been developed subsequently (Pollack et al., 2011; Sadanaga et al., 2010) with variations implementation, though similar operation and results. 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 wave-length 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).

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

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

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

In Eq. (3) *j* is the rate constant (s⁻¹), *F* is the spectral photon flux (photons cm⁻² s⁻¹ nm⁻¹), *a* is the absorption cross section of NO₂ (cm²), *φ* is the quantum yield (dimensionless) of NO₂ photo-dissociation, 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 is attached a cooling fan. The ends are bolted to a central section with rubber gaskets forming an air-tight 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 inch 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 0.96s. 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...0.6s⁻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 at with sample gas at ambient temperature and pressure; 20°C, 1 atm.

2.2.2 High power BLC

The high power BLC of the aircraft instrument is designed to operate at a higher flow rate (1.5 standard L min⁻¹), 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 [2W, 395nm, Nichia Corp] are used in order that the conversion efficiency be 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 power BLC lamps are actively (Peltier) cooled to 47°C, and without Peltier cooling ~~reach~~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% ($j = 6.5s^{-1}$).

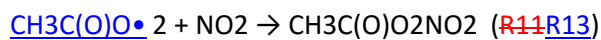
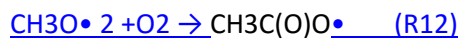
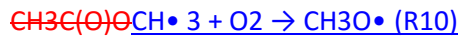
2.3 TD-LIF analyser

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 “~~arte~~artifact” NO₂ signal.

The Thermal Dissociation Laser Induced Fluorescence (TD-LIF) system is a custom in-strument developed for aircraft and ground-based observations of NO₂, >PNs, >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. It uses ~~laser induced fluorescence (LIF)~~ to detect NO₂ concentrations directly (Dari-Salisburgo et al., 2009; Matsumoto and Kajii, 2003; Matsumoto et al., 2001; Thornton et al., 2000) and, coupled with a thermal dissociation inlet system, allows measurement of peroxy nitrates (>PNs), alkyl nitrates (>ANs), and HNO₃ after conversion into NO₂ (Day et al., 2002). The TD-LIF comprises four main parts: the laser source, the detection cells system, the inlet system and the pumps. The laser source is a Nd:YAG pulse doubled laser (Spectra-Physics, model Navigator I) that emits light at 532nm with a power of 3.8W, a repetition rate of 15 kHz and 20 ns pulse-width. The detection cells 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 in four channels: one at ambient temperature to measure NO₂, and the last three heated at 200, 400 and 550°C, to thermally dissociate >PNs, >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 (3–4Torr). 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 over-flow of zero air in the detection cells; and calibrated by standard addition of 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 10Hz and the detection limits are: 9.8, 18.4, 28.1, and 49.7 pptv (1 s, S/N = 2) for NO₂, >PNs, >ANs, and HNO₃ cells, respectively (Di Carlo et al., 2013).

2.4 PAN preparation

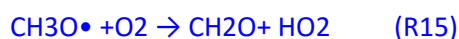
In order to test the sensitivity of the instrument to peroxy-acetyl nitrate (PAN) interferences it was prepared by the photolysis in air of acetone and NO as described by (Meyrahn et al., 1987) and later by (Warneck and Zerbach, 1992; ZellwegerFlocke et al., 20002005). Reactions (R9)–(R11R13) show the reaction sequence by which PAN is formed by acetone photolysis (Singh et al., 1995) describe the mechanism by which PAN is formed from acetone photolysis.



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Here, NO₂ reacts stoichiometrically with the acylperoxy acetyl 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 thermo-stated (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 centered 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 is shown in Reactions (R12)–(R16). (Williams et al., 2014) is shown in Reaction (R14) and formaldehyde which is formed as a major by-product is shown in (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). Reactions (R15), (R17) (Fischer and Nwankwoala, 1995) show that the formation of nitro-methane and HONO is also possible from PAN synthesis by acetone photolysis.





~~A dedicated "PAN generator", as used by Whalley et al. (2004), was employed to produce a consistent source of PAN. The generator consists of: flow control elements for the NO standard gas, the acetone flow, and the zero air diluent flow; an 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, all thermo-stated at 300C; 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).~~

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 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). A Laser Induced Fluorescence instrument, described in Sect. 2.2.3, was used to ~~find if any~~ quantify NO₂ produced directly in the PAN generator ~~with the results presented in Sect. 2.4.1, 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°C dew point T_d) compressed air by subsequent filtering through a cartridge of molecular sieve (13x, 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 volatile organic compounds (VOC) 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 below the LOD levels of NO (< 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 PAG 003 and filter stack was sampled by the NO₂ LIF analyser. Additionally, high grade bottled zero air (BTCA 178, BOC Specialty Gasses) was analyzed for NO₂. Table 1 shows the photomultiplier ~~counts per second~~ counts s⁻¹ 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~~ 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 LIE NO₂ channel was ~ 180 cps counts s⁻¹ ppb⁻¹, thus a 4–4.5 cps 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 analysers were first calibrated for sensitivity/converter efficiency and 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°C) and the sensitivity of the NO analyser is reduced by high humidity in the ambient sample gas. This means that switching the NO 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 specialty specialty 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 analyser was then shut off so that the NO 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 analyser with excess flow vented to the atmosphere. The system was then allowed to stabilize until a stable consistent NO value was recorded on the NO_x analyser. Next, the acetone photolysis lamp of the PAN 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 analyser fell to ~ 0 ppbv after the acetone/NO mixture was illuminated by the photolysis lamp; $\geq 99.5\%$ 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 to 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 signal relative to zero air during the NO or NO₂ measurement cycle was observed during these experiments at any mixing ratio.~~ 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 ~~also. No additional signal over zero air during~~ 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 measurement cycle was observed in either case, photolysed indicating that peroxy radicals from acetone with or without nitric oxide addition. Thus, it was concluded that acetone does not interfere photolysis within the BLC and that peroxy radicals PAN generator do not exist outside of the broadband photolysis cell of the PAN generator. have a long enough lifetime (self reaction or surface loss) before entering the BLC, to cause an interference or 'PERCA' (Clemishaw et al., 1997) like chemistry within the BLC.

It should be noted that sampling acetone does cause ~~an~~ 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 photochemical zero taken every 5 minutes described in Sect. 2.1.1.](#)

To test whether the PAN generator produced any NO₂ directly (i.e. rather than as a consequence of ~~conversion~~ [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 ~~less than 1~~ [< 10](#) ppt NO₂ at 1000 ppt PAN (~~0~~ [\(< 1 %\)](#)) 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 ~~analyser~~ [analysers \(shown in Table 2\)](#) was varied by varying the flow rate. This was achieved by altering the sample flows through each of the NO_x analyser channels (which share a common inlet). [Residence times were 2.10 and 1.05 s⁻¹ for 1 and 2 channel operation respectively.](#)

3 Impact of PAN on NO₂ measurements

In this section we ~~discuss~~ [describe](#) experiments investigating ~~the potential~~ [the](#) impact of PAN on the two NO₂ instruments ~~measurements~~. In Sect. 3.1 and 3.2 we explore the interference in the laboratory 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 ~~was recorded and~~ 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 NO2 signal is proportional to increasing PAN mixing ratios. The measured mixing ratios of NO2 were 8–25% of the initial PAN mixing ratio.~~

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.

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 are 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 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 ~~an~~-interference and estimate a small (2 to 4 pptv) positive bias. The photolytic converter designs in ~~the aforementioned~~[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 ~~the inlet to~~ PAN decomposition. [in the inlet to any artifact signal.](#) The inlet in this case consists of ~~ca. ~~~ 2.7m 1/4 inch 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 [58](#) 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 ~~artefact~~[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 **plainly** 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). The light source is a 1000W quartz-halogen tungsten coiled-coil filament lamp with spectral irradiance standard F-1128. The lamp was operated at 8 Amps DC (125V), 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 ~ 1cm 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 layer of Teflon contaminated. The porosity also gives rise to the artifact NO₂ signal as new material off-gasses (as can other surfaces e.g. LED die). 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 ~~PCL~~[photolytic converter \(PLC\)](#) optics e.g. Eco Physics ~~PCL-762~~[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, 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 either with methyl, ethyl or isopropyl nitrate – methyl nitrate being a minor impurity in PAN synthesis. There is only very minor overlap in the ~~PCL~~[PLC](#) optics spectrum with PAN, methyl ethyl, and isopropyl nitrate. ~~There is~~[PLC optics exhibit](#) a great deal of overlap with HONO which the UV-LEDs do not ~~possess however~~. 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 other types of photolytic converter, 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. ~~some overlap with NO₃ radicals and BrONO₂, more so in the case of PCL optics than for UV-LEDs.~~](#)

3.6 Possible thermal interferences in BLCs

The thermal and electronic characteristics of the standard BLC lamps were ~~ascertained~~[found](#) in bench tests and are summarized in Table 3. Each lamp was run constantly ~~on the bench~~ whilst recording 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 ~~details~~[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 correlate positively with the power drawn by each lamp (R² = 0.96) and indeed with output intensity (Fig. 2), but with each lamp pair there is only weak correlation (R² = 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 experienced 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 (~~R18~~[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~~measurable PAN decomposition to NO₂ occurs above ~~ca. ~~~ca. ~ 50°C. At the maximum LED surface temperature recorded (80°C) the model predicts ~~ca. ~~~ca. ~ 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 0.96s residence is somewhat lower. ~~Also,~~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, their 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 ~~artefact~~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. 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 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 % 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) with 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 (~~R18~~R16) may be ~~excited~~vibrationally excited (likely NO₂ (2A1)) through the dissipating of internal energy from the parent PAN molecule (Mazely et al., 1995), this NO*₂ 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 “~~artefact~~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 ~~58~~58 to ~~20-25~~20-25% of the PAN supplied. The UV-LED light source ~~employed~~employed ~~by~~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.](#)

The positive bias in NO₂ measurements by NO chemiluminescence using BLCs has implications for ~~data in both~~ remote background sites ~~and polluted areas~~. 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 ~~which become more important at higher latitudes and altitudes~~.

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 ~~relaxation~~ [mixing](#) timescale (τ s) for temperature from the ambient temperature (T₀) to that of the BLC (TBLC) as in Eq. (4).

()

- t

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

τ

The rate at which thermal equilibrium is reached within the cell, τ, is calculated as 0.42s from the observed PAN decomposition of 4.6% ~~(from which T(t) is derived), %~~, 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 1st order loss of the PAN like compound and a temperature profile within in the instrument as described in 4 we have 5:

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

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 9.3.2, <http://www.geos-chem.org>, Bey et al., 2001) run at 2° x 2.5° resolution, plus updates described in Sherwen et al. ([2015](#)[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; ~~ClONO₂~~; N₂O₅; CH₃O₂NO₂, HO₂NO₂. Thermal decomposition information are taken from IUPAC evaluated kinetic data (Atkinson et al., 2003, 2006, 2007). Interferences are calculated for each month of a one year simulation and the maximum value shown. The 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), ~~and/or~~

in the upper troposphere. Here, [the concentration of](#) compounds such as PAN and HO₂NO₂ are ~~in~~ high ~~concentrations compared relative~~ to NO_x and it is not surprising that thermal decomposition can have an impact. Upper tropospheric over estimates 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 ~~value is~~ [values are](#) in general close to 1. In ~~the~~ blue the same calculation is performed but including the interferences on the NO₂ channel ~~from~~. The instrumental decomposition of [NO_y over](#) a range of BLC lamp temperatures between ~~60~~20 and ~~105~~95°C [are shown](#) (described by τ of 0.42s 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 ~~by all available measurements given the NO₂ bias we have shown exists with photo-lytic~~ [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 \(Bauguitte et al., 2012; Cantrell et al., 2003; Frey et al., 2013, 2015; This has led Griffin et al., 2007; Hosaynali Beygi et al., 2011; Kanaya et al., 2007; Yang et al., 2004\) 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 un-accounted for instrument bias our study has suggested. It is noteworthy that the studies of Bauguitte, Cantrell, Frey, Griffin, Hosaynali Beygi, Kanaya, and Yang were all in locations where we predict a significant interference \(indicated on Fig. 9\), 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. \(Bauguitte et al., 2012; Cantrell et al., 2003; Frey et al., 2013, 2015; Hosaynali Beygi et al., 2011\).](#)

~~As a practical example with an analogous system to that used in this study, the NOT observations of Hosaynali Beygi et al. (2011) taken in the South Atlantic during the “OOMPH” project (Ocean Organics Modifying Particles in both Hemispheres) serve as a case study. During this cruise a BLC photolytic NO₂ converter (Droplet Measurement Technologies, Colorado, USA), with a residence time of 1 s, as described in this study—coupled to an NO chemiluminescence analyser was deployed aboard the French research vessel Marion Dufresne II. The cruise track covered the South Atlantic Ocean from Cape Town, South Africa to Punta Arenas, Chile, reaching 60° S during March 2007.~~

~~The results presented by Hosaynali Beygi et al. (2011) show an NO₂ : NO ratio which is a factor c.a. 7 greater than can be explained given the available supporting observations of O₃, CO, OH, HO₂, ROT (RO + RO₂ + HOT), i.e. measured NO₂ is much greater than the Leighton relationship would predict. This apparent Leighton ratio is attributed by the author to an “unknown oxidant” which selectively converts NO to NO₂.~~

The authors estimate a minimal photolytic interference from atmospheric nitrates using their BLC, consistent with our analysis (Sect. 3.5 and Fig. 6). Only PAN decomposition within the inlet line is considered as a potential interference, but is estimated to be minimal (< 7 ppt) due to the low ambient temperature range of 3 to 11 °C. Our results have shown that thermal, rather than photolytic decomposition of atmospheric NO_y species with the converter itself is the major source of over-reporting in NO₂ measurements made with BLCs. Indeed, our model study predicts interference of 50 to 100% in the region of the cruise, assuming an NO₂ converter efficiency of 100%, whereas in the OOMPH observations the efficiency was 59% thus, a multiplying factor may apply to any PAN interference of ~ 1.7.

Presented in Fig. 4 of Hosaynali Beygis' paper on page 8503 (Hosaynali Beygi et al., 2011) is the Leighton ratio calculated from their NO₂ data and ancillary measurements. The ratio in the pristine background appears to be significantly biased towards NO₂, exceeding what the authors are able to explain given their measurements of HO₂, RO₂ and OH. Their values fit well within the modelled Leighton ratios shown in Fig. 10 when an instrumental bias is included however. This is suggestive of an instrumental NO₂ bias caused by a BLC with a lamp temperature of around 90°C, however does not include any multiplying effect of having an NO₂ conversion efficiency less than unity. As the efficiency is 59% the actual temperature would not necessarily be so high as 90°C. Eliminating this NO₂ over-reporting closes the oxidative balance implied by their other data and removes the need to invoke any compound X or mystery oxidant.

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 produces 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 theorization 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.

~~which cannot be explained with any available measurements. This has led to theorization of an unknown "compound X" which selectively oxidizes NO to NO₂, however this is likely anomalous and simply due to error in the NO₂ determination.~~

In order to mitigate ~~this~~ overestimation of the NO₂ mixing ratio by ~~the dissociation of~~ 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 ~~mitigate the~~ minimise uncertainty in NO₂ and to remove any multiplying effect of ~~having lower conversion efficiencies. High conversion efficiency is now achievable thanks to advancements in the power density of UV-LEDs currently available; new generation BLCs have a CE > 95% for example. Additionally, actively cooling the UV emitting elements or separating them from the gas stream is essential in order~~ more easily photolysable vibrationally excited NO₂. It would also seem prudent that the sample gas should ~~not contact any surface which is above ambient temperature. Failure to achieve this may result in spuriously high NO₂ observations~~ contact only chemically inert, and non-porous materials in order to mitigate any heterogeneous processes or memory effect; quartz being an ideal material for photolysis cells.

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Table 1. Comparison of the NO₂ ~~signal~~ observed from measurement of three zero air sources. (Eco Physics AG PAG 003, BOC Specialty Gasses 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 ~~per seconds-1~~ as well as the standard deviation of those averages.

	PAG 003	BTCA 178	Sofnofil/Carbon
Normalized concentration (pptv)			23.06 26.17 -
Signal (epscountss-1)	88.10	88.66	83.95
Standard Deviation	1.64	1.56	1.81

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

Inlet residence time (s-1)

0.84 1.05 1.40 2.10

~~NO2 (ppt) 60.2 61.3 60.6 61.5~~

NO2 (%) 5.4 5.4 5.2 5.3

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) ±0.005	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

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

Converter

efficiency (%) ±1

42 <u>33</u> <u>41</u> <u>35</u>	22
Measured %	10.8 15.9 19.6
Normalized %	4.4 5.2 4.3

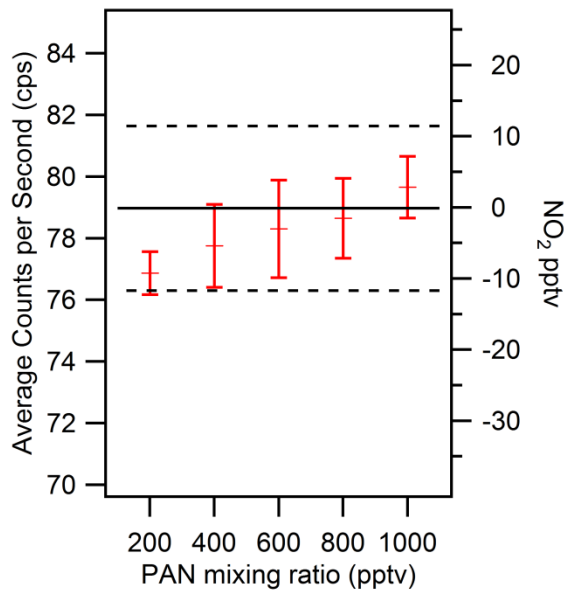


Figure 1. The average raw [counts-per-second](#) [counts s-1](#) (left) and [pptv](#) (right) recorded by a LIF instrument when sampling various mixing ratios of PAN (in red) and zero air (black). The variance of the zero air signal is also shown (dashed black). The average signal while sampling PAN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

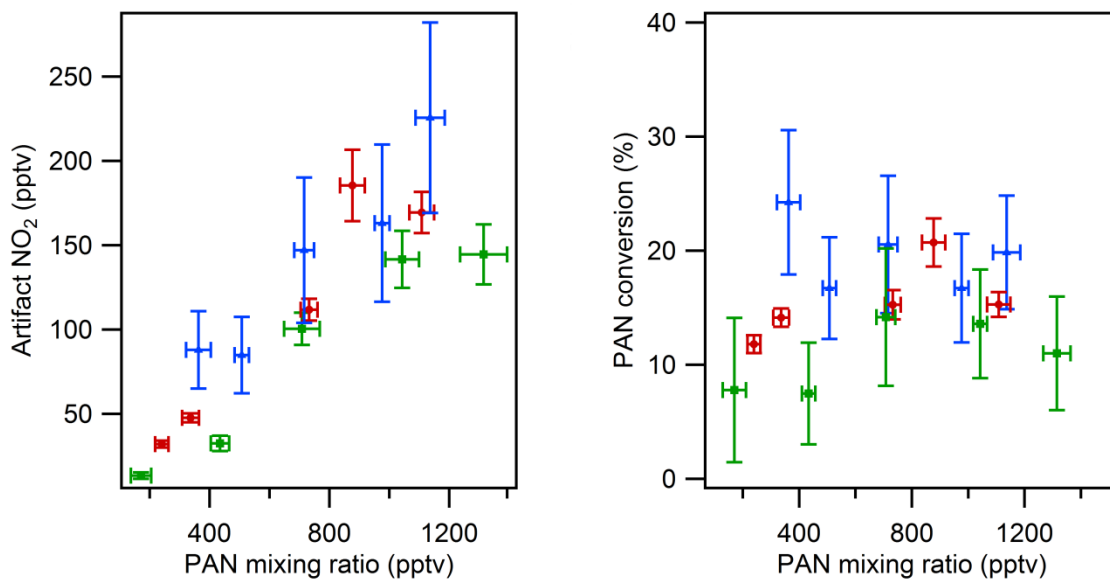


Figure 2. The measured [absolute-NO2 artifact](#) signal (left panel) of the supplied PAN mixing ratio, and as a percentage (right panel), for three BLC units operating in constant mode: [separated by NO2 conversion efficiency](#): Green = 41% CE, Red = 35% CE, Blue = 22% CE.

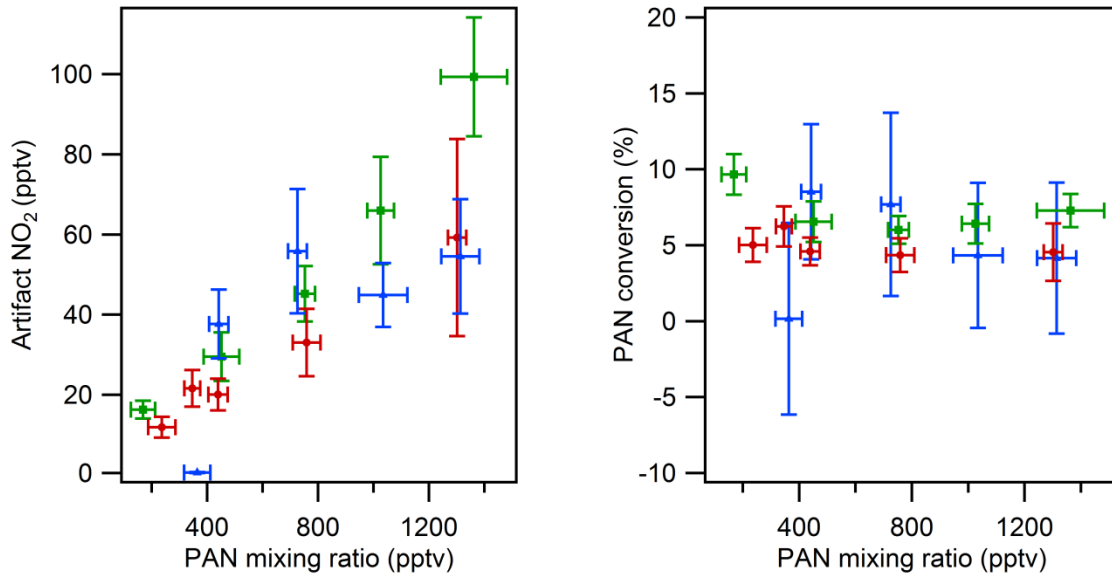


Figure 3. The measured **absolute-NO₂ artifact** signal as a function of the supplied PAN mixing ratio (left panel), and as a percentage (right panel), for three BLC units operating in switching mode-
separated by NO₂ conversion efficiency: Green = 41% CE, Red = 35% CE, Blue = 22% CE.

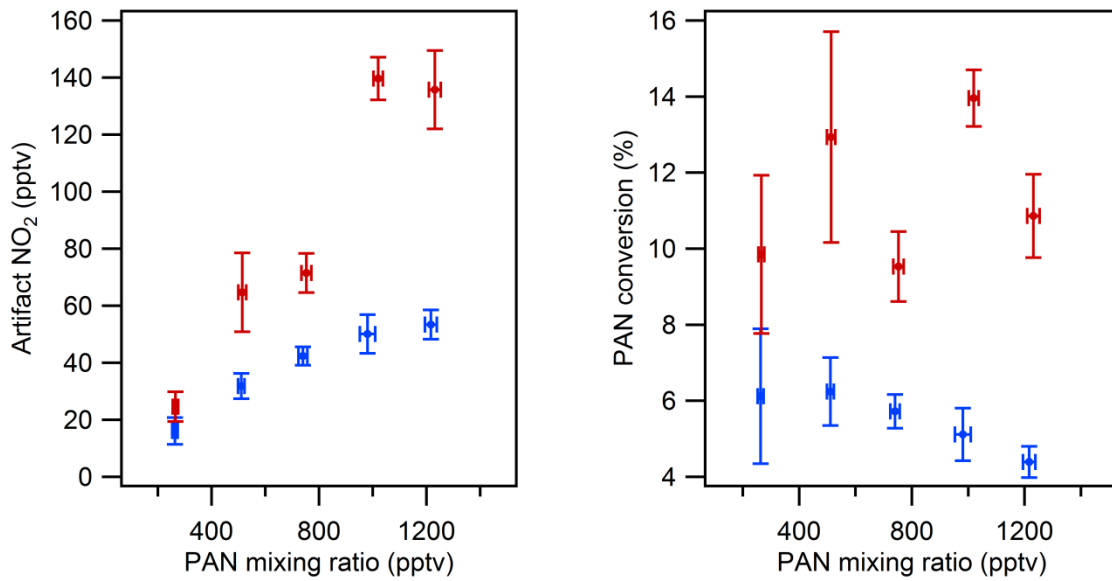


Figure 4. The measured NO₂ **artifact** signal as a function of the supplied PAN mixing ratio (left panel), and as a percentage (right panel), for the cooled (blue) and uncooled (red) high powered BLC.

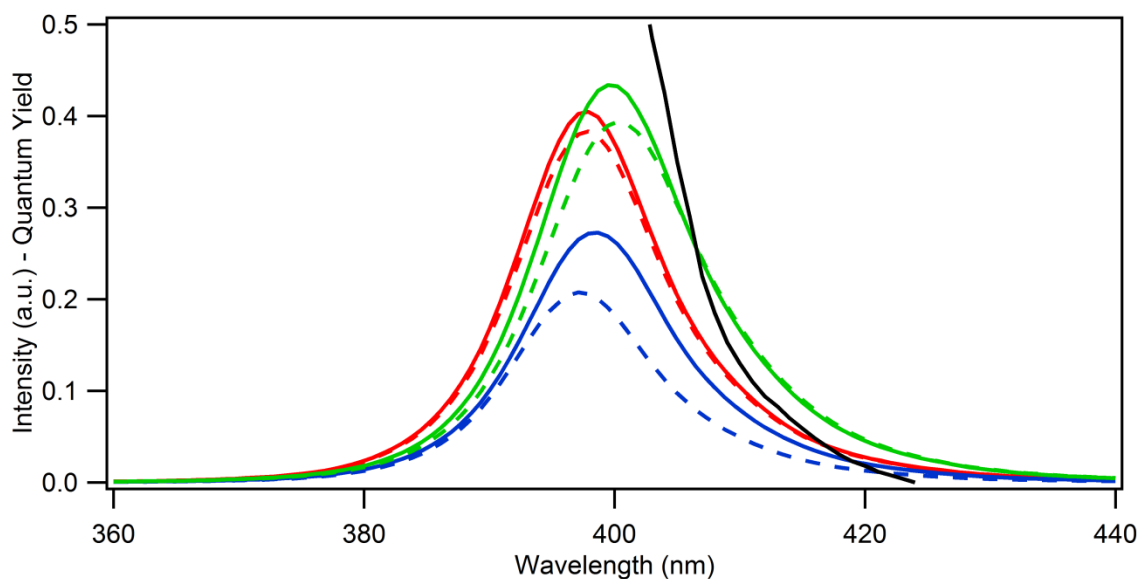


Figure 5. Shown is the spectral output vs. wavelength of two new, previously unused BLC lamps No. 1 (solid) and 2 (dashed) in green, two used lamps No. 3 (solid) and 4 (dashed) in red; still within acceptable conversion efficiency, and two which fall below acceptable limits No. 5 (solid) and 6 (dashed)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

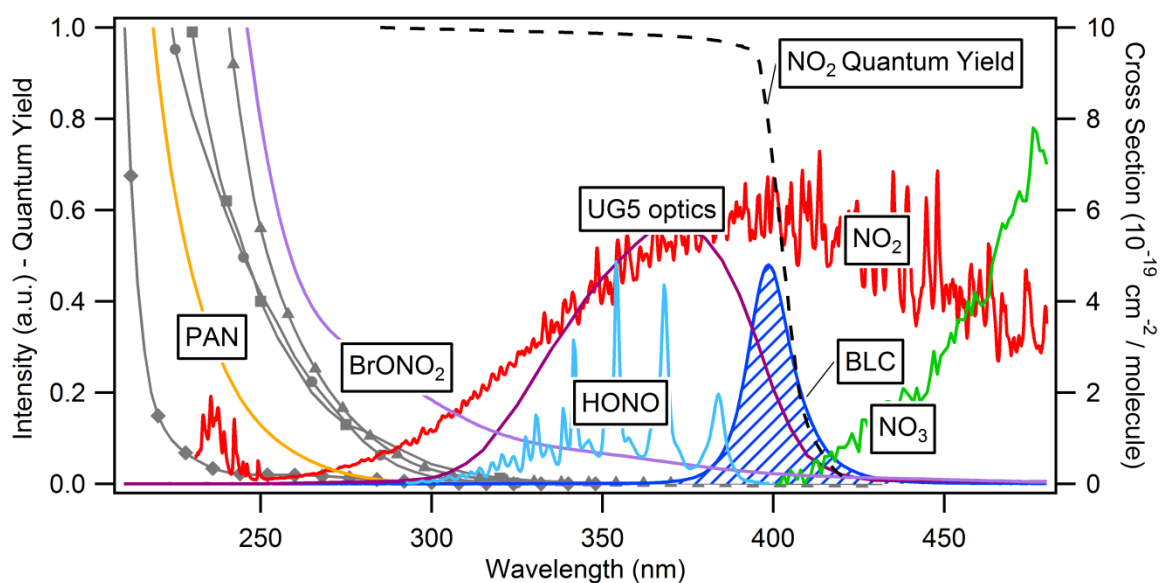


Figure 6. Absorption cross section (red) and quantum yield (dashed black) of NO₂, presented with the spectral output of UG5 optical filtering (purple) and an average of the six BLC lamps used in this study output (dark blue). Shown are interfering species; NO₃ radicals (green), HONO (light blue), BrONO₂ (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 clearly is not overlapped by either UG5 or BLC light sources. Additional non-interfering species; ClONO₂ (triangles), N₂O₅ (squares), HO₂NO₂ (circles), HNO₃ (diamonds) shown for reference.

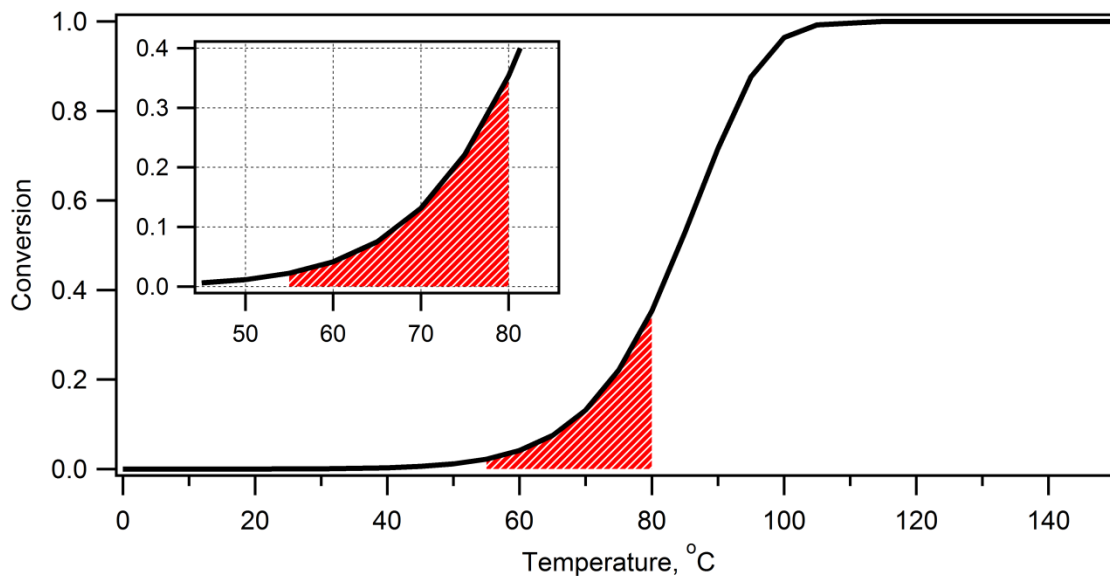


Figure 7. Model of thermal decomposition of PAN to NO₂ with a residence time of 0.96 s at temperatures between 0 to 150°C. Inset is detail of ~~30 to 90°C~~. [45 to 85°C](#). The [red shaded area](#) corresponding to the temperature range of the UV LEDs of a BLC. Kinetic data from IUPAC (Atkinson et al., 2006)

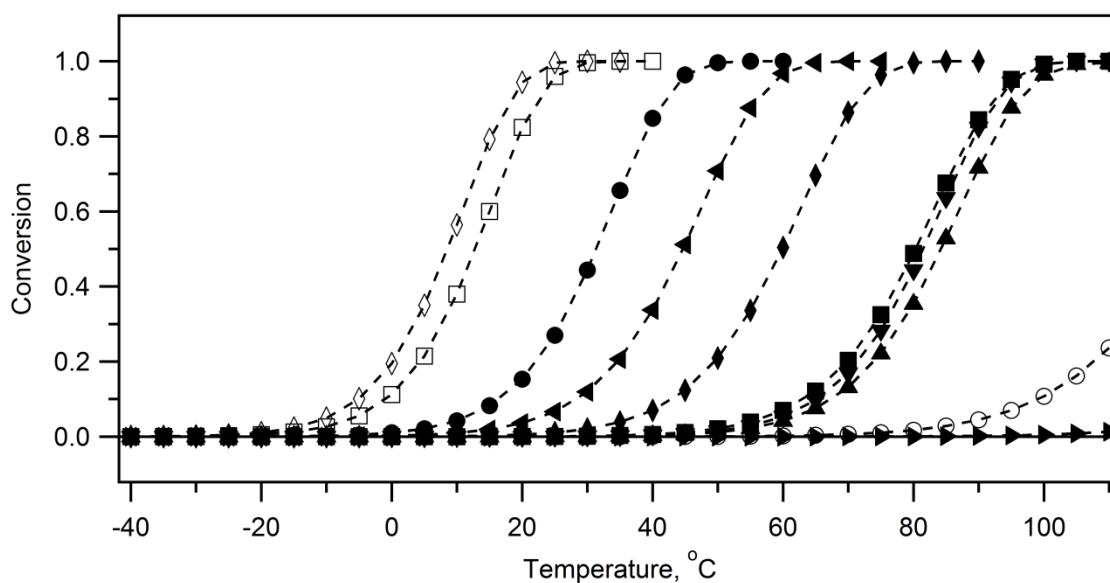


Figure 8. Thermal decomposition profiles of IONO₂ ; BrONO₂ Q; ClONO₂ ; HO₂NO₂ •; N₂O₅ J; C₂H₅O₂NO₂ ; CH₃C(O)CH₂O₂NO₂ EI; MPAN •; PAN A; PPN V. Calculated from IUPAC recommended kinetic data (Atkinson et al, 2004, 2006, 2007) using FACSIMILE [kinetic modelling](#) software (MCPA Software Ltd.) based on 1 s residence time. Note CH₃O₂NO₂ is not shown but has the same profile as ~~HO₂NO₂~~ [CH₃C\(O\)CH₂O₂NO₂](#).

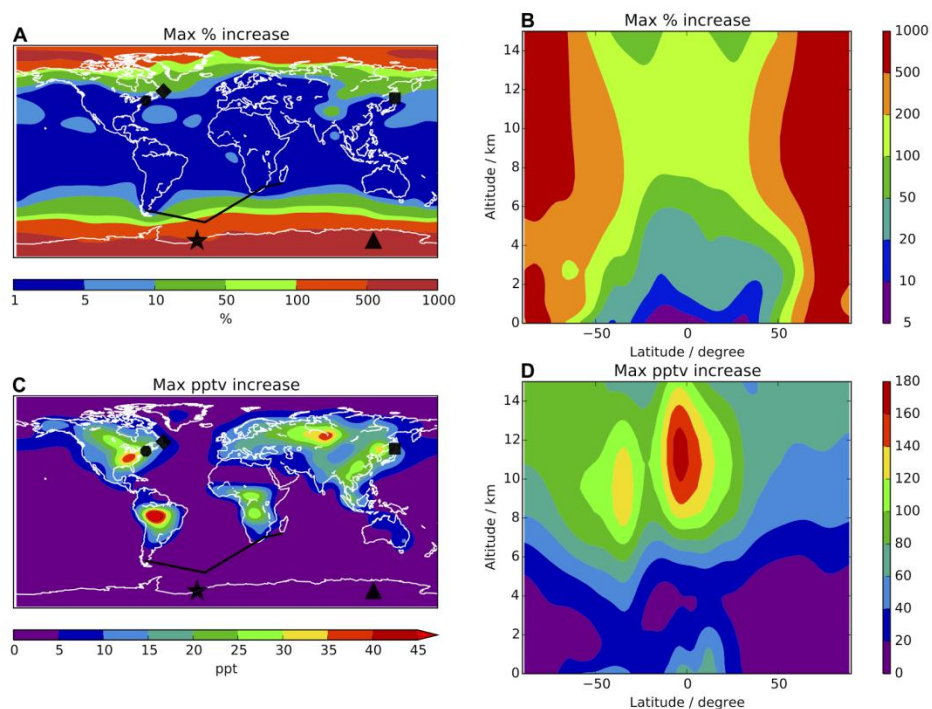


Figure 9. GEOS-Chem model [output](#) showing the monthly maximum percentage over-reporting of NO₂ [determined by BLC/Chemiluminescence](#) (a) zonally and (b) by altitude in any month of a 1 year simulation. Panels (c) and (d) show the same in absolute pptv values. ~~Note; the area over the Amazon in plot (c) is over the maximum range of the colour scale.~~ 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. \(2013, 2015\) a](#); [Griffin et al., \(2007\) •](#); [Kanaya et al., \(2007\) •](#); [Yang et al., \(2004\) .](#)

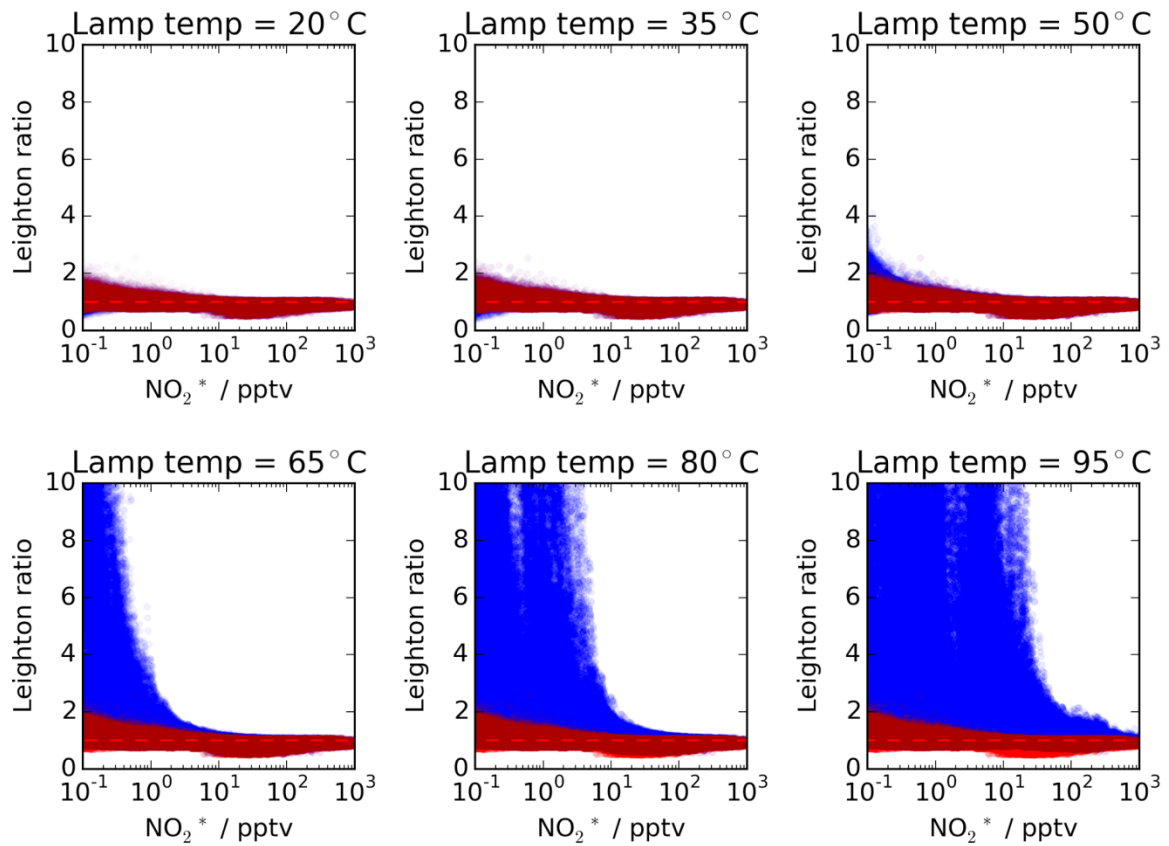


Figure 10. Leighton ratio calculated for each [surface](#) model grid-box for each daylight hour for March by the [GEOS-Chem](#) model as a function of the grid box NO₂ concentration. The instrument interference is characterized by a numerical solution of Eq. (5) with $\tau = 0.42$ s and a residence time of 1 s. Red shows the values calculated without the interference on the NO₂ concentration and the blue indicated the values calculated with the interference. The interferences are calculated for different lamp temperatures, [65](#)[20](#) to [105](#)[95](#)°C.