We thank the reviewers for their time and constructive comments that have improved our manuscript. Below we include specific responses to the reviewer's comments. The reviewer's comments are in black. Authors' responses are in blue, quotes from the manuscript are in *italic*, and changes to the text are shown in red.

Thank you for giving me the opportunity to review this manuscript. I hope my input will be useful to the authors.

I appreciate this paper very much. The paper describes results from an intercomparison of different measurement techniques for what many would call "basic" photochemical tracers but the validity and precision of these tracer measurements are in fact critical for the success of any atmospheric chemistry mission.

This paper is a timely and very relevant contribution at a time during which measurement capabilities are expanding rapidly. It is well structured and clearly written using precise language. The scientific methods are sound. The content is entirely appropriate for publication in AMT. The reference list is appropriate. I recommend accepting the manuscript for publication after considering the following suggestions.

HONO:

I have a bit of a hard time wrapping my mind around the HONO comparison numbers and illustrations.

1. How can the distribution of the factional errors be so tight around a value of 2 (Figure S1)? When plugging into the equation CES/CIMS values mentioned at various places in the manuscript (1.36, 1.8, 2.48 and 3.9) I calculate values for FE between 0.3 and 1.2. This should center the gaussian somewhere in the middle of that range and show a much broader distribution.
2. Figure S4e shows that the CES measures anywhere from zero to 25 ppb while the CIMS measures between 0 and 3 ppb. How does this reconcile with the gaussian distribution shown in Figure 5 and the mean difference plots in figure S9?

This might require a bit more explanation than what is currently presented in the text.

Response:

1. In Figure S1, only data from smoke is presented (as indicated in the caption) whereas the slopes in the main manuscript are for all 1Hz data (i.e., smoke + background). Even so, there is very little HONO left in most of the data collected in smoke: about 90% of HONO data in smoke is below 1 ppbv, which is about the precision of the CES instrument. The fractional error (FE) expression is as follows:

FE = (CES HONO – CIMS HONO) / Average HONO

Since Average HONO = (CIMS HONO + CES HONO) / 2 we get

FE = 2*(CES HONO – CIMS HONO) / (CIMS HONO + CES HONO)

When HONO mixing ratios are close to 0, CES HONO >> CIMS HONO because of the lower precision of the CES. Hence, FE becomes tightly distributed around a value of 2.

We added a sentence in the caption of Figure S1 (now Figure S3) to emphasize this point.

"*The tight distribution of FE-HONO$_{CES-CIMS}$ around a value of 2 is due to the lower precision of the CES instrument when HONO mixing ratios were close to 0 (~90% of the data in smoke).*"

2. Few data points actually contributed to the pattern identified by the reviewer. We realized that this figure may be misleading and we replaced it with a new figure (now Figure S6) showing the same plots but color coded by data density.

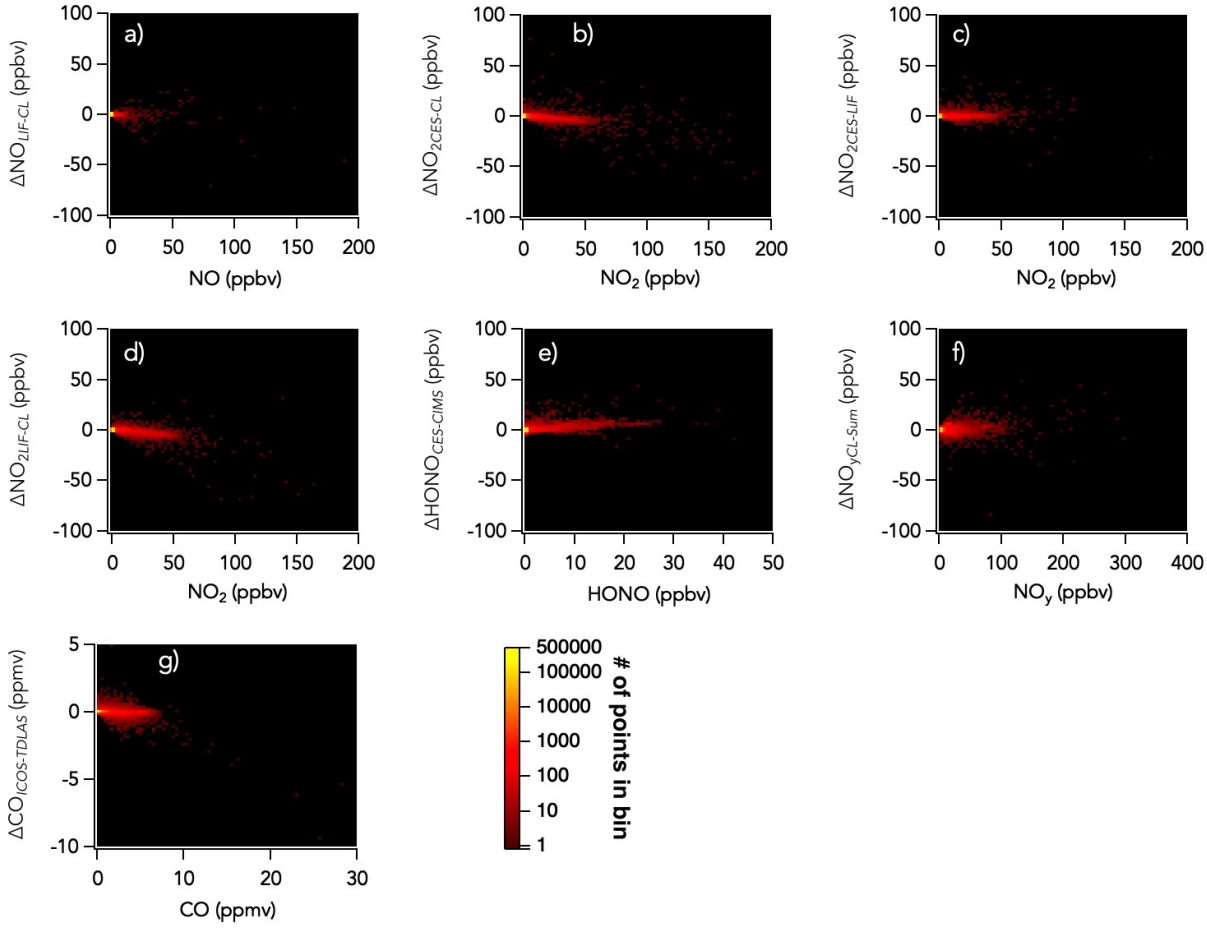


Figure S6 Measurement differences (1Hz data) of a) NO, b)–d) NO_2, e) HONO, f) NO_y, g) CO as a function of the species mixing ratios for the entire campaign. The color bar indicates the number of individual data points per bin of mixing ratios (bin size is 2.5×2.5 ppbv).

While I can appreciate that the IMR temperature may have an influence on sensitivity I'd be curious to know why this would only affect HONO and not also other analytes. Other readers might be left wondering about this.

Response: Other analytes do show temperature dependences to varying degrees. See response and reference below, where this subject is discussed in detail.

Was there an attempt made to correct the HONO values for IMR temperature, and how does the comparison look like then?

Response: A correction has indeed been derived for the CIMS HONO value based on the temperature. The details of this correction are beyond the scope of this manuscript and is the object of a follow-up paper focusing specifically on this issue that is currently under review in *AMTD* (Robinson et al., 2022). We added the new reference to the text lines 743-745.

"*This intercomparison has yielded new insights into the CIMS HONO detection sensitivity, and future work will identify and implement appropriate corrections to this measurement (Robinson et al. 2022).*"

NOy:

For lack of a better word, I find the assessment of the NOy measurements somewhat sugarcoated. In my view there are too many uncertainties to make these measurements ultimately useful, at least for fire smoke research. The facts I gather are the following:

1. Particulate nitrate makes up the largest fraction of total NOy in western wildfire smoke and a significant fraction in the eastern fires.
2. The sampling efficiency of particulates is highly dependent on airspeed but the real airspeed at the inlet tip (and the dependency on type of aircraft, banking and attack angle, or install location on the aircraft) is unknown.
3. Particulates used in the model described are assumed to be ammonium nitrate. The exact composition of the nitrates contained in fire smoke particulates is not known. There could be a significant fraction of organics, in particular nitroaromatics, but their volatilization behavior and conversion efficiency in the gold converter is unknown.
4. In the best case of sampling efficiency, 25% of the nitrate could be unaccounted for. Looking at the graph in Figure 10a, that fraction could be more than 50% in the worst case.

I'd agree with the authors if you call this a devil's advocate assessment, but at the end of the day my impression is that NOy measurements and "oxidized nitrogen closure" calculations based on these measurements or their use as photochemical clocks, etc. still need to be taken with a (fairly large) grain of salt. Just like they had to in the past.

We appreciate the reviewer's summary and agree with it to some extent.

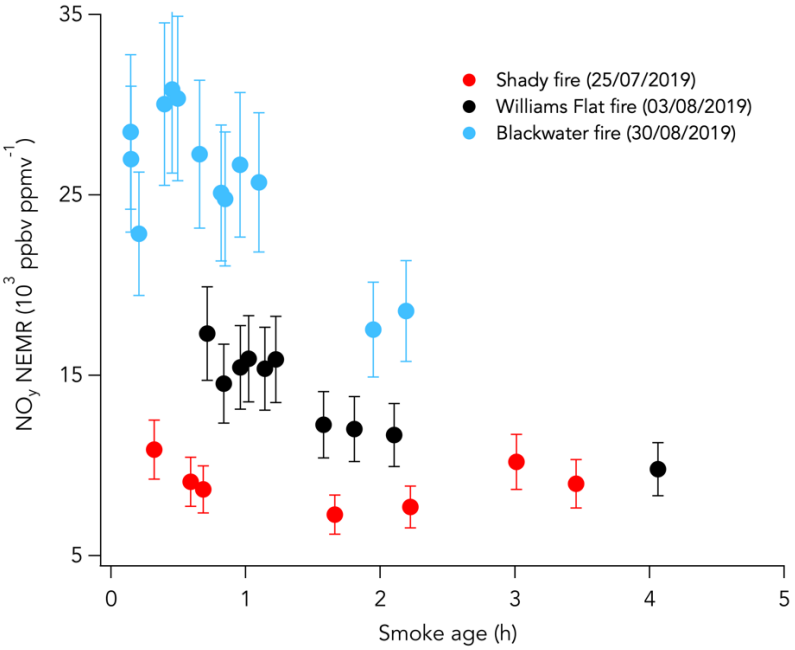
1) Particulate nitrate makes up the largest fraction of total NO_y in western wildfire aged smoke and a significant faction in western wildfire fresh smoke and in the eastern fires based on the speciated measurements.
2) The impact of air speed on the CL sampling efficiency of particles has been examined in depth in the Supplementary Information (see Section S1 - Estimation of particle losses and sensitivity to air speed). We show in Figure SB that correcting for the CL inlet transmission of particles significantly improves the correlation between ΣNO_y and measured total NOy (without biasing the residuals), meaning that the uncertainty associated with the airspeed at the inlet tip is significantly smaller than the full range of uncertainties shown in Figure 12.

3) It is explicitly stated in section S1 that the volatility that matters for the NO_y converter is the bulk aerosol volatility, not the NH_4NO_3 volatility. During FIREX-AQ, pNO_3 volatility was on par/slightly lower than that of organic aerosols but significantly higher than that of ammonium sulfate, based on in-situ measurements (Pagonis et al., personal communication). So again, this shows that using the work from Clarke et al. (1991) as done in the section S1 is justified and that indeed all non-refractory material excluding ammonium sulfate but including all organic N compounds are likely volatilized in the CL inlet. The conversion efficiency of organic pNO_3 and in particular of nitro-aromatics in the CL gold converter has not been characterized so far, although a previous study reports overall excellent conversion of several nitro-compounds (including nitro-aromatics) in a similar CL inlet with a gold converter (Bradshaw et al., 1998).
4) As noted in 2) the worst case called out by the reviewer is unlikely given the sensitivity test performed on sampled air speed in section S1.

What would a comparison of plume dilution calculated using CO versus a similar calculation using NOy look like?

Response: We appreciate the suggestion from the reviewer to compare the NO_y to CO normalized excess mixing ratios (NEMR). A figure is shown below but not included in the manuscript. Because of changing fire conditions during the course of a day, smoke of different nominal ages may have different initial NO_x to CO ratios. We do not interpret the changes in nominally conserved tracers as indicative of either aging or sampling artifacts as a result. We have added a sentence to the paper lines 884-887 to this effect:

"*The NO_y to CO ratio was approximately conserved with smoke age, but showed both increasing and decreasing trends with different fires, likely as a result of variability in the NO_x to CO emission ratio during the course of a day with changing fire conditions.*"



Minor suggestions:

Section 2 intro: Maybe a figure with a plumbing diagram of the manifolds described in the manuscript could be helpful

Response: We thank the reviewer for this suggestion. Such a figure is already included in the FIREX_AQ overview paper (Warneke et al., 2022). We added a citation for this article in the manuscript line 65.

"*The focus of the joint National Oceanic and Atmospheric Administration (NOAA) / National Aeronautics and Space Administration (NASA) Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ) airborne campaign was to provide comprehensive observations to investigate the impact of summer time wildfires, prescribed fires and agricultural burns on air quality and climate across the conterminous US (Warneke et al., 2022).*"

Section 2.2.1.: What was the conversion efficiency of the photolysis converter?

Response: The conversion efficiency is 40 ± 1 %. We added this information lines 171-173.

"*In the NO_2 channel, NO_2 is photolyzed to NO with a 40 ± 1 % conversion efficiency using two ultraviolet (UV) LEDs (Hamamatsu, model L11921) at 385 nm in a 45 cm long quartz cell (inner diameter of 1.2 cm) pressure-controlled at 209.8 ± 0.3 Torr.*"

Line 134: Suggest replacing "minimal" with "least possible"

Response: Done.

Line 169: NOy is missing in the list

Response: Fixed.

Section 2.2.3.: What is the inlet material? What was is shared with?

Response: The inlet tube is Silcosteel (Restek) coated with FluoroPel. It was shared with another four instruments during FIREX-AQ, two instruments from NASA Goddard (ISAF HCHO and ROZE O3) and two instruments from NOAA (SO2 and NO). We added a clarification to the text lines 240-242.

"*The inlet tube is a 45 cm length of 0.94 cm inner diameter Silcosteel (Restek) coated with FluoroPel* (Cazorla et al., 2015). *The CANOE instrument pulled its 750 sccm sample flow from a shared manifold (with another four instruments) at the instrument rack.*"

Line 305: How can the addition of 1% flow of saturated nitrogen stabilize the I- / I-*H20 clusters to such a precise ratio?

Response: We vary the water addition by controlling between 0 and 50 sccm of N_2 saturated with water, and adjusting the flow to maintain a constant reagent ion cluster ratio. This compensates for the changes in ambient humidity. The ambient airflow into the instrument is ~1 slm, with specific humidity that goes up to about 2%. Since the water addition has up to ~50x greater mixing ratio than the ambient sample, the additional water flow that is about 50x smaller than the ambient sample is sufficient to compensate for changes in ambient humidity.

Line 401: should be CH3NO2

Response: Fixed.

Line 511: If this uncertainty is based only on the spread of the trajectory ensemble, does this mean that there is additional uncertainty arising from the plume rise time, calculated using a fixed vertical transport speed?

Response: The age uncertainty provided in the data files includes multiple factors:

- Spread of trajectory ensemble (as mentioned by the reviewer)
- Uncertainty in updraft speed (±50%)
- For large fires, ages are calculated from several possible emission locations within the fire
- Uncertainty due to upwind trajectories not passing directly over the source fire (due to model wind errors)
- Wind speed uncertainty: since met field wind speeds don't exactly match observed wind speeds, an additional age estimate is derived by rescaling the trajectory age based on the ratio of model/observed wind speed. The uncertainty due to this effect is taken to be half of the difference between the unscaled and rescaled ages.

All of these uncertainties are added together in quadrature (i.e. assuming independent) to get the provided age uncertainty. This methodology will be described in full detail in a paper that is still in progress.
We added this precision to the text lines 546-549

"*The median uncertainty in smoke age is about 27%, as determined by the sum in quadrature of the spread among the ensemble of estimates, the uncertainties in the updraft speed, the fire location and the wind speed, and uncertainties in the model.*"

Line 575: I am not certain what the logic is behind putting some figures into the supplement and others into the main manuscript. Maybe this could be revisited.

Response: We appreciate the suggestion but have chosen main text figures in order to keep the manuscript as short as possible while placing the most important figures in the text.

Line 633: Could the positive artifact in the CL instrument be caused by thermal decomposition of peroxynitrate species inside the photolytic converter cell (which might be warmed by the heat output of the LEDs?)

Response: We thank the reviewer for this comment, but we do not believe peroxynitrates (i.e., HO_2NO_2 and RO_2NO_2) thermal dissociation to be the source of the artifact. The comparison did not depend on altitude or outside air temperature, suggesting that the artifact did not result from thermally labile species. The following sentence has been added to lines 681-682:

"*Further, $\Delta NO_{2CES-CL}$ or $\Delta NO_{2LIF-CL}$ did not depend on altitude or outside temperature, which also suggests little influence from thermally labile species.*"

Line 699: Suggest starting the paragraph with "The interpretation of literature…."

Response: We thank the reviewer for the suggestion. We modified the paragraph line 748.

Line 733: If there is an obvious problem with the CIMS HONO measurements, why are these being used here?

Response: The CIMS HONO measurements were used because they have much better precision than the CES HONO. Precision matters more than accuracy for plots like Figure 5, that are more weighted by background data than by smoke data. Using CES HONO rather than CIMS HONO only affects the slope of the correlation between measured NO_y and ΣNO_y by 6%. We clarified this aspect lines 370-372.

"*Using LIF NO, CES NO_2 and CES HONO as primary measurements changed the correlation slope between ΣNO_y and measured NO_y by -2%, -6% and 6%, respectively (Table S1).*"

Line 749: one or more?

Response: We agree with the reviewer's point. We changed the text line 802.

Line 757: see NOy discussion. How is this known?

Response: See our response to the NO_y discussion above.

Line 787: "…higher than…"

Response: Fixed.

Line 936: see NO_y discussion above

Response: See our response to the NO_y discussion above.

Conclusions point 6: Averaging data always results in less scatter. How useful really are instrument comparisons when averaging data spanning orders of magnitude?

Response: Here, we did not average the data but we integrated the signal across each transects (so more analogous to a sum than an average). Comparison of integrated datasets should reduce the scatter that may occur when rapid variations in mixing ratios occur faster than the measurement period and/or with greater spatial heterogeneity than the distance between the sampling locations on a large aircraft.

References:

Bradshaw, J., Sandholm, S., and Talbot, R.: An update on reactive odd-nitrogen measurements made during recent NASA Global Tropospheric Experiment programs, J. Geophys. Res. Atmospheres, 103, 19129–19148, https://doi.org/10.1029/98JD00621, 1998.

Cazorla, M., Wolfe, G. M., Bailey, S. A., Swanson, A. K., Arkinson, H. L., and Hanisco, T. F.: A new airborne laser-induced fluorescence instrument for in situ detection of formaldehyde throughout the troposphere and lower stratosphere, Atmospheric Meas. Tech., 8, 541–552, https://doi.org/10.5194/amt-8-541-2015, 2015.

Robinson, M. A., Neuman, J. A., Huey, L. G., Roberts, J. M., Brown, S. S., and Veres, P. R.: Temperature dependent sensitivity of iodide chemical ionization mass spectrometers, EGUsphere, 1–17, https://doi.org/10.5194/amt-2022-295, 2022.

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