Referee 3:

The authors describe an implementation of a photolytic NO2 converter demonstrating it's' use in airborne atmospheric research – specifically high altitude aircraft measurements. The selective photolysis of NO2 using a narrow band UV source illuminating a quartz cell, followed by detection of the resulting NO by chemiluminescence has been the reference method of NOx determination since the early 2000s'.

With some comments addressed the manuscript can make a valuable contribution to AMT.

We thank the referee for the positive feedback and the time to review our manuscript.

General comments:

The authors don't give a clear rational for modifying of the Droplet Measurement Technologies (also Air Quality Design, and now Teledyne API) Blue Light Converter in the way they have, especially given the sub-optimal results.

Some laboratory studies were performed prior to the CAFE Africa campaign as part of a master thesis project and showed the mentioned surface effects. The modification of the Droplet Measurement Technologies BLC with a quartz tube was implemented to account for these effects. Due to a small time frame for the preparations at that point it was not possible to develop a new converter as alternative and undergo the full authorization /certification process for the implementation. Therefore, a quartz tube was inserted which was a compromise regarding the available time frame and the reduction of surface effects. The results of the NO2 measurements from the campaign show that the modification was by far not sufficient and post-campaign a converter entirely made from quartz was developed and tested. We have conducted the laboratory experiments with the modified conventional converter in order to enable comparison with the aircraft experiments. We have added text for clarification and added the names of the successor companies distributing the commercial blue light converter. We changed the description of the converter to type 1 for the modified blue light converter and type 2 for the alternative quartz converter for easier distinction.

Line 132 f.: We use a blue light converter (type 1) purchased from Droplet Measurement Technologies in 2005 (later Air Quality Design, now Teledyne API) (…)

Line 138 f.: Please note that this modification was made prior to the CAFE Africa research campaign within a limited time frame and did not have the desired outcome.

Why reuse the low-powered 1 W, 395 nm, UV Hex, Norlux Corp. LEDs when much more powerful units are available – and in fact are used in more recent BLCs (see: https://doi.org/10.5194/amt-9-2483-2016)?

Thank you for noting this. We have implemented the use of new LEDs which fit the modified converter design and added text regarding the specifications.

Lines 150 ff.: The applied LEDs were purchased from LED ENGIN (San Jose, California, USA) (High Efficiency VIOLET LED Emitter LZ1-10UB00-01U6, 2-2.2W, 395-400nm peak wavelength).

What is the rational for moulding the PTFE around the quartz envelope? Were no alternatives tried? Similar aircraft implementations from NOAA, NCAR and FAAM, plus the paper cited by Andersen et al., 2021 use quartz cells wrapped in baking foil! Vapour deposition of optical silver has also been used in the past with no benefit over simply wrapping.

I realise in advance the answer to the two previous questions may be due to certification hurdles of HALO/DLR.

We have performed an experiment with aluminum foil instead of PTFE and found a slightly (by a few %) lower conversion efficiency. At the same time, the PTFE envelope provides a stable housing for the sensitive quartz tube. We have added some text in the manuscript:

Lines 147 ff.: The PTFE material was found to provide a higher conversion efficiency in the converter compared to aluminum foil and additional provides a stable housing for the sensitive quartz tube.

The authors should note that their PLC/BLC implementation has remarkably similar characteristics to a once commercially available unit also marketed by Droplet Measurement Technologies – a glass envelope, shrouded in PTFE, with arrays of Norlux UV-LEDs at either end. In this case the volume is ~ 115 cm3 which is the main difference. It is well described in the paper by Pollack et al., 2010 which the authors cite. These NO2 converters were previously operated by NCAR and FAAM on their aircraft, though are long since retired.

We have added this information in the manuscript.

Lines 95 ff.: The use of quartz glass in a blue light converter was also reported by Pollack et al. (2010) who compared the commercially available converter BLC-A manufactured by Droplet Measurement Technologies to other photolytic converters.

There is a marked drop in photolysis frequency between the two BLC modifications (0.66 to 0.46) using presumably the same LEDs. The authors should discuss why this is the case; is it the design, or aging of the LEDs, change in sample gas temperature etc.

Thank you for noting this. We have added the information of the new LEDs which are likely responsible for the drop in photolysis frequency. We will investigate further improvements regarding the photolysis frequency and the conversion efficiency in more detail in the future.

Lines 150 ff.: The applied LEDs were purchased from LED ENGIN (San Jose, California, USA) (High Efficiency VIOLET LED Emitter LZ1-10UB00-01U6, 2-2.2W, 395-400nm peak wavelength).

There is no description of the aircraft inlet from which the NOx instrument samples. Is that heated? What is the residence time to the instrument? What is the sample line/cabin temperature? When discussing the uncertainty of airborne measurements these must be taken into account.

The NOx instrument sampled from the aircraft inlet via a bypass line of an approximate length of 1.5 - 2m and an inner diameter of 3/8 inches (1/2 tubing) (≈0.95cm) giving a volume of around 500 cm³ (±20%). The flow was around 80 SLM and the pressure in the line depended on the aircraft altitude. At ground level pressure the residence time to the instrument was around 0.4s. At 12km altitude the residence time was only <0.1s. The aircraft inlet was not heated, the cabin/sample line temperature was approximately 25°C. We have added this information to the manuscript.

Lines 194 ff.: A bypass line provided the instruments with air from the aircraft inlet for which the residence time depended on the ambient pressure level (for high altitudes <0.1s). The sample line temperature was approximately 25°C.

There is no schematic of the instrument given so I must assume it is identical to F2 given in Tadic et al., 2020. Several elements of the design shown there may skew measurements, especially during your discussion of the effects of humidity.

Firstly, the sample flows through mass flow controllers in the high pressure side of the inlet system which a) increases hold-up/lag, but also provides plenty of stainless steel surfaces to form layers of water on. Secondly, the NO and NOx channels appear to have different volumes due to there only being an NO2 converter on the NOx channel and no dead cell on the NO channel. Necessarily, there are different surface areas between the two, and different volumes, thus data must be offset between the two channels to compensate for the different residence times which themselves must either be very carefully measured or modelled. I doubt for instance that the true residence time if the BLC is 0.34 seconds – this is more likely 1 e-folding time. Lastly, and most crucially, the flow of humidified ozone is switched between reaction and pre-chamber of the CLD, with the sample (of varying humidity) constantly passing through the pre-chamber. This results in wildly fluctuating humidity within the pre-chamber. Many airborne CLDs follow the scheme in Pollack et al. 2010 whereby the humidified ozone constantly passes through the pre-chamber and the sample is switched – this also acts to decrease the response time of the instrument by removing dead volume.

Ultimately, I don't think flaws in the instrument design can account for the humidity effects described, though they should be considered.

The referee is correct that the schematic of the instrument is identical to Figure 2 in Tadic et al. (2020). We have clarified this in the text.

Thank you for pointing out the possible effects of humidity that could result from the design of the instrument. Please note that the NO and the NOc channel are structurally identical apart from the photolytic converter and two short (~20cm) Teflon lines for the gas in and outlet. We do not observe any humidity effects in the NO channel and therefore we can exclude that stainless steel surfaces or the varying humidity in the pre-chamber account for the described effects. These components are equally present in both channels. The referee is correct about the different residence times in the two channels, however we only observe the humidity effects in the type 1 blue light converter with the porous surface, not in the type 2 quartz converter. The additional residence time using either converter is the same (0.33 and 0.34s). We therefore conclude that the different residence times cannot account for the observed humidity effects either. We have added a note on this to the manuscript.

Lines 124 ff.: All NOx measurements were performed using a modified two-channel chemiluminescence instrument originally purchased from ECO Physics, Dürnten, Switzerland (CLD 790 SR) as described by Tadic et al. (2020) (Figure 2 presets the instrument schematic) (…).

Lines 432 f.: As we do not observe these effects in the NO channel (and the two channels are structurally identical), we can exclude that any of the humidity effects are caused by components in the instrument other than the photolytic converter.

The whole discussion on possible mechanisms for NO/H2O selective/competitive sorption is highly speculative and hard to follow at times.

We regret that the referee finds the discussion on possible mechanisms hard to follow. We agree with the referee that we cannot finally prove the exact mechanism taking place in the photolytic converter which is why we use the word “hypothesis” in our discussion. We would like to offer our readers a possible explanation for our observations which is consistent with the results of the experiments we performed. For our work, knowing the exact mechanism is not imperative, but our observations and ideas might be helpful for other researchers who would like to solve similar questions.

A typical test flight when commissioning a new NOx instrument is to fly whilst adding an amount of NO well above ambient to the inlet, performing profiles, orbits, in-cloud, boundary layer, and free troposphere runs – a system which is performing well will show no deviation throughout the entire flight envelope.

We would like to thank the referee for this advice. We aim to conduct these experiments when using the quartz converter during our next aircraft campaign. We will then get the chance to test our quartz converter under ambient conditions.

Specific comments:

Line 86: this was also the conclusion of Reed et al., 2016 which is cited.

We have added the citation of Reed et al., 2016 to this sentence.

Line 90 f.: The correct adjustment of the conditions, preferably including low pressure, high flow rates and small temperature variations, can minimize interferences which was also concluded by Reed et al. (2016).

Line 117: ‘commercially available’ – all four example of the CLD 790 SR were built for DLR on special order, no?

We purchased our instrument from ECO Physics around 2000. The reviewer is correct that four examples (as far as we know) exist. We have rephrased this sentence.

Lines 124 ff.: All NOx measurements were performed using a modified two-channel chemiluminescence instrument originally purchased from ECO Physics, Dürnten, Switzerland (CLD 790 SR) as described by Tadic et al. (2020) (...).

Line 123: State the reason why the photolysis cell is operated at 110 mb i.e. this is a pressure height of ~50kft which is the service ceiling of HALO/G550.

We operate the converter at a pressure level lower than the minimum ambient pressure so that the conversion efficiency from NO2 to NO is not dependent on the aircraft altitude, but a constant value in order to prevent an additional uncertainty from calculating altitude-dependent CEs. We have added some text for clarification.

Lines 152 ff.: Please note that the low conversion efficiencies in both converters result from the operation at low pressures which we have implemented in regard to aircraft measurements where altitude changes are accompanied by pressure variations. Operating the converter at lower than minimum ambient pressure levels (max. ~15km flight altitude) has the benefit of a constant conversion efficiency. The fractional dissociation of thermally unstable NOx reservoir species increases with increasing pressure in the converter which can be seen in Figure S1a of the Supplement. On the other hand, a higher conversion efficiency would be desirable for improved accuracy of the measurement.

Line 124: The stated wavelength is 398 nm of the UV LEDs – the design wavelength is 395 nm – is this a typo or was it measured (and not shown/described)? If the latter then a lot of energy is being wasted outside of the quantum yield of NO2 which drops rapidly at ~400 nm.

We have characterized the UV LEDs in the laboratory and the spectral emission showed a maximum at 397 nm with a full width at half maximum of 14 nm. We have corrected this in the main text.

Lines 132 ff.: We use a blue light converter (type 1) purchased from Droplet Measurement Technologies in 2005 (later Air Quality Design, now Teledyne API) equipped with UV-LEDs emitting at a wavelength of 397 nm (FWHM = 14 nm, as characterized in the laboratory) (…).

Line 132: please state the j value along with the conversion efficiency i.e. 0.656 s-1

We have added the j value in the main text.

Line 143: (j = 0.66 s-1)

Line 138: please state the j value along with the conversion efficiency i.e. 0.457 s-1

We have added the j value.

Line 150: (j = 0.46 s-1)

Line 138: presumably the gas flow doesn't contact the LEDs either in the design depicted in F1b? This would in-turn lead to much less sample heating and have a large impact on any thermal artefacts.

We agree with the referee. We have added this information to the manuscript.

Lines 159 ff.: Additionally, the sample gas flow in the type 2 quartz converter does not have contact with the LEDs which likely minimizes the sample gas heating and consequently the thermal interferences when passing through the converter.

Line 178: limits of detection are only useful when an averaging time is stated, please add this, how many standard deviations are included in the determination of LOD and uncertainty? e.g. 5 pptv averaged over 10 seconds, 3 sigma uncertainty of 6% etc.

Thank you for noting this. We have added the information.

Line 207: 5 pptv detection limit at 1 min integration time and 6 % relative uncertainty (1σ)

Line 146: What is the residence time of the pre-chamber; same as the reaction chamber? What is the efficiency? What is the material?

The pre-chamber volume is approximately 160 cm³ with a gas flow of 1.5 SLM and a pressure of ~100 hPa. This gives a residence time of approximately 0.6 s. Please note, that we do not measure the pre-chamber pressure and the residence time is therefore an estimate. The volume of the main chamber is approximately 380 cm³ and a pressure of 10 hPa which yields a residence time of around 0.15 s. The efficiency of the pre-chamber is >96% for the NO channel and ~100% for the NOc channel. The material of the chambers is gold-plated stainless steel. We have added this information to the manuscript.

Lines 166 ff.: The residence time in the pre-chamber allows for the reaction of O3 and NO and the relaxation of NO2* before entering the main reaction chamber (pre-chamber efficiency >96% for the NO channel and ~100% for the NOc channel).

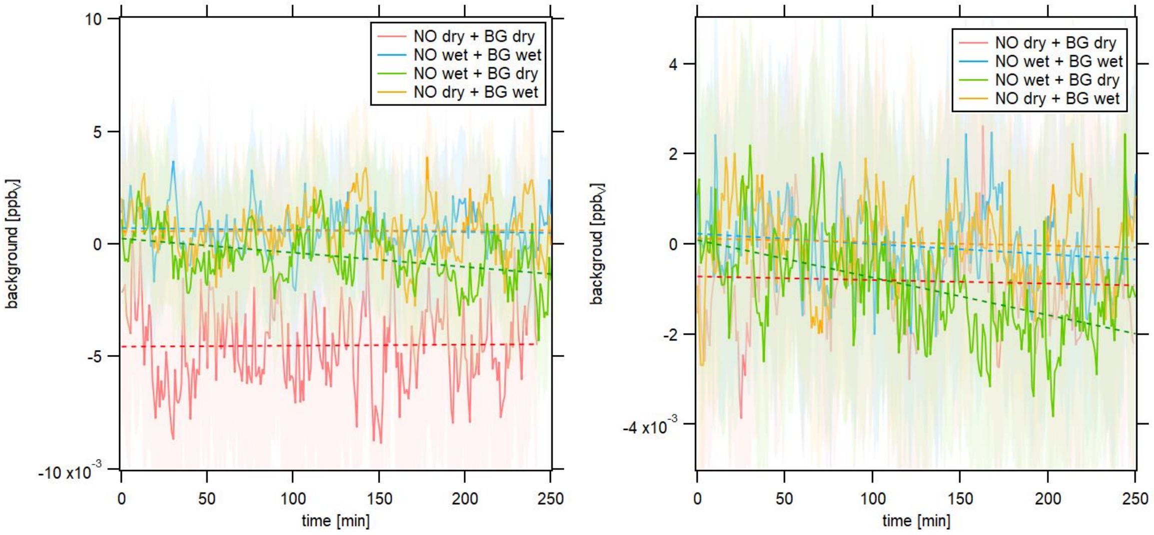
Line 172 f.: The material of both the pre- and the main-chambers is gold-plated stainless steel.

Line 282: '…monitoring system for pressure…' in an airborne system the pressure must always be known and/or controlled otherwise the conversion efficiency of NO2 to NO is unknowable, regardless of potential artefacts or not!

We agree with the referee and have rephrased the sentence for clarification.

Lines 312 ff.: Based on these results, we recommend the implementation of a monitoring system for both temperature and pressure within the photolytic converter (…).

Line 370: I'm not sure it is true that there are no trends in the NO channel signal – I think the scale may be helping here – perhaps fit the trends to remove any doubt or adjust the scale.



We have added a linear fit to the measured background in the NO channel vs time for the two experiments and changed the scale for investigating the suggestion of the referee. There is no trend for most lines and if at all a downward tendency for the measurement NO wet + BG dry which could be due to surface effects on other components such as metal surfaces within the instrument. However, the change is very small compared to the observations in the NOc channel and more importantly, the 3σ uncertainty is larger than (the 2σ uncertainty approx. equal) the observed decrease over 250 minutes and therefore not significant. We have added text in the manuscript to point that out.

Lines 403 ff.: For comparison, the instrumental background signal in the NO channel over time is presented in Figure S5 of the Supplement. The lines show no significant trend over time.

Line 411 -414: the logic in this statement is flawed – you can only measure NO with a CLD, therefore you only saw NO in your experiment. You could do the same experiment with the BLC connected to a direct NO2 measurement, or a PAN-GC or a CIMS for that matter and would likely see may compounds desorb.

We intended to say that NO has to be part of the observed effect in the blue light converter. We showed this by switching off the converter, so that only NO could be detected. The observed signal in the NOc channel increased when applying heat which we see as proof that NO is involved. However, other molecules can play a role, too, which we show exemplarily with the HNO3 uptake experiment (Figures in Supplement). We agree with the referee that our wording might be misleading and have rephrased the sentence.

Lines 447 ff.: Our assumption that the observed effect is - at least partly - associated with NO molecules is supported by an experiment where we heated the type 1 blue light converter with switched-off LEDs with a heat gun and observed a sharp increase in the NOc channel during zero air measurement (following NO calibration measurement).

Sect 2.5: please define all the acronyms for the NOy species (MPN,PAN…) at their first use.

The acronyms for the NOy species are first used and defined in the Introduction Section 1. However, we agree with the referee that it benefits the reading flow if we provide the acronyms in Sect 2.5, again and have adjusted the text accordingly.

Line 255: We consider the NO2 reservoir species PAN (peroxyacetyl nitrate), MPN (methyl peroxy nitrate) and PNA (pernitric acid).