Interactive comment on “Interferences in photolytic NO$_2$ measurements: explanation for an apparent missing oxidant?” by C. Reed et al.

C. Reed et al.

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We, the authors, would like to thank the reviewer for their extensive comment, which, with many great points and suggestions has contributed to improving our initial submission.

We will address the reviewers points in turn below.

"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 NO$_2$ 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 characterize their instruments for e.g. PAN decomposition, and that the optimal method for doing this would be with a pure PAN source.

We have endeavored 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 NO$_2$, but also the PA radical, which can oxidize NO to NO$_2$ 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 NO$_2$ 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 characterize their instruments with a pure PAN source, or a source of any other readily available NOy 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 ppts". Technically low NOx is an ozone
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 with the reviewers suggestion.

"line 16 "thermally breakdown to release the NOx". Much of the NOx (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 vapor 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 NOx SIP Call - Methods for Ambient Air Monitoring of NO, NO2, NOy, and Individual NOz 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 NOx environments including nighttime offset, 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"."

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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 NOx 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/ppt". 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 vapor are mitigated by all experiments and calibration occurring in stable (Td) 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

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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" or "counts s⁻¹". 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 none-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.”

Noed

"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 \( \Delta G_{\text{ij}} = 1 \times 10^{-8} \text{cm}^3 \text{molecule}^{-1} \). 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 peroxy radicals 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 NOx 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/NOy. 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 (page 28720, line 5) and account for cooling, what we call mixing timescale (ðH), in our model. We also account for the temperature differential of the incoming gas.

"pg 28724 line 19 " ancillary " should be ancillary"
Corrected
"line 21 "measurements"
Corrected

"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 (Bauguitte et al., 2012; Cantrell et al., 2003; Frey et al., 2013, 2015; Griffin et al., 2007, 2011; Kanaya et al., 2007; Yang et al., 2004).

"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


Villena, G., Bejan, I., Kurtenbach, R., Wiesen, P. and Kleffmann, J.: Interferences of commercial NO2 instruments in the urban atmosphere and in a smog chamber, Atmos. C13396

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