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.

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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 $NO_2$ 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 $NO_y$ budget by comparing $NO_y$ measured by CL with a sum of individually measured components, $\Sigma NO_y$, calculated by adding NO, $NO_2$, HONO, $HNO_3$ (measured by another CIMS), $pNO_3$ (measured using an aerosol mass spectrometer, AMS) and acyl peroxynitrates (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 $NO_2$, 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.

Response: We thank the reviewer for the suggestions. We have added a table that lists measurements, instruments and uncertainties (now Table 1). After careful consideration, we decided not to add any additional table to the manuscript for the following reasons:

- a table of flights schedules, including date and time will be provided in the FIREX-AQ overview paper (Warneke et al. 2022), that has been referenced in the manuscript in response to Reviewer 1.

- a table with mixing ratios statistics would be difficult to provide since those statistics depend on the environmental conditions (e.g., smoke vs background, aged smoke vs fresh smoke, wildfires vs eastern fires) and also on the instruments. Most important for the manuscript is the range of mixing ratios being sampled, which are well shown in the correlation plots such as Figures 2, 7, 8, 9 and 14.

- a table with the various correlation slopes/intercepts would not bring new information to the manuscript but add to its (already considerable) length.

| SPECIES | INSTRUMENT | UNCERTAINTY |
|---|---|---|
| **NO** | CL | ± (4 % + 6 pptv) |
| | LIF | ± (8 % + 1 pptv) |
| **$NO_2$** | CL | ± (7 % + 20 pptv) |
| | CES | ± (5% + 0.26 ppbv) |
| | LIF | ± (10% + 100 pptv) |
| **HONO** | CIMS | ± (15% + 3 pptv) |
| | CES | ± (9% + 0.6 ppbv) |
| **$NO_y$** | CL | ± (12 % + 15 pptv) |
| | Sum | ~ 25% |
| **CO** | TD-LAS | 2–7% |
| | ICOS | ± (2.0 ppb + 2%) |

**Table 1** List of measured species and instruments, including the corresponding uncertainties, during FIREX-AQ

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

Response: The design of FIREX-AQ was to conduct a scientific campaign where a double blind intercomparison between measurement techniques was not the main objective. Several individual measurements of important species were present on the research aircraft during the campaign, and we seized the opportunity to conduct this intercomparison. All PIs had access to other instruments measurements throughout the campaign, so we could not qualify the comparisons as "blind".

We added a sentence to the text lines 568-569 to clarify this point:

"*Comparisons in this manuscript are not blind as all PIs had access to other instruments measurements throughout the campaign.*"

(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 $NH_3$ concentrations were quantified (Figure S14) but their measurement is not described at all.

Response: Thank you for raising this point. We added a description of individual APNs compounds that were quantified as well as the associated measurement uncertainties lines 425-428.

"*APNs species measured during FIREX-AQ include PAN, acryloyl peroxynitrate (APAN), propionyl peroxynitrate (PPN), and peroxybenzoyl nitrate (PBN) with an uncertainty of 20%, 30%, 30% and 30%, respectively.*"

We also included a brief description and appropriate references of HCN and $NH_3$ measurements in the caption of Figure S14 (now Figure S16).

"*HCN was measured by CIMS* (Crounse et al., 2009, 2006). *$NH_3$ was measured by PTR-MS* (Norman et al., 2007)."

In addition, we added the description of the HCN measurement in the Caltech CIMS instrument section lines 376-394. We did not include a description of the $NH_3$ measurement in the main text for the sake of brevity and also because $NH_3$ measurements are presented in Figure S14 (now Figure S16) only.

"*Observations of $HNO_3$, HCN, and hydroxyl nitrates produced from the oxidation of ethane, propene, butane, and isoprene were made by the California Institute of Technology Chemical Ionization Mass Spectrometer (CIT-CIMS) compact time-of-flight (cToF, TofWerk/Caltech) sensor using $CF_3O^-$ ion chemistry* (Crounse et al., 2006). *In short, a large flow of ambient air (about 40 $m^3$ $s^{-1}$) was rapidly brought into the aircraft through a Teflon coated glass inlet (warmed slightly above ambient temperature), where it was subsampled, diluted with dry $N_2$, reacted with $CF_3O^-$, and underwent subsequent product ion analysis by time-of-flight mass spectrometry. The $HF{\bullet}NO_3^-$ (m/z 82) product ion is used to quantify $HNO_3$. The HCN and hydroxy nitrates are detected as cluster ions. Laboratory-generated, T-dependent and water-dependent calibration curves were performed to produce ambient mixing ratios from raw signals for $HNO_3$ and hydroxy nitrates The HCN sensitivity is tracked in situ based on the continuous addition of isotopically labeled $H^{13}C^{15}N$ into the instrument from a custom-made gravimetrically based compressed gas cylinder. In-flight instrumental zeros were performed every ~15 minutes using dry $N_2$ and ambient air passed through $NaHCO_3$-coated nylon wool. Continuous data, with the exception of zero and calibration periods, are reported with 1Hz frequency. The uncertainties for $HNO_3$, HCN, and hydroxy nitrates are ± (30% + 50 pptv), ± (25% + 70 pptv), and ± (25% + 3 pptv), respectively.*"

(4) Measurements of $HNO_3$, APNs, $ClNO_2$, $N_2O_5$, $pNO_3$, 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 $NO_y$ (judging from Figure 10).

Response: We added two supplemental figures to the SI that show timeseries of $HNO_3$, APNs, $ClNO_2$, $N_2O_5$ and $pNO_3$ (Figures S1 and S2).

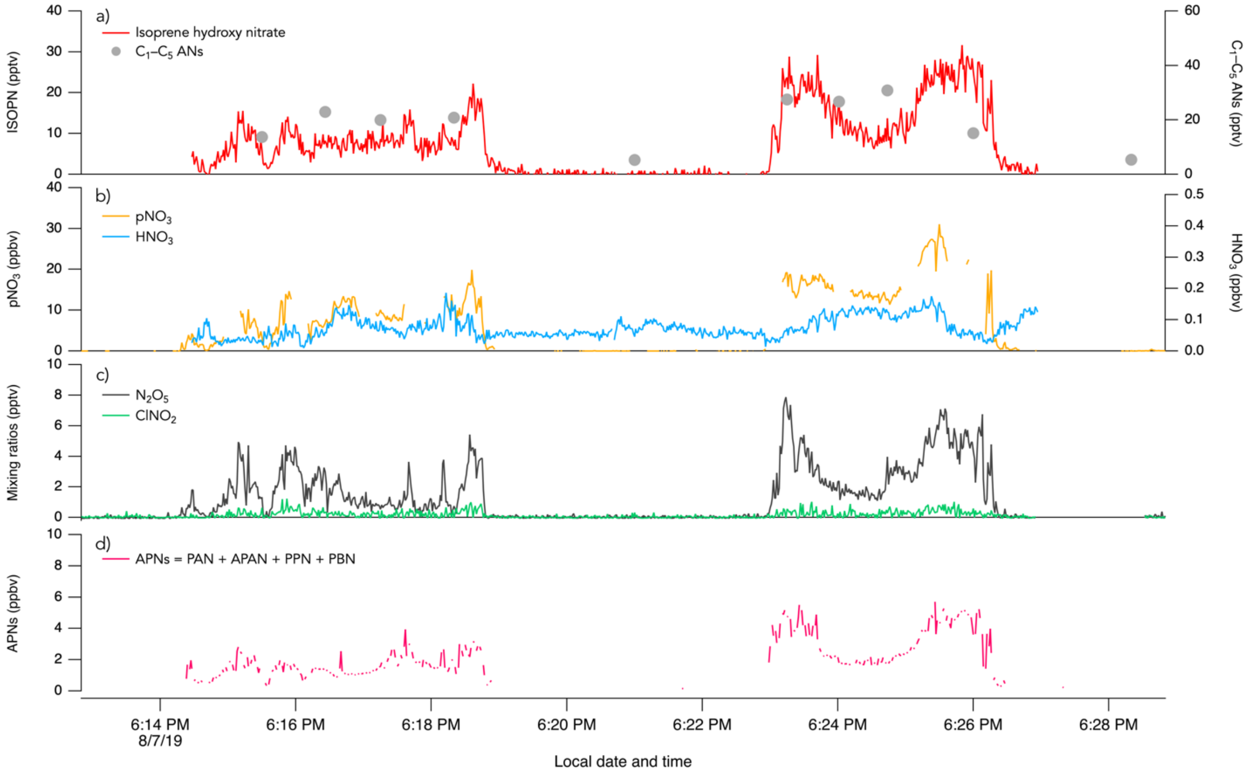


**Figure S1** 1 s measurements of a) Isoprene hydroxy nitrate (ISOPN) and $C_1$–$C_5$ alkyls nitrates (ANs), b) particulate nitrate ($pNO_3$) and $HNO_3$, c) $N_2O_5$ and $ClNO_2$ and d) APNs during two crosswind plume transects of smoke from the Williams Flat fire on 07/08/2019. The plume transects were chosen due to the significant enhancement of all species at that time.

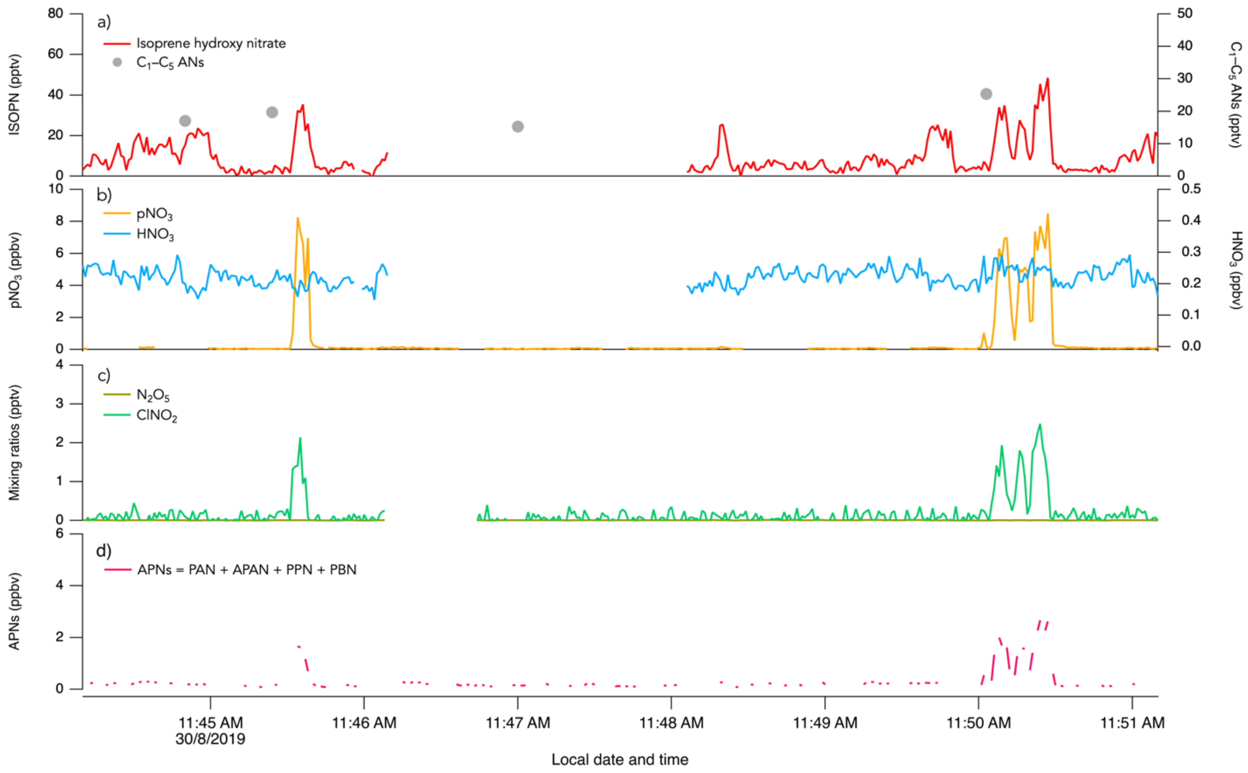


**Figure S2** 1 s measurements of a) Isoprene hydroxy nitrate (ISOPN) and $C_1$–$C_5$ alkyls nitrates (ANs), b) particulate nitrate ($pNO_3$) and $HNO_3$, c) $N_2O_5$ and $ClNO_2$ and d) APNs during crosswind plume transects of smoke from crop burning in southeastern US on 30/08/2019.

(5) The definition and choices/explanations as to what species to include in $\Sigma NO_y$ 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 $NO_y$ (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 $NO_y$ are omitted from equation (2). Please note more prominently the (many) omissions from $\Sigma NO_y$ in the abstract, such as higher molecular weight alkyl nitrates ("total alkyl nitrates", line 846), coarse nitrate, peroxynitrates ($HO_2NO_2$, $RO_2NO_2$), and the nocturnal nitrogen oxides $NO_3$, $N_2O_5$ and $ClNO_2$.

Since the expression given here for $\Sigma NO_y$ is a simplification, the right-hand side of equation (2) only approximates $\Sigma NO_y$ and an equal sign should not be used (use $\approx$ instead).

Further, since the expression for $\Sigma NO_y$ omits nocturnal nitrogen oxides, the definition of $\Sigma NO_y$ 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.

Response: We thank the reviewer for the great suggestions. We added the definition from Fahey et al. 1986 to the introduction lines 99-109.

"*Fahey et al. (1986) define* $\Sigma NO_y$ *as the sum of important nitrogen species as illustrated by Eq. 1:*

$\Sigma NO_y = NO + NO_2 +$ *nitric acid* ($HNO_3$) + *HONO* + *peroxynitric acid* ($HO_2NO_2$) + *nitrate* ($NO_3$) + *dinitrogen pentoxide* ($2*N_2O_5$) + *peroxyacetyl nitrate (PAN)* + *particulate nitrate* ($pNO_3$) + … *(Eq. 1)*

*Other nitrogen compounds that can contribute to* $\Sigma NO_y$ *include alkyl nitrates* (Day et al., 2003)*, acyl peroxynitrates (APNs; Juncosa Calahorrano et al., 2021), non-acyl peroxynitrates* ($RO_2NO_2$ *; Murphy et al., 2004), nitryl chloride* ($ClNO_2$ *; Kenagy et al., 2018), nitro compounds and nitroaromatics (Decker et al., 2021).*"

As suggested, we clarified the definition of $\Sigma NO_y$ in the abstract lines 15-19.

"*Other* $NO_y$ *species were not included in* $\Sigma NO_y$ *as they either contributed minimally to it (e.g.,* $C_1$*-*$C_5$ *alkyl nitrates, nitryl chloride* ($ClNO_2$)*, dinitrogen pentoxide* ($N_2O_5$)*) or were not measured during FIREX-AQ (e.g., higher oxidized alkyl nitrates, nitrate* ($NO_3$)*, non-acyl peroxynitrates, coarse mode aerosol nitrate).*"

We also used the recommended formalism in Equation 2 line 361.

"$\Sigma NO_y \approx NO_x + HONO + HNO_3 + pNO_3 + APNs$ *(Eq. 2)*"

(b) Organization.

It is clear from the outset that several components of $NO_y$ 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 $\Sigma NO_y$ (e.g., line 14 and 339). If I counted correctly, there are (at least) 36 different ways $\Sigma NO_y$ could have possibly been calculated for this data set (NO from either one of two instruments or average NO which gives 3 possibilities, $NO_2$ from one of three instruments or average $NO_2$ to give 4 possibilities, HONO from one of two instruments or average HONO to give 3 possibilities, 3×4×3 = 36 possible combinations). The reader is only told on line 732 which measurements were actually used.

Response: We thank the reviewer for raising this issue. We moved the description of instruments that were used to calculate $\Sigma NO_y$ to section 2.2.6 lines 368-374.

(c) Closure.

Having so many choices (data from several instruments to choose from, and which compounds to include in $\Sigma NO_y$) is great, but ultimately undermines the conclusion that $NO_y$ 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 $\Sigma NO_y$ once the slope relative to $NO_{y,CL}$ 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 $NO_x$ and HONO data from the LIF & CES instruments).

Response: As explained in the manuscript lines XXX, other nitrogen oxides (alkene hydroxy nitrates, nitromethane ($CH_3NO_2$), $N_2O_5$, $ClNO_2$, and $C_1$–$C_5$ alkyl nitrates) were also measured during FIREX-AQ but were not included in this equation as they contributed on average less than 7% to the $NO_y$ budget (see section 3.4). Further, including these measurements would have decreased data availability for comparison with the total $NO_y$ measurement by more than 60%.

We added a plot (Figure S14) showing the $NO_y$ comparison when all measurements were available (except for $C_1$-$C_5$ alkyl nitrates as those are discrete measurements). We also added a discussion to the text lines 786-789.

"*Including minor $NO_y$ species (= $ClNO_2$, $N_2O_5$, $CH_3NO_2$, and alkene hydroxy nitrates) in the $\Sigma NO_y$ had little effect on the correlation between $\Sigma NO_y$ and CL $NO_y$ and resulted in a slope of 1.02 ± 0.25 ($R^2$ =0.94) and an intercept of –0.68± 0.01 ppbv (Figure S14).*"

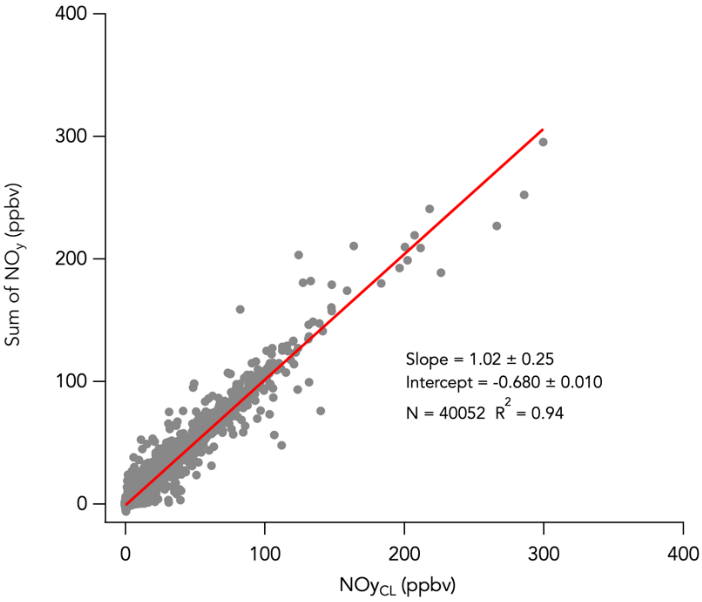


Figure S14: Comparison of the sum of individually measured $NO_y$ species (= $NO_x$ + HONO + $HNO_3$ + APNs + $pNO_3$ + alkene hydroxy nitrates + $CH_3NO_2$ + $ClNO_2$ + $N_2O_5$) with the total $NO_y$ measurement by CL. Data from the entire campaign are presented in panels a) and b). Here LIF NO, CES HONO and CES $NO_2$ are used in the sum of $NO_y$.

And please discuss the elephant in the room: The unquantified components of $NO_y$. If closure was indeed achieved, it would imply that those unquantified components were negligible, which in my opinion is doubtful.

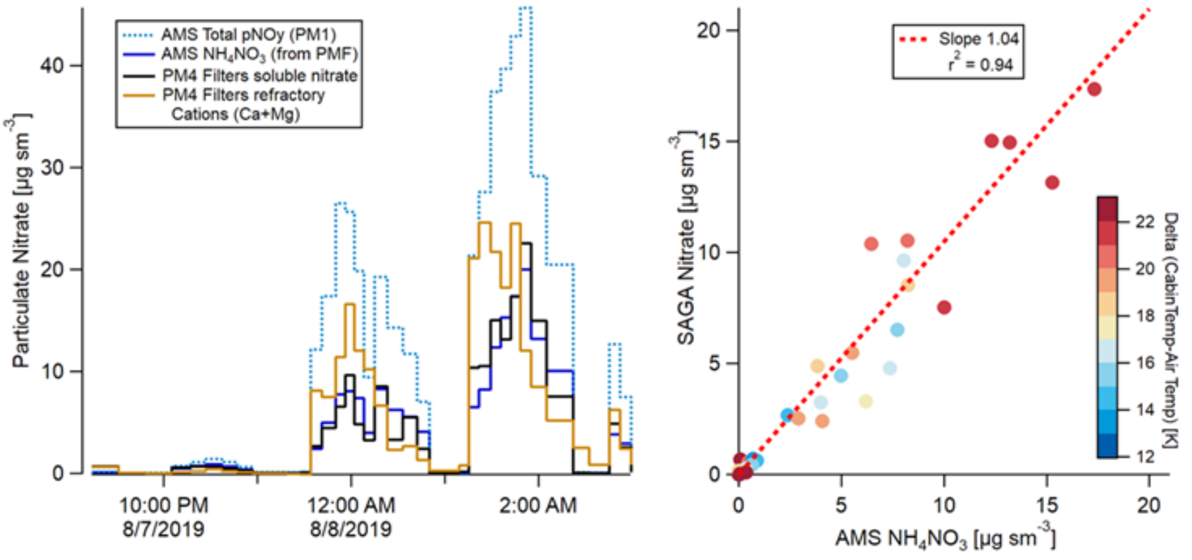
It is stated on line 846, that FIREX-AQ did not include a measurement of total alkyl nitrates, but the thought is left hanging. What if the suite of instruments had included such a measurement? Would the $NO_y$ budget have blown up? I'd be surprised if the Cohen group had not quantified ΣAN in fire plumes at some point to help constrain this "known unknown" and to guide this discussion.

Response: We thank the reviewer for raising this point. Wolfe et al. (2022) presents total alkyl nitrate measurements from the Rim Fire during the SEAC$^4$RS campaign. They find that about 10% of the NO$_y$ budget consists of total alkyl nitrate (ANs), and that ANs are typically one order of magnitude less abundant than peroxynitrates. We added this discussion to the text lines 914-918.

“*A recent analysis of the California Rim Fire during the 2013 NASA Studies of Emissions, Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC$^4$RS) mission report that total alkyl nitrates measured by TD-LIF accounted for ~10% of the NO$_y$ budget* (Wolfe et al., 2022).”

Also, if submicron pNO$_3$ constituted ~40% or so of 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.

Response: We thank the reviewer for raising this issue. During FIREX-AQ, the large majority of coarse mode aerosols were in the form of ash, not dust, with very little nitrate associated to them (Adachi et al., 2022). Furthermore, a PMF analysis of the flight (on 07/08/2019) with the largest amount of coarse mode particulate calcium and nitrate (as measured by a bulk aerosol sampling system coupled to an ion chromatograph (SAGA instrument) with an approximated PM$_4$ cutoff (Dibb et al., 2002; Brock et al., 2019)) shows that the amount of coarse mode particulate nitrate reported by the SAGA instrument was consistent with the amount of submicron inorganic pNO$_3$ measured by the HR-AMS measurements:



This result indicate that particulate nitrate is almost exclusively in the accumulation mode, with little to none contribution from the coarse mode, which may be explained by the low HNO$_3$ concentrations in the sampled smoke plumes resulting in a slow uptake on coarse aerosols.

During FIREX-AQ, measured coarse mode particulate nitrate was greater than measured submicron $pNO_3$ for ~10% of the data, and only under conditions where $pNO_3$ was a small contributor to the total $NO_y$ (2 µg $sm^{-3}$ or less total aerosol nitrate). Therefore, the overall contribution of coarse mode particulate nitrate to the $NO_y$ budget is should be minimal.

Additionally, neither the CL instrument nor the HR-AMS instrument measured super-micron aerosol because of inlet cut-off, meaning that coarse mode aerosol nitrate is not accounted for on either side of equation 2 and should not have consequences on $NO_y$ budget closure. We added a sentence to the main text lines 774-779 to reflect this point:

"*Based on comparisons of HR-AMS $pNO_3$ with on-board filters collecting aerosols with a size cut around 4µm (Brock et al., 2019; Dibb et al., 2002), coarse mode particulate nitrate did not significantly contribute to the total $NO_y$ budget during FIREX-AQ. Additionally, coarse mode particulate nitrate was not measured by either the HR-AMS or the $NO_y$ inlet in the CL instrument and therefore does not contribute to the intercomparison presented 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.

Response: We thank the reviewer for the suggestion. We would like to keep the CO comparison into this paper, as we believe that this comparison fits well in the current manuscript. CO is an essential component to fire science, similar to nitrogen compounds. It provides a reference species that is only affected by dilution on the timescales usually considered when investigating chemistry in smoke plumes (i.e., a couple of hours) and it is extensively used in the calculation of normalized excess mixing ratios as well as important fire parameters such as the modified combustion efficiency. Ensuring that CO was measured accurately during FIREX-AQ is thus crucial to get all following analyses right.

Specific/Minor comments

line 21. a slope of 1.8 - yikes!

Response: We agree with the reviewer that this is a large slope. It is adequately discussed in the manuscript and does not require further justification in the abstract.

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

Response: We have added this table in the figures (Table 1) and a reference to it line 78.

"*During FIREX-AQ, a large suite of airborne instruments, detailed in the following sections, performed independent in situ tropospheric measurements of one or more fire-science relevant reactive nitrogen species and CO aboard the NASA DC-8 aircraft (Table 1).*"

lines 95-98. Please insert an equation here, defining $NO_y$ (similar to equation (1) of Fahey et al., J. Geophys. Res., 91, 9781-9793, 10.1029/JD091iD09p09781, 1986).

Response: Please refer to our response above regarding this point.

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

Response: We thank the reviewer for the suggestion. We added Decker et al. lines 106-109.

"*Other nitrogen compounds that can contribute to* $\Sigma NO_y$ *include alkyl nitrates* (Day et al., 2003)*, acyl peroxynitrates (APNs; Juncosa Calahorrano et al., 2021), non-acyl peroxynitrates (*$RO_2NO_2$ *; Murphy et al., 2004), chlorine nitrite (*$ClNO_2$ *; Kenagy et al., 2018), nitro compounds and nitroaromatics (Decker et al., 2021).*"

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, $NO_2$ photolysis frequency, temperature etc.

Response: We thank the reviewer for the correction. It is a new system – we removed the reference to Pollack et al. and we added the relative data of the LEDS 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 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.

Response: Done.

line 180. "5% HONO interference". The magnitude of this interference will depend on the ratio of HONO to $NO_2$ in ambient air. Please clarify what is meant by 5% (stated on lines 615-617: 5% of the HONO sampled converts to NO).

Response: We mean that at a wavelength of 385nm, about 5% of the HONO signal will be converted into $NO_2$ and cause an interference in the $NO_2$ measurement. We corrected the text lines 193-194 to clarify this aspect of the instrument description.

"*Finally,* $NO_2$ *data were further corrected for a HONO interference (5% of the HONO mixing ratios) due to HONO photolysis at 385 nm quantified from theoretical calculation and confirmed in the laboratory using a HONO source described in Lao et al. (2020).*"

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

Response: We thank the reviewer for the suggestion. We added the estimate lines 225-226 and also in Table 1.

"*The NO measurement uncertainty is estimated to be ± (8% + 1 pptv).*"

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

Response: We used zero air from a cylinder, and we added the correction to the text lines 266 and 279.

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

Response: The filters were changed prior to each flight. We clarified this point in the manuscript line 278.

line 271. a $0^{th}$ order polynomial - interesting way to say "offset".

Response: The polynomial order can be something other than 0, but was zero in this case. Thus this term is more accurate than the term “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.

Response: The absorption spectra are not pressure dependent, and measurements took place at ambient temperature inside the cabin. Therefore, we don't expect the cross sections to change under our experimental conditions, and we don't anticipate any additional error here.

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

Response: During FIREX-AQ, the effective path length was about 5.3 km. We do not provide this information in the manuscript as instrument precision is already described.

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

Response: The dynamic range for the instrument is species dependent. For compounds that are measured with high sensitivity, the dynamic range is the smallest, since the product ions may deplete the reagent ions. For high sensitivity compounds, the response remains linear up to tens of ppbv. For HONO, which is measured with relatively lower sensitivity, the response remains linear up to 100s of ppbv.

line 310. "normalized by the iodide signals" - $I^-$ or $I^- \cdot H_2O$ or both? The Pratt group has recently used the water cluster to normalize.

Response: We normalize by IH2O, we added the precision in the text.

line 313-314. "Calibrations with $Cl_2$ and $HNO_3$ 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).

Response: The standard deviation of inflight calibrations is typically 10%. We added this information lines 334-335.

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?

Response: The temperature dependence to sensitivity results in background variations roughly from 10 to 160 ppt. Importantly, the backgrounds did not increase following sampling of concentrated fire plumes. There is no evidence that HONO, nor any other compound, sticks to the instrument surfaces and later desorbs.

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

Response: We moved the description of instruments used in equation 2 to section 2.2.6 lines 368-370.

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

Response: Please refer to our response above to comment #5.

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).

Response: We added the uncertainty estimate lines 425-428.

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 ±(15% + 2 pptv) accuracy?

Response: We now present $N_2O_5$ and $ClNO_2$ data in Figures S1 and S2. As described in Robinson et al. (2022), the temperature dependence does not affect $N_2O_5$.

line 431. "at approximately 4.6 µm" 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.

Response: The ICOS instrument measures CO at 2190.0cm$^{-1}$, or 4.566µm. We modified the text accordingly and we added an additional reference (Arévalo-Martínez et al., 2013) to the manuscript lines 465-467:

"*CO was measured using a modified commercial off-axis ICOS instrument (Los Gatos Research (LGR) $N_2O$/CO-30-EP; Arévalo-Martínez et al., 2013; Baer et al., 2002) at 4.566 µm.*"

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 ~4.7 µm and whose data would have equally been affected by the presence of water vapor?

Response: Both instruments report dry air mole fraction. The correction is made for displacement purposes, since the water vapor mixing ratio is often on par with the uncertainty of the measurement. We modified the text line 477.

"*(…) (both ICOS-CO and TDLAS-CO mixing ratios are reported as dry air mole fractions).*"

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

Response: Yes, this is the 1-Hz precision. We clarified the text line 486.

"*The 1-Hz precision of the measurement in flight is estimated to be 0.4 ppb.*"

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

Response: We added a reference for Orthogonal Distance Regression line 572.

"*We first calculated the slope of the linear least-squares (LLS) orthogonal distance regression (ODR; Boggs et al., 1987) to characterize the percent difference between measurements of a pair of instruments weighted by the inverse of the instrument precision.*"

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

Also, please state how combined uncertainties were calculated.

Response: We updated the figures to reflect an error that corresponds to that defined in the text. Combined uncertainties were calculated be adding in quadrature individual instrument uncertainties. We added a sentence to clarify this point lines 589-591.

"*In the following sections, combined instrument uncertainties were calculated by adding in quadrature individual instrument uncertainties.*"

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

Response: Thank you.

line 609. "ranging from 0.88±0.12 to 0.90±0.11". This large difference is interesting. Wouldn't that suggest that the CL $NO_y$ data may also be 10% - 12% too low, since it would have been calibrated using $NO_x$ calibration standards?

Response: It is unlikely that the difference between CL $NO_2$ and other $NO_2$ measurements was due to a calibration issue. If so, the CL NO measurement, which was calibrated using the same standard as for the CL $NO_2$ measurement, would also have been 10-12% higher than the NO LIF measurement (which was calibrated using an independent standard). This was not the case during FIREX-AQ (see section 3.1). Therefore, there is no reason to suspect a calibration error in the CL $NO_y$ measurement.

We added this discussion to the main text lines 654-659.

"*However, it is unlikely that the difference between CL $NO_2$ and other $NO_2$ measurements was due to a calibration issue. If so, the CL NO measurement, which was calibrated using the same standard as for the CL $NO_2$ measurement, would also have been 10-12% higher than the NO LIF measurement (which was calibrated using an independent standard). This was not the case during FIREX-AQ (see section 3.1).*"

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

Response: We modified the text accordingly.

line 618. how much HONO was there relative to $NO_2$?

Response: HONO to $NO_2$ ratio was typically between 0.2–0.4 during FIREX-AQ. 5% of that ratio means that at most 2% of the $NO_2$ signal was due to HONO interference. We added this precision in the text lines 660-664.

"*However, this interference was determined to be low (less than 5% of HONO concentration; typical HONO to $NO_2$ ratios ranged between 0.2-0.4 during FIREX-AQ) following laboratory tests using a HONO calibration source* (Lao et al., 2020)*, and the $NO_2$ measurement by CL was corrected for it*"

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 $^{15}N^{18}O_2H$ 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 $NO_2$ can convert on surface to HONO. Has the CES inlet transmission of $NO_2$ been tested using an "aged" filter?

Response: Yes, the CES had a filter. But CES-HONO tended to be higher than CIMS-HONO during FIREX-AQ. If the filter were causing transmission loss, then CES-HONO would have been lower. We did not test an "aged" filter, but there wasn't any trend in $\Delta NO_{2\,CES-CL}$ or $\Delta HONO_{CES-CIMS}$ with flight time which indicates no significant loss on the filters. Additionally, filters were changed prior to each flight (see response above).

line 720. "$NO_y$". Usually, $NO_x$ constitutes the largest fraction of $NO_y$. Since there was good agreement between $NO_x$ measurements, good agreement can also be expected for $NO_y$. Consider a section on $NO_z = NO_y$ â©‘$NO_x$.

Response: This is true in most urban settings. However, in smoke plumes $pNO_3$ and APNs rapidly become the most prevalent $NO_y$ components. For this reason, adding a section on $NO_z$ would actually be redundant with the current section on $NO_y$.

line 723. Section 2.2.8 should be section 2.2.6.

Response: Fixed.

line 817. How were HCN and $NH_3$ quantified?

Response: We added a brief instrument description and appropriate reference in the caption of Figure S16 (see also our comment above).

line 817. "Here, we find no evidence for a potential interference of HCN or $NH_3$" - thats' good news! Is there an explanation as to why this instrument outperforms others in this regard?

Response: $NH_3$ and HCN interferences in CL instruments have been demonstrated in laboratory settings and in dry air conditions (Fahey et al., 1985). However, the same study showed that those interferences accounted for less than 1% of measured $NO_y$ for air of 20% relative humidity. During FIREX-AQ, ambient air relative humidity was typically higher than 20% (average value of 37%), so negligible interference from those compounds were expected.

line 846. "However, FIREX-AQ did not include a measurement of total alkyl nitrates." And if it had, would the result have been $\Sigma NO_y >> NO_{y,CL}$? I wonder ...

Response: Please refer to our response above to comment #5

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

Response: Fixed.

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

Response: All data are included in panels 2a and 9a, and we clarified this in the captions. However, as stated in Figure 12a caption, the data shown is from one individual fire smoke (Williams Flat fire on 08/07).

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).

Response: The local time is given in the x-axis of Figure 3. The smoke plume form the Williams Flat fire sampled on 08/07 (presented in Figure 3) was wide and thick, creating "nocturnal" conditions at the heart of the plume. This explained the elevated mixing rations of HONO sampled 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 ($N_2O_5$/$ClNO_2$) is needed.

Response: We thank the reviewer for raising this point. See previous comment regarding the time of the day. Decker et al., 2021 recently showed that in smoke plumes $NO_3$ reactivity is largely dominated by VOCs leading to the production of nitro-aromatics or $HNO_3$. As a result, there was little to no formation of $N_2O_5$ and $ClNO_2$ in smoke during FIREX-AQ (see Figures S& and S2).

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

Response: Done.

Supplement

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

Response: We thank the reviewer for the suggestion. We'd like to keep the numbering as it is as Figures SA-SD belong with the modeling work on $pNO_3$ transmission in the $NO_y$ inlet rather than with the main text.

Figure S12. I am surprised not to see a larger difference in the slopes of Figures S12a and 9c, considering $NO_x$ (~30% of $NO_y$ 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.

Response: Using CES NO2 actually decreases the slope by 6%, while using CES HONO increases the slope by 6%. Using NO LIF decreases the slope by 2%. As a consequence, the slope shown in Figure S12 (now Figure S14), where CES HONO, CES NO2 and NO LIF were used in the sum of $NO_y$ did not change compared to Figure 9. In smoke, using LIF NO, CES $NO_2$ and CES HONO as primary measurements changed the correlation slope between $\Sigma NO_y$ and measured $NO_y$ by -1%, -8% and 9%, respectively. We added Table S1 where we provide the various slopes calculated depending on the instrument used. We also added a clarification in the main text lines 370-374:

"*Using LIF NO, CES $NO_2$ and CES HONO as primary measurements changed the correlation slope between $\Sigma NO_y$ and measured $NO_y$ by -2%, -6% and 6%, respectively (Table S1). In smoke, using LIF NO, CES $NO_2$ and CES HONO as primary measurements changed the correlation slope between $\Sigma NO_y$ and measured $NO_y$ by 1%, -8% and 9%, respectively (Table S1).*"

## References:

Adachi, K., Dibb, J. E., Scheuer, E., Katich, J. M., Schwarz, J. P., Perring, A. E., Mediavilla, B., Guo, H., Campuzano-Jost, P., Jimenez, J. L., Crawford, J., Soja, A. J., Oshima, N., Kajino, M., Kinase, T., Kleinman, L., Sedlacek III, A. J., Yokelson, R. J., and Buseck, P. R.: Fine Ash-Bearing Particles as a Major Aerosol Component in Biomass Burning Smoke, J. Geophys. Res. Atmospheres, 127, e2021JD035657, https://doi.org/10.1029/2021JD035657, 2022.

Arévalo-Martínez, D. L., Beyer, M., Krumbholz, M., Piller, I., Kock, A., Steinhoff, T., Körtzinger, A., and Bange, H. W.: A new method for continuous measurements of oceanic and atmospheric $N_2O$, CO and $CO_2$: performance of off-axis integrated cavity output spectroscopy (OA-ICOS) coupled to non-dispersive infrared detection (NDIR), Ocean Sci., 9, 1071–1087, https://doi.org/10.5194/os-9-1071-2013, 2013.

Baer, D. S., Paul, J. B., Gupta, M., and O'Keefe, A.: Sensitive absorption measurements in the near-infrared region using off-axis integrated-cavity-output spectroscopy, Appl. Phys. B, 75, 261–265, https://doi.org/10.1007/s00340-002-0971-z, 2002.

Boggs, P. T., Byrd, R. H., and Schnabel, R. B.: A Stable and Efficient Algorithm for Nonlinear Orthogonal Distance Regression, SIAM J. Sci. Stat. Comput., 8, 1052–1078, https://doi.org/10.1137/0908085, 1987.

Brock, C. A., Williamson, C., Kupc, A., Froyd, K. D., Erdesz, F., Wagner, N., Richardson, M., Schwarz, J. P., Gao, R.-S., Katich, J. M., Campuzano-Jost, P., Nault, B. A., Schroder, J. C., Jimenez, J. L., Weinzierl, B., Dollner, M., Bui, T., and Murphy, D. M.: Aerosol size distributions during the Atmospheric Tomography Mission (ATom): methods, uncertainties, and data products, Atmospheric Meas. Tech., 12, 3081–3099, https://doi.org/10.5194/amt-12-3081-2019, 2019.

Crounse, J. D., McKinney, K. A., Kwan, A. J., and Wennberg, P. O.: Measurement of Gas-Phase Hydroperoxides by Chemical Ionization Mass Spectrometry, Anal. Chem., 78, 6726–6732, https://doi.org/10.1021/ac0604235, 2006.

Crounse, J. D., DeCarlo, P. F., Blake, D. R., Emmons, L. K., Campos, T. L., Apel, E. C., Clarke, A. D., Weinheimer, A. J., McCabe, D. C., Yokelson, R. J., Jimenez, J. L., and Wennberg, P. O.: Biomass burning and urban air pollution over the Central Mexican Plateau, Atmos Chem Phys, 16, 2009.

Day, D. A., Dillon, M. B., Wooldridge, P. J., Thornton, J. A., Rosen, R. S., Wood, E. C., and Cohen, R. C.: On alkyl nitrates, O3, and the "missing NOy," J. Geophys. Res. Atmospheres, 108, https://doi.org/10.1029/2003JD003685, 2003.

Decker, Z. C. J., Robinson, M. A., Barsanti, K. C., Bourgeois, I., Coggon, M. M., DiGangi, J. P., Diskin, G. S., Flocke, F. M., Franchin, A., Fredrickson, C. D., Gkatzelis, G. I., Hall, S. R., Halliday, H., Holmes, C. D., Huey, L. G., Lee, Y. R., Lindaas, J., Middlebrook, A. M., Montzka, D. D., Moore, R., Neuman, J. A., Nowak, J. B., Palm, B. B., Peischl, J., Piel, F., Rickly, P. S., Rollins, A. W., Ryerson, T. B., Schwantes, R. H., Sekimoto, K., Thornhill, L., Thornton, J. A., Tyndall, G. S., Ullmann, K., Van Rooy, P., Veres, P. R., Warneke, C., Washenfelder, R. A., Weinheimer, A. J., Wiggins, E., Winstead, E., Wisthaler, A., Womack, C., and Brown, S. S.: Nighttime and daytime dark oxidation chemistry in wildfire plumes: an observation and model analysis of FIREX-AQ aircraft data, Atmospheric Chem. Phys., 21, 16293–16317, https://doi.org/10.5194/acp-21-16293-2021, 2021.

Dibb, J. E., Talbot, R. W., Seid, G., Jordan, C., Scheuer, E., Atlas, E., Blake, N. J., and Blake, D. R.: Airborne sampling of aerosol particles: Comparison between surface sampling at Christmas Island and P-3 sampling during PEM-Tropics B, J. Geophys. Res. Atmospheres, 107, PEM 2-1-PEM 2-17, https://doi.org/10.1029/2001JD000408, 2002.

Fahey, D. W., Eubank, C. S., Hübler, G., and Fehsenfeld, F. C.: Evaluation of a catalytic reduction technique for the measurement of total reactive odd-nitrogen NO y in the atmosphere, J. Atmospheric Chem., 3, 435–468, 1985.

Fahey, D. W., Hübler, G., Parrish, D. D., Williams, E. J., Norton, R. B., Ridley, B. A., Singh, H. B., Liu, S. C., and Fehsenfeld, F. C.: Reactive nitrogen species in the troposphere: Measurements of NO, NO2, HNO3, particulate nitrate, peroxyacetyl nitrate (PAN), O3, and total reactive odd nitrogen (NO y ) at Niwot Ridge, Colorado, J. Geophys. Res. Atmospheres, 91, 9781–9793, https://doi.org/10.1029/JD091iD09p09781, 1986.

Juncosa Calahorrano, J. F., Lindaas, J., O'Dell, K., Palm, B. B., Peng, Q., Flocke, F., Pollack, I. B., Garofalo, L. A., Farmer, D. K., Pierce, J. R., Collett, J. L., Weinheimer, A., Campos, T., Hornbrook, R. S., Hall, S. R., Ullmann, K., Pothier, M. A., Apel, E. C., Permar, W., Hu, L., Hills, A. J., Montzka, D., Tyndall, G., Thornton, J. A., and Fischer, E. V.: Daytime Oxidized Reactive Nitrogen Partitioning in Western U.S. Wildfire Smoke Plumes, J. Geophys. Res. Atmospheres, 126, e2020JD033484, https://doi.org/10.1029/2020JD033484, 2021.

Kenagy, H. S., Sparks, T. L., Ebben, C. J., Wooldrige, P. J., Lopez-Hilfiker, F. D., Lee, B. H., Thornton, J. A., McDuffie, E. E., Fibiger, D. L., Brown, S. S., Montzka, D. D., Weinheimer, A. J., Schroder, J. C., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Dibb, J. E., Campos, T., Shah, V., Jaeglé, L., and Cohen, R. C.: NOx Lifetime and NOy Partitioning During WINTER, J. Geophys. Res. Atmospheres, 123, 9813–9827, https://doi.org/10.1029/2018JD028736, 2018.

Lao, M., Crilley, L. R., Salehpoor, L., Furlani, T. C., Bourgeois, I., Neuman, J. A., Rollins, A. W., Veres, P. R., Washenfelder, R. A., Womack, C. C., Young, C. J., and VandenBoer, T. C.: A portable, robust, stable, and tunable calibration source for gas-phase nitrous acid (HONO), Atmospheric Meas. Tech., 13, 5873–5890, https://doi.org/10.5194/amt-13-5873-2020, 2020.

Murphy, J. G., Thornton, J. A., Wooldridge, P. J., Day, D. A., Rosen, R. S., Cantrell, C., Shetter, R. E., Lefer, B., and Cohen, R. C.: Measurements of the sum of $HO_2NO_2$ and $CH_3O_2NO_2$ in the remote troposphere, Atmospheric Chem. Phys., 4, 377–384, https://doi.org/10.5194/acp-4-377-2004, 2004.

Norman, M., Hansel, A., and Wisthaler, A.: O2+ as reagent ion in the PTR-MS instrument: Detection of gas-phase ammonia, Int. J. Mass Spectrom., 265, 382–387, https://doi.org/10.1016/j.ijms.2007.06.010, 2007.

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.

Warneke, C., Schwarz, J. P., Dibb, J., Kalashnikova, O., Frost, G., Seidel, F., Al-Saadi, J., Brown, S. S., Washenfelder, R., Brewer, A., Moore, R. H., Anderson, B. E., Yacovitch, T., Herndon, S., Liu, S., Jaffe, D., Johnston, N., Selimovic, V., Yokelson, B., Giles, D., Holben, B., Goloub, P., Popovici, I., Trainer, M., Pierce, B., Fahey, D., Roberts, J., Soja, A., Peterson, D., Saide, P. E., Holmes, C., Wang, S., Coggon, M. M., Decker, Z. C. J., Ye, X., Stockwell, C., Xu, L., Gkatzelis, G., Lefer, B., Crawford, J. Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ). To be submitted. 2022

Wolfe, G. M., Hanisco, T. F., Arkinson, H. L., Blake, D. R., Wisthaler, A., Mikoviny, T., Ryerson, T. B., Pollack, I., Peischl, J., Wennberg, P. O., Crounse, J. D., St. Clair, J. M., Teng, A., Huey, L. G., Liu, X., Fried, A., Weibring, P., Richter, D., Walega, J., Hall, S. R., Ullmann, K., Jimenez, J. L., Campuzano-Jost, P., Bui, T. P., Diskin, G., Podolske, J. R., Sachse, G., and Cohen, R. C.: Photochemical evolution of the 2013 California Rim Fire: synergistic impacts of reactive hydrocarbons and enhanced oxidants, Atmospheric Chem. Phys., 22, 4253–4275, https://doi.org/10.5194/acp-22-4253-2022, 2022.