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## Comment on amt-2021-432

Anonymous Referee #2

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Referee comment on "Comparison of airborne measurements of NO, NO<sub>2</sub>, HONO, NO<sub>y</sub> and CO during FIREX-AQ" by Ilann bourgeois et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-432-RC2>, 2022

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Bourgeois et al. report aircraft measurements made on board the NASA DC-8 during the FIREX-AQ campaign in 2019. In this paper, the authors compare duplicate measurements of NO mixing ratios by chemiluminescence and by laser-induced fluorescence (LIF), of NO<sub>2</sub> by photolysis coupled to CL (P-CL), cavity-enhanced absorption spectroscopy (CES), and LIF, HONO by chemical ionization mass spectrometry (CIMS) and CES, and of CO by tunable diode laser absorption spectroscopy (TLDas) and integrated cavity output spectroscopy (ICOS). The authors also attempt to close the NO<sub>y</sub> budget by comparing NO<sub>y</sub> measured by CL with a sum of individually measured components, ΣNO<sub>y</sub>, calculated by adding NO, NO<sub>2</sub>, HONO, HNO<sub>3</sub> (measured by another CIMS), pNO<sub>3</sub> (measured using an aerosol mass spectrometer, AMS) and acyl peroxy nitrates (APNs) that were quantified by a third CIMS.

This is a well written manuscript though perhaps a bit too long. There is a lot of interesting results, for example, a great validation of the new LIF instrument and excellent agreements for NO and NO<sub>2</sub>, but there were also a few questionable items (see below) that the authors will hopefully be able to address in the finalization of this manuscript.

### General/Major comments

(1) Tables are, strangely, absent from this paper. Having tables would have helped consolidate this rather long manuscript. Specifically:

Please add a table of measurements/instruments.

Please also add a table of the flight schedule(s), indicating time of day and whether there were nighttime flights analyzed here.

Please add a table which summarizing statistics on the mixing ratios observed (e.g., median, average, percentiles, max and min etc.).

Please consolidate the various correlation slopes/intercepts in one or more tables as well.

(2) Please clarify if the comparisons made here were "blind" or if kibitzing was allowed/possible before individual PIs reported their data.

(3) Some instrument descriptions are very thorough (and thank you for that!) yet important details are missing for others. For example, APN data presented, but it is unclear which individual compounds were actually quantified (PAN, PPN, MPAN, APAN etc.) and included in the sum. There was also no statement as to how good or uncertain these data are. HCN and NH<sub>3</sub> concentrations were quantified (Figure S14) but their measurement is not described at all.

(4) Measurements of HNO<sub>3</sub>, APNs, ClNO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, pNO<sub>3</sub>, C1-C5 alkyl nitrates were made but sample time series of those data are not shown, which is an odd omission considering that some of these compounds contribute the most to NO<sub>y</sub> (judging from Figure 10).

(5) The definition and choices/explanations as to what species to include in  $\Sigma\text{NO}_y$  in this manuscript (abstract line 14; equation 2, line 339) would benefit from some polishing.

(a) Definitions.

Please add (to the introduction - see comment on lines 95-98) a comprehensive definition of what species contribute to NO<sub>y</sub> (e.g., equation (1) of Fahey et al., J. Geophys. Res., 91, 9781-9793, 10.1029/JD091iD09p09781, 1986), if only to provide a contrast to equation (2) of this manuscript.

Many components of NO<sub>y</sub> are omitted from equation (2). Please note more prominently the (many) omissions from  $\Sigma\text{NO}_y$  in the abstract, such as higher molecular weight alkyl

nitrates ("total alkyl nitrates", line 846), coarse nitrate, peroxy nitrates ( $\text{HO}_2\text{NO}_2$ ,  $\text{RO}_2\text{NO}_2$ ), and the nocturnal nitrogen oxides  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$ .

Since the expression given here for  $\Sigma\text{NO}_y$  is a simplification, the right-hand side of equation (2) only approximates  $\Sigma\text{NO}_y$  and an equal sign should not be used (use  $\approx$  instead).

Further, since the expression for  $\Sigma\text{NO}_y$  omits nocturnal nitrogen oxides, the definition of  $\Sigma\text{NO}_y$  as in equation (2) should perhaps be referred to as the sum of daytime nitrogen oxides, and the time of day of the measurements should be added to the title.

#### (b) Organization.

It is clear from the outset that several components of  $\text{NO}_y$  were measured by multiple instruments, yet the reader is kept in the dark for far too long what the authors included in this sum and what they mean by  $\Sigma\text{NO}_y$  (e.g., line 14 and 339). If I counted correctly, there are (at least) 36 different ways  $\Sigma\text{NO}_y$  could have possibly been calculated for this data set (NO from either one of two instruments or average NO which gives 3 possibilities,  $\text{NO}_2$  from one of three instruments or average  $\text{NO}_2$  to give 4 possibilities, HONO from one of two instruments or average HONO to give 3 possibilities,  $3 \times 4 \times 3 = 36$  possible combinations). The reader is only told on line 732 which measurements were actually used.

#### (c) Closure.

Having so many choices (data from several instruments to choose from, and which compounds to include in  $\Sigma\text{NO}_y$ ) is great, but ultimately undermines the conclusion that  $\text{NO}_y$  budget closure was achieved (lines 22/23).

Even though I know this wasn't the case, the manuscript somehow gave me the vibe that data were cherry-picked and the authors stopped adding compounds to  $\Sigma\text{NO}_y$  once the slope relative to  $\text{NO}_{y,\text{CL}}$  reached unity. Can you be more convincing - for example, why not add all components that were quantified - surely, there would have been times when all instruments were operational? Please add such a plot (and use the larger  $\text{NO}_x$  and HONO data from the LIF & CES instruments).

And please discuss the elephant in the room: The unquantified components of  $\text{NO}_y$ . If closure was indeed achieved, it would imply that those unquantified components were negligible, which in my opinion is doubtful.

It is stated on line 846, that FIREX-AQ did not include a measurement of total alkyl nitrates, but the thought is left hanging. What if the suite of instruments had included such a measurement? Would the  $\text{NO}_y$  budget have blown up? I'd be surprised if the Cohen group had not quantified  $\Sigma\text{AN}$  in fire plumes at some point to help constrain this "known unknown" and to guide this discussion.

Also, if submicron  $\text{pNO}_3$  constituted  $\sim 40\%$  or so of  $\text{NO}_y$  in wildfire plumes (Figure 10a), surely there would have been coarse nitrate as well, which would have consequences on closure. More discussion is needed. There were measurements of coarse mode size distributions (Schoeberl et al., Coarse mode aerosol in biomass burning aerosol layers during FIREX-AQ, TBD, in prep, 2021 - listed on <https://csl.noaa.gov/projects/firex-aq/science/pubs.html> and Noyes et al., Remote Sensing 12(22), 3223, <https://doi.org/10.3390/rs12223823>) that may provide some constraints here.

#### (6) Carbon monoxide

The sections on CO seem like an afterthought and do not add much to the remainder of the paper. I'd recommend splitting this off into a separate to reduce the size of this already very long paper.

#### Specific/Minor comments

line 21. a slope of 1.8 - yikes!

line 72. Please add a table summarizing this large suite of airborne instruments.

lines 95-98. Please insert an equation here, defining  $\text{NO}_y$  (similar to equation (1) of Fahey et al., J. Geophys. Res., 91, 9781-9793, 10.1029/JD091iD09p09781, 1986).

line 112. There have been other papers from this campaign (e.g., Decker et al.) that would be worth calling out here.

lines 159. Pollack et al. describe two converters with LEDs at 365 nm and one converter at 395 nm, but not one at 385 nm. Is this a new system? If so, please provide relative data

such as make/power of the LEDs, NO<sub>2</sub> photolysis frequency, temperature etc.

line 160. Pollack et al. - the Journal of Atmospheric Chemistry lists this citation as a 2010 paper (even though it was only accepted in 2011). Please update.

line 180. "5% HONO interference". The magnitude of this interference will depend on the ratio of HONO to NO<sub>2</sub> in ambient air. Please clarify what is meant by 5% (stated on lines 615-617: 5% of the HONO sampled converts to NO).

line 209. please provide an uncertainty estimate for the NO-LIF instrument similar to lines 183, 220 and 280.

line 247. please state how the zero air was generated (cylinder or scrubbed air).

line 259. Please state how often the Teflon filters were changed.

line 271. a 0<sup>th</sup> order polynomial - interesting way to say "offset".

lines 270-276. Please comment on errors introduced from using reference absorption cross-sections are measured at near 1 atm pressure and near room temperature to fit absorption spectra collected at reduced pressure and ambient (I am guessing) temperature.

line 281. What is the effective optical path of this instrument?

line 307. What is the linear dynamic range of this instrument?

line 310. "normalized by the iodide signals" - I<sup>-</sup> or I<sup>-</sup>·H<sub>2</sub>O or both? The Pratt group has recently used the water cluster to normalize.

line 313-314. "Calibrations with Cl<sub>2</sub> and HNO<sub>3</sub> permeation sources ... to diagnose the stability of instrument sensitivity" - please comment on how stable that response turned out to be (perhaps further down in the results section).

line 321. background typically equivalent to 40 ppt - what was the range of backgrounds observed? Does the background increase after sampling high concentrations of HONO?

line 339. Data from which instruments were used to account for the species in equation (2)?

line 372-373. Can you speculate how much coarse nitrate there might be in a biomass burning plume?

line 393. please provide an uncertainty estimate for the CIMS measuring APNs instrument similar to lines 183, 220 and 280 (see also comment for line 209).

line 404-415. Are the  $N_2O_5$  data presented anywhere? If these data are from the same instrument that underestimated HONO by a factor of 1.8, how confident can one be in the  $N_2O_5$  data and stated  $\pm(15\% + 2 \text{ pptv})$  accuracy?

line 431. "at approximately  $4.6 \mu\text{m}$ " Since these types of instruments monitor a specific absorption line and derive mole fractions based on that particular line's line strength, please be more specific here.

In general, more detail (or a more appropriate citation) is needed in this section since the Baer et al. (2002) reference does not describe an instrument quantifying CO via its absorption in the mid-IR.

line 442 and 456-457 "dry air mole fraction". Is this correction made purely because the water vapour variability is sufficiently large to cause deviations to mole fractions, or are there other effects in play, too, such as spectral broadening or overlap with water lines in the IR? Please add an explanation and justification for this correction to the text.

In practice, how much of a correction was made, and perhaps most importantly, why were only the ICOS data corrected and not also the TDLAS instrument described in 2.2.8 which used an absorption line  $\sim 4.7 \mu\text{m}$  and whose data would have equally been affected by the presence of water vapor?

line 451. "precision" - is that for 1-second data?

line 533. Please cite a paper for orthogonal distance regression or describe the algorithm.

line 556. Figure 2a shows a slope of  $0.98 \pm 0.00$  whereas the text has  $0.98 \pm 0.08$ . The meaning of the error is defined for the text ( $\pm$ combined instrument uncertainties) but not for the Figures since the values there are different. Please clarify.

Also, please state how combined uncertainties were calculated.

lines 554 - 577. Impressive performance by a new instrument! Well done!

line 609. "ranging from  $0.88 \pm 0.12$  to  $0.90 \pm 0.11$ ". This large difference is interesting. Wouldn't that suggest that the CL  $\text{NO}_y$  data may also be 10% - 12% too low, since it would have been calibrated using  $\text{NO}_x$  calibration standards?

line 609. "comparable" is probably not the best word in this context - suggestion: "on the upper end of the combined uncertainties" or similar.

line 618. how much HONO was there relative to  $\text{NO}_2$ ?

lines 666-697. Sounds like the CIMS would benefit from an internal standard to track its HONO sensitivity, e.g., continuous addition of a calibrated amount of  $^{15}\text{N}^{18}\text{O}_2\text{H}$  to the inlet.

If I understood this correctly, one HONO instrument sampled through a filter, the other did not. Please comment on what role, if any, the filter on the CES may have played? There are indications that  $\text{NO}_2$  can convert on surface to HONO. Has the CES inlet transmission of  $\text{NO}_2$  been tested using an "aged" filter?

line 720. " $\text{NO}_y$ ". Usually,  $\text{NO}_x$  constitutes the largest fraction of  $\text{NO}_y$ . Since there was good agreement between  $\text{NO}_x$  measurements, good agreement can also be expected for  $\text{NO}_y$ . Consider a section on  $\text{NO}_z = \text{NO}_y \hat{=} \text{NO}_x$ .

line 723. Section 2.2.8 should be section 2.2.6.

line 817. How were HCN and  $\text{NH}_3$  quantified?

line 817. "Here, we find no evidence for a potential interference of HCN or NH<sub>3</sub>" - that's good news! Is there an explanation as to why this instrument outperforms others in this regard?

line 846. "However, FIREX-AQ did not include a measurement of total alkyl nitrates." And if it had, would the result have been  $\Sigma\text{NO}_y \gg \text{NO}_{y,\text{CL}}$ ? I wonder ...

line 953. My browser displayed: "Hmm. We're having trouble finding that site." Please verify the link to the archive.

Figures 2a, 9a, and 12a. Are all data included in these panels, or a selection? Please clarify in the caption(s).

Figure 3. Please clarify in the caption at what time of day these plumes were observed (>20 ppbv of daytime HONO would seem like a lot during daytime).

Figure 8. Since the CES data are likely more accurate, consider switching the axes (plotting CIMS vs CES data). Were photolysis frequencies quantified? Are these daytime HONO levels? If there was truly this much HONO in the daytime, more justification as to the suggested absence of other photolabile compounds (N<sub>2</sub>O<sub>5</sub>/ClNO<sub>2</sub>) is needed.

Figure 10. Please state what percentiles are used of the box-and-whisker plots.

Supplement

The figures here are labeled SA, SB, SC, ... and S1, S2, S3, but could have just been numbered consecutively to avoid unnecessary confusion.

Figure S12. I am surprised not to see a larger difference in the slopes of Figures S12a and 9c, considering NO<sub>x</sub> (~30% of NO<sub>y</sub> in background air judging from Figure 10) would have been increased by 10%-12% and HONO (which was abundant at times also - Figure 8) by 80%, yet the slopes are virtually identical (1.00±0.01 and 1.01±0.00). Since a distinction was made in Figure 10 between background air and "in smoke", please also make that distinction in Figures 9 and S12.