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Comment on amt-2021-180

Anonymous Referee #1

Referee comment on "Modification of a conventional photolytic converter for improving aircraft measurements of NO_2 via chemiluminescence" by Clara M. Nussbaumer et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-180-RC3, 2021

This manuscript describes a photolytic converter for airborne measurements of NO_2. The focus of the paper is measurements of NO_2 in remote areas where mixing ratios are sub 1 ppb. The authors describe interferences and artefacts associated with a commercial photolytic converter that complicate these sub-1 ppb measurements and suggest modifications to the commercial converter that reduce the effects of artefacts. There is not an overabundance of publications about the nuances of NO_2 photolytic converters, and thus I believe this manuscript can be a value contribution to the atmospheric community.

I agree with the assessments and comments posted by the other referees. I had many of the same concerns. Thus, in an effort to streamline the review process, I have only included my additional thoughts here. I hope they are helpful.

Comments:

Title: I do not think that the word “new” is appropriate for the title. This is because there is not anything particularly novel about the modified converter. The use of a fully enclosed quartz cell with and without a reflective Teflon shroud is not new among the airborne research community. However, these PCL systems are typically custom built (e.g., Pollack et al., 2010, Jordan et al., 2020). I wonder if a better title could be “Modification of a commercial photolytic converter for improved aircraft measurements of NO_2 via chemiluminescence”.

Abstract: Please add another sentence or two to the abstract about the aircraft measurement findings related to the NO_2 reservoir species. This is first and foremost in the results section but seems to be lacking mention in the abstract. Also, the abstract is a bit misleading in that it highlights the memory effect as the key phenomenon. Yet, the observations from CAFÉ are likely a combination of phenomena that also include an artefact from the subtraction of two signal channels and a changing background.

Line 6 and throughout: Maybe it is just me, but I find the use of the word “conventional” to be a bit bothersome. This is because the photolytic converters typically used aboard aircraft do not use the porous Teflon material with ring channel for gas introduction. The word “conventional” seems more appropriate for ground-based applications that utilize commercial monitors and commercial converters. It might help to clarify the difference in the text.

Line 124: Can you add the year the BLC was purchased from DMT? This could help readers distinguish between the version of "conventional" BLC that you are using compared to other versions of "conventional" commercial BLCs.

Line 134-142: I don’t think the use of the words “new” or “newly-developed” are appropriate here since several existing converters already separate the sample flow from direct contact with the porous Teflon surfaces. Maybe a better word for the converter shown in Figure 1b is “modified” or “updated”.

Section 2.2: I understand the elimination of a night flight (MF11), but why were only MF10 and MF12 through MF15 used in this study? Were MF01 through MF09 not good candidates, was NO_2 data not collected during those flights, or was this phenomenon not observed during those flights?

Line 170: Can you add a figure (either here or in the SI) that shows the J-curve for your converters? The conversion efficiencies of the “conventional” BLC (20%) and your “updated” converter (14%) are very low. This is likely a function of your very low cell pressure, which when combined with the high flow rate, results in a short residence time in the photolysis cell. It would be helpful to see how each converter (the conventional versus the updated BLC) behaves over a range of residence times. Regardless, a note should be included in the text to associate the low conversion efficiency with the low cell pressure, which is needed for high altitude measurements.

Line 180: Is it reasonable to utilize a nighttime NO concentration instead of zero measurements for determining c(NO) when the c(NO_2) is determined from the subtraction of the NO measurement from c(NOc) and c($background_{NOc}$) determined from a zero? What is the magnitude of the difference between NO zeros at night versus NO zeros with an overflow of zero air? Has this difference been factored into an uncertainty calculation for c(NO) and c(NO_2)? What is the overall measurement uncertainty for NO and NO_2? Also, what was the concentration and uncertainty of the NO standard used for calibrations. What was the effective calibration mixing ratio after dilution into the sample flow? It would be helpful to add these details to the manuscript.

Line 305: I wonder if the changes in background can be more carefully characterized in a future flight by overblowing the instrument inlet with zero air for the duration of a test flight (aka. a “null” flight). The in-flight instrument performance can be evaluated from changes in the background signal levels during vertical profiles and maneuvers, which can

inform about precision, detection limit, motion sensitivity, and fluctuations with pressure and temperature. It can also inform about lags in the recovery of background signals with these perturbations. For high altitude chemiluminescence applications, it might also be interesting to characterize the PMT dark counts versus background in a future test flight by periodically turning off the reagent O3 injection.

Line 329: How do the NO_2 measurements change if you assume a constant background signal per altitude level? My first instinct would be that subtracting an interpolated background signal would contribute a good bit to the negative excursions in NO_2. Since the CLD 790 SR has two separate channels, is the BG trace in Figure 5 meant to be the background signal of the NO_2 channel? How does the background of the NO channel differ from that of the NO_2 channel with the LEDs on and off? Does the NO channel background also change with altitude or only the background measured through the converter? Can you add the NO channel BG as a trace in the Figure?

Section 3.1.3: I admit, I found the logic of this section a little hard to follow. If I have this correct, the bulk of the discussion in this section is about the instances when NO2_CLD is enhanced yet there are no enhancements in NO2_PSS nor NO2_DOAS. The authors are claiming that the NO2_CLD enhancements are correlated with increases in water vapor as the aircraft descends. The authors associated the discrepancy to a hysteresis in the photolysis cell upon the introduction of water vapor. If this were the case, then I agree that a decrease in NO_2 back to baseline levels following the increase in water vapor with the lag time representing the memory effect time would be expected. However, the rising edge of the enhancement in NO_2 that starts to increase as a large step change in NO starts to decrease and that occurs earlier in time than the step change in water vapor concentration is not something that I would have expected from a memory effect phenomenon. This leads me to believe that the NO_2 peaks are more of an artefact of the NO channel subtraction, which is enhanced by a factor of 4 due to the correction for Ce, and less so from a memory effect of water vapor on the photolysis cell sampling surfaces.

From the manuscript (mainly the abstract, introduction, and conclusions), I am led to believe that the authors think the memory effect is the key phenomenon at play with the "conventional" converter. However, the results and discussion of the CAFÉ observations suggest that the signal subtraction, low Ce, fluctuations in background, and large changes in NO concentrations could also have been significant contributors to the observations. Thus, it seems a little misleading to only mention memory effects in the abstract and conclusions. It is my recommendation that the text in the abstract and conclusions be updated to reflect the observations and all possible factors that could have impacted the CAFÉ observations.

Section 3.2: The UV artefact (Figure S5) of 0.1 ppb seems substantial for a sub-1ppb ambient measurement. How does the UV artefact factor into your subtraction calculations (e.g., eq. 4) and into the overall measurement uncertainty? What does Figure S5 look like for the updated converter?