

Interactive comment on “Interferences in photolytic NO₂ measurements: explanation for an apparent missing oxidant?” by C. Reed et al.

Anonymous Referee #1

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My apologies to the authors for not reviewing this manuscript in a more timely fashion.

Review

Reed et al. report that they have found measurement artifacts in certain NO₂ instruments equipped with blue light convertors (BLCs) that arise from thermal dissociation of peroxyacyl nitrate (PAN). The authors suggest that ambient NO₂ measurements using the BLC technique are generally biased high as a result of conversion of PAN and possibly other species (HO₂NO₂, CH₃O₂NO₂) to NO₂. Interference from decomposition of PAN and other peroxy nitrates in NO₂ instruments is well-known for conventional NO₂ instruments that use heated Mo convertors but this type of interference (we have been told) was supposed to be absent in instruments where NO₂ is selectively photodissociated to NO with a BLC. The observation that PAN does convert to NO₂ after all

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in commercial BLC instruments is an important finding that users of such instruments should be aware of and test their instruments for. Reed et al. performed GEOS-CHEM modeling to deduce that data collected remote regions and the upper layers atmosphere would be most affected by this measurement bias. The manuscript should be published after my concerns below have been addressed.

Major comments

- 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 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).

- 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?

- 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

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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.

Specific comments

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).

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

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, halogen oxides, and the nitrate radical do exist (really) and have been quantified and shown to perturb

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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).

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

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.

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

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.

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).

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

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.

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".

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

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.

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

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).

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

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".

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).

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).

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.

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).

pg 28712 line 20. Please be consistent and use only of "counts per second", "cps",

"counts s⁻¹" (line 22) Table 1 gives concentrations in cps which is somewhat useless. State concentrations or mixing ratios instead.

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.

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?

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 \rightleftharpoons PAN is $\sim 1 \times 10^{-8}$ 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.

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

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reader know at this point what the residence times typically were - for example, by referring to the table that is presented later on.

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.

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")

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?

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

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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.

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

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.

pg 28724 line 19 " ancillary " should be ancillary

line 21 "measurments"):

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

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

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

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

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.

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

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the location of the Hosaynali Beygi et al. (2011) study.

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

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