Comparison of airborne measurements of NO, NO₂, HONO, NO₃ and CO during FIREX-AQ

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Abstract

We present a comparison of fast-response instruments installed onboard the NASA DC-8 aircraft that measured nitrogen oxides (NO and NO$_2$), nitrous acid (HONO), total reactive odd nitrogen ($\Sigma$NO$_y$) and carbon monoxide (CO) in the troposphere during the 2019 Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ) campaign. By targeting smoke from summertime wildfires, prescribed fires and agricultural burns across the continental United States, FIREX-AQ provided a unique opportunity to investigate measurement accuracy in concentrated plumes where hundreds of species coexist. Here, we compare NO measurements by chemiluminescence (CL) and laser induced fluorescence (LIF); NO$_2$ measurements by CL, LIF and cavity enhanced spectroscopy (CES); HONO measurements by CES and iodide-adduct chemical ionization mass spectrometry (CIMS); and CO measurements by tunable diode laser absorption spectrometry (TDLAS) and integrated cavity output spectroscopy (ICOS). Additionally, total NO$_y$ measurements using the CL instrument were compared with $\Sigma$NO$_y$ (= NO + NO$_2$ + HONO + nitric acid (HNO$_3$) + acyl peroxy nitrates (APNs) + submicron particulate nitrate (pNO$_3$)). The aircraft instrument intercomparisons demonstrate the following: 1) NO measurements by CL and LIF agreed well within instrument uncertainties, but with potentially reduced time response for the CL instrument; 2) NO$_2$ measurements by LIF and CES agreed well within instrument uncertainties, but CL NO$_2$ was on average 10% higher; 3) CES and CIMS HONO measurements were highly correlated in each fire plume transect, but the correlation slope of CES vs. CIMS for all 1 Hz data during FIREX-AQ was 1.8, which we attribute to a reduction in the CIMS sensitivity to HONO in high temperature environments; 4) NO$_y$ budget closure was demonstrated for all flights within the combined instrument uncertainties of 25%. However, we used a fluid dynamic flow model to estimate that average pNO$_3$ sampling fraction through the NO$_y$ inlet in smoke was variable from one flight to another and ranged between 0.36 and 0.99, meaning that approximately 0–24% on average of the total measured NO$_y$ in smoke may have been unaccounted for and may be due to unmeasured species such as organic nitrates; 5) CO measurements by ICOS and TDLAS agreed well within combined instrument uncertainties, but with a systematic offset that averaged 2.87 ppbv; and 6) integrating smoke plumes followed by fitting the integrated values of each plume improved the correlation between independent measurements.
1. Introduction

Biomass burning (BB) can take multiple forms (e.g., wildfires, prescribed fires, agricultural burns, grass fires, peat fires) and accounts for a large fraction of global carbon emissions with consequences for climate (Bowman et al., 2009; van der Werf et al., 2010, 2017) and biogeochemical cycles (Crutzen & Andreae, 2016). BB also contributes substantially to the atmospheric burden of trace gases and aerosols (Andreae, 2019), causing poor air quality on regional to continental scales (Jaffe et al., 2020; O’Dell et al., 2019; Wotawa, 2000) and posing a major threat to public health (Johnston et al., 2012, 2021). In the United States (US), wildfires mainly occur in the western states and in Alaska and burned over 4.5 million acres in 2019 (US National Interagency Fire Center, https://www.nifc.gov/fire-information). Wildfires frequency and severity are predicted to increase in response to a warmer, drier climate (Burke et al., 2021; Westerling, 2016) and also to increasing human-caused ignition (Balch et al., 2017). In comparison, prescribed fires, which are common practice in the southeastern US, burned an estimated 10 million acres in 2019, to which agricultural burns added another 2–3 million acres (Melvin, 2020). While agricultural burns are usually smaller and less intense than wildfires or prescribed fires, they occur more frequently and throughout the whole year, and can significantly impact local air quality (Dennis et al., 2002; McCarty, 2011).

Rising interest in the impact of fires on climate and air quality over the past decades has resulted in a series of laboratory studies of BB emissions in the US such as the FLAME-4 experiment in 2012 (e.g., Stockwell et al., 2014) and the FIRELAB study in 2016 (e.g., Selimovic et al., 2018). Recent, large-scale field studies such as AMMA (e.g., Liousse et al., 2010), BBOP (e.g., Collier et al., 2016) and WE-CAN (e.g., Calahorrano et al., 2020) have been dedicated to sampling and characterizing emissions and atmospheric chemistry from fires. 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.

Accurate measurements facilitate understanding of fire emissions, processing and impacts. In situ, fast-response measurements of trace gases in the atmosphere conducted from airborne platforms provide unique data sets that enhance our understanding of atmospheric composition and chemistry. One method for evaluating measurement accuracy is by comparison of independent measurements using different techniques. A relatively small body of literature reported comparisons of methods for in flight detection of tropospheric carbon monoxide (CO) and reactive odd nitrogen species measured both as the total (NO\textsubscript{y}) and from the sum of individually measured species (\Sigma NO\textsubscript{x}), and these studies have shown that such comparisons are valuable for identifying instrument artifacts and quantifying measurement uncertainties (Eisele et al., 2003; Gregory et al., 1990; Hoell et al., 1987; Hoell et al., 1987; Sparks et al., 2019). 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.
Additionally, FIREX-AQ provides a unique opportunity to investigate measurement accuracy in concentrated smoke plumes where hundreds of species coexist.

Nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}) are among the largest components of the reactive nitrogen budget emitted by biomass burning and are produced by the oxidation of reduced nitrogen species present in the fuel in the flaming stage of combustion (Roberts et al., 2020). NO\textsubscript{x}, defined as the sum of NO and NO\textsubscript{2}, directly affects atmospheric oxidation rates and ozone (O\textsubscript{3}) production within fire plumes (Robinson et al., 2021; L. Xu et al., 2021). It also contributes to the formation of secondary aerosols and N transport and deposition to ecosystems downwind (Galloway et al., 2003; Kroll & Seinfeld, 2008; Ziemann & Atkinson, 2012). Therefore, two independent NO and three independent NO\textsubscript{2} measurements were part of FIREX-AQ to provide continuous in situ observations, as described in section 2 below. Nitrous acid (HONO) is emitted directly to the atmosphere through various combustion processes including BB. The rapid production of OH from HONO at the early stage of smoke plume formation (Peng et al., 2020) results in rapid initiation of photochemistry, with a strong influence on downwind chemical evolution of smoke plumes (Robinson et al., 2021; Theys et al., 2020). Total NO\textsubscript{y} can be measured through conversion of individual species to NO (Fahey et al., 1985). It is a more conserved tracer for NO\textsubscript{x} emissions than NO\textsubscript{x} itself since it accounts for NO\textsubscript{x} oxidation products, and it provides a mean to assess from a mass-balance approach the accuracy of $\Sigma$NO\textsubscript{y} budget closure (Bollinger et al., 1983; Fahey et al., 1986; Williams et al., 1997). $\Sigma$NO\textsubscript{y} usually consists of NO\textsubscript{x}, HONO, nitric acid (HNO\textsubscript{3}), nitrogen pentoxide (N\textsubscript{2}O\textsubscript{5}), peroxynitric acid (HNO\textsubscript{4}), acyl peroxy nitrates (APNs), halogen-nitrogen species such as ClNO\textsubscript{2}, other organic nitrates such as alkyl nitrates, and particulate nitrate (pNO\textsubscript{3}). Carbon monoxide (CO) is emitted from incomplete combustion in fires and other sources, and is especially important for characterizing the combustion stage of fires (i.e., flaming vs. smoldering) through the use of the modified combustion efficiency (Yokelson et al., 1996). Due to its relatively long chemical lifetime, CO is commonly used as a conserved tracer to account for dilution with ambient air as smoke plumes are transported downwind, and accurate CO measurements are necessary to better constrain emission factors (EFs) used in emission inventories.

This study builds on past airborne instrument comparisons and extends these analyses to a new species (HONO), new measurement techniques (first airborne deployment of the NOAA NO-LIF (laser induced fluorescence) and the NOAA CO-ICOS (integrated cavity output spectroscopy) instruments) and new environments (concentrated fire smoke). In this paper we present a comparison of NO, NO\textsubscript{2}, HONO, NO\textsubscript{y} and CO measurements, which are compounds of major interest for fire-related science, air quality and climate. In the first part of this paper, we describe the FIREX-AQ campaign, the deployed instruments and the methodology used to perform the comparisons. In the second part, we provide a detailed instrument comparison for each species.

2. FIREX-AQ overview and instruments
2.1 FIREX-AQ airborne mission
The FIREX-AQ campaign ([https://www-air.larc.nasa.gov/missions/firex-aq/](https://www-air.larc.nasa.gov/missions/firex-aq/); [https://www.esrl.noaa.gov/csl/projects/firex-aq/](https://www.esrl.noaa.gov/csl/projects/firex-aq/)) took place from July to September 2019. FIREX-AQ included the deployment of multiple aircraft and mobile platforms over the course of the campaign, however this study focuses on the heavily instrumented NASA DC-8 aircraft. The NASA DC-8 portion of the project achieved two flights over the Los Angeles (LA) Basin and the Central Valley in California, 13 flights originating from Boise, Idaho, and 7 flights based out of Salina, Kansas. The flights from Boise were conducted over the Western US to sample smoke from wildfires, while the flights from Salina focused on agricultural and prescribed burns (hereafter referred to as eastern fires) in the Southeastern US.

Most wildfire flights were designed to sample background mixing ratios, fresh emissions, and aged smoke, whereas the eastern fire flights typically transected numerous fresh smoke plumes several times each. For wildfires, the NASA DC-8 first flew upwind of the fire to characterize ambient conditions unaffected by targeted fire emissions. Subsequent cross-wind plume transects were conducted as close as possible to the fire to sample the emissions with the minimal atmospheric ageing. Plume transects were designed to be perpendicular to the wind direction and through the center of the vertical extent of the plume, terrain permitting.

The vertical structure of the plume was systematically assessed using a differential absorption lidar during a lengthwise overpass above the plume from end to start. The aircraft transected the smoke plume successively further downwind, at approximately 15–40 km intervals, to characterize smoke evolution in a “lawnmower” pattern (Figure 1a). For several wildfires, the DC-8 also executed flight transects along the plume axis, both toward and away from the fire source. Most eastern fires sampled during FIREX-AQ did not produce plumes large enough to enable regularly spaced plume transects. Most smoke plumes were therefore sampled repetitively at the same location, sometimes with varying altitude and/or approach angle (Figure 1b).

2.2 Instruments

2.2.1 Chemiluminescence (NO/NO$_2$/NO$_y$)

The NOAA CL instrument has been frequently used for both ground-based and airborne measurements of NO, NO$_2$ and NO$_y$ and uses the CL detection of NO with O$_3$ added as reagent gas (Fontijn et al., 1970; Ridley & Grahek, 1990; Ridley & Howlett, 1974; Ryerson et al., 1999, 2000). NO, NO$_2$ and NO$_y$ are measured on three independent channels of the instrument. The NO channel measures NO, the NO$_2$ channel measures the sum of NO and photolyzed NO$_2$ as NO, and the NO$_y$ channel measures the total reactive nitrogen oxides species reduced to NO. NO$_2$ is determined from the difference between signals from the NO and NO$_2$ channels. Ambient air is continuously sampled from a pressure-building ducted aircraft inlet to the instrument at a typical flow of 1045.1 ± 0.2, 1030.2 ± 0.2 and 1029.5 ± 0.2 standard cubic centimeters per minute (sccm) in flight for NO, NO$_2$, and NO$_y$, respectively. In the NO$_2$ channel, NO$_2$ is photolyzed to NO using ultraviolet (UV) LEDs at 385 nm in a 45 cm long quartz cell (inner diameter of 1.2 cm) pressure-controlled at 209.8 ± 0.3 Torr (Pollack et al., 2011). In the NO channel, a similar quartz cell wrapped in aluminum foil to avoid NO$_2$ photolysis and pressure controlled at 209.7 ± 0.3 Torr, ensures similar
residence time of sampled air in both channels. In the NO\textsubscript{y} channel, reactive odd nitrogen species are first sampled through an inlet heated at 90.0 ± 0.1°C then catalytically reduced to NO on a gold tube surface heated at 300.0 ± 0.2°C in the presence of added pure CO flowing at 3.19 ± 0.01 sccm. Approximately 5% O\textsubscript{3} in oxygen is produced by corona discharge, delivered at 73.80 ± 0.02 (NO channel), 74.11 ± 0.03 (NO\textsubscript{2} channel), and 74.60 ± 0.04 (NO\textsubscript{y} channel) sccm, and mixed with sampled air in a pressure (8.65 ± 0.02, 8.79 ± 0.02, 8.56 ± 0.02 Torr for NO, NO\textsubscript{2}, and NO\textsubscript{y} respectively) and temperature (25.0 ± 0.2 and 25.1 ± 0.2°C for NO and NO\textsubscript{2}, respectively) controlled reaction vessel. O\textsubscript{3}-induced CL is detected with a red-sensitive photomultiplier tube controlled at −78°C with dry ice, and the amplified digitized signal is recorded using an 80 MHz counter. Pulse coincidence at high count rates was calculated after the mission by fitting an inverse function to the curve between observed and theoretical count rates for known NO mixing ratios ranging from ppbv to ppmv levels. Instrument calibrations were routinely performed both on the ground and during flight by standard addition of NO from a gravimetrically determined NO in N\textsubscript{2} mixture (1.38 ± 0.03 ppmv) delivered at 4.04 ± 0.02 (NO channel), 4.84 ± 0.02 (NO\textsubscript{2} channel), and 4.96 ± 0.02 (NO\textsubscript{y} channel) sccm. All measurements were taken at a temporal resolution of 0.1 second (s), averaged to 1 s, and corrected for the dependence of instrument sensitivity on ambient water vapor content (Ridley et al., 1992). Finally, NO\textsubscript{2} data were further corrected for a 5% HONO interference 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). Under these conditions the total estimated 1Hz uncertainty at sea level was ± (4 % ± 6 pptv), ± (7 % ± 20 pptv), and ± (12 % ± 15 pptv) for NO, NO\textsubscript{2}, and NO\textsubscript{y}, respectively.

2.2.2 Laser Induced Florescence (NO)

The NOAA NO-LIF measurements were performed using a custom-built laser-induced fluorescence instrument as detailed in Rollins et al. (2020). Air was continuously sampled from outside the aircraft through an optical cell in the DC-8 cabin held to near 90 hPa. The instrument utilizes a fiber laser system with a narrow-band laser tuned to a rotationally resolved NO spectral feature near 215 nm. Rapid dithering on and off of this resonance achieves 0.1 s measurements with a continuously monitored background to reduce uncertainty in the instrument zero. The laser induced excitation of NO is followed by red-shifted fluorescence which is detected by a photomultiplier tube operated in single-photon counting mode. The laser is directed through both a sampling and reference cell in a single pass for continuous monitoring of any changes in the instrument sensitivity due to changes in the laser spectrum, or pressure of the optical cells. 500 ppbv of NO in air was flown at 50 sccm through the reference cell to ensure that measurements are occurring with the laser tuned to the peak online wavelength. A constant flow of approximately 2500 sccm is maintained within the sampling cell through the use of a custom inlet valve (Gao et al., 1999) and the exhaust of both cells are tied together allowing for any changes in sensitivity due to pressure fluctuations to be accounted for during data reduction. Hourly calibrations were performed during each flight in which 2–10 sccm of 5 ppmv NO in N\textsubscript{2} mixture was added to the sample flow resulting in mixing ratios of 4–20 ppbv. The sensitivity of the instrument was determined using the in-flight calibrations to be typically 10 counts per second (CPS).
pptv\(^{-1}\) with 10 CPS background achieving a detection limit of 1 pptv for 1 s integration. The uncertainty of the instrument sensitivity is ±6–9%. The effect of water vapor, which reduces the sensitivity by quenching of the electronically excited NO, was accounted for during data reduction using water vapor measurements provided by an ICOS instrument on the DC-8.

2.2.3 Laser Induced Fluorescence (NO\(_2\))

The NASA Compact Airborne NO\(_2\) Experiment (CANOE) measured NO\(_2\) using non-resonant LIF. The instrument is a modified version of a formaldehyde (HCHO) instrument (St. Clair et al., 2019) with the excitation wavelength changed to 532 nm. The technique utilizes the pulsed (80 kHz) output of a fixed wavelength, 2W, 532 nm laser to excite NO\(_2\) molecules and detects the resulting fluorescence with two identical detection axes consisting of a photomultiplier tube (PMT) and optical filters that transmit > 695 nm. Delayed time gate PMT counts are recorded at 10 Hz and a laboratory calibration, along with an intercept determined by preflight zeroing, are used to provide 1Hz NO\(_2\) data. The NO\(_2\) measurement uncertainty is estimated to be ±(10% + 100 pptv).

During FIREX-AQ, ambient air was sampled using a shared inlet that provided a large (10–25 standard liter per minute (slpm)) bypass flow to the instrument rack. The CANOE instrument pulled its 750 sccm sample flow from a shared manifold at the instrument rack. An inline particle filter on the sample line prevented laser scatter by fine aerosol that were not removed by the particle-rejecting inlet. A manual three-way valve outside the instrument was used to sample from a scrubber (Drierite/molecular sieve) and provide a zero before and periodically during the flight. Pressure in the CANOE detection cell was maintained at 40 Torr by a pressure controller that precedes the cell in the flow path.

2.2.4 Cavity Enhanced Spectroscopy (NO\(_2\)/HONO)

NO\(_2\) and HONO were also measured by the NOAA airborne cavity enhanced spectroscopy (ACES) instrument. This technique is based on incoherent broadband cavity enhanced spectroscopy (CES, Fiedler et al., 2003). The CES instrument is described in full detail by Min et al. (2016) with only minor changes for FIREX-AQ. Briefly, the system consists of two parallel 45 cm optical cavities capped by highly reflective mirrors, with reflectivity curves centered at 365 nm (R = 0.99987) and 455 nm (R = 0.99992). Each cavity is illuminated by a broadband LED light source (centered at 365 and 455 nm respectively) collimated by an off-axis parabola, and passively coupled into the cavity. The light makes many passes before exiting the cavity into a fiber optic cable, which transmits the light to a grating spectrometer spanning 350–475 nm. The LEDs are modulated on for 0.4 s and off for 0.08 s for charged-couple device (CCD) readout, giving a total integration time of 0.48 s per light intensity spectrum. An absorption spectrum of the ambient air sample is determined using the procedure presented by Washenfelder et al. (2008). The procedure requires comparing the measured light intensity spectrum to a background spectrum of the cavity filled with zero air, which is determined here every 10 minutes. The mirror reflectivity is measured every hour using the Rayleigh scattering difference between helium and zero air, and the spectrometer dark counts and wavelength calibration are measured every two hours.
A small flow from a mixture of 25 ppm NO₂ in air is diluted into the cavity every hour, resulting in NO₂ concentrations between 50 and 100 ppbv, to assess the NO₂ spectral retrieval features on the spectrometer. The absolute concentration was not used for calibration of the NO₂ response, but rather for providing a reference NO₂ spectrum. Glyoxal reference spectra was obtained by bubbling zero air through a Teflon bubbler with 40% glyoxal in water as in Min et al. (2016).

Ambient air is pulled through the inlet into the two optical cavities at a flow rate of 5.4 volumetric liters per minute per cavity by a scroll pump. The air passes through two 1 μm pore size Teflon filters before entering the instrument to remove any aerosol particles. Mirror cleanliness is maintained by flowing 150 sccm zero air over each mirror to prevent condensation of semi-volatile species. A pressure controller consisting of a Teflon orifice and a variable flow to a bypass maintains the internal pressure at one of two pressure set points: 400 mbar when the aircraft was below 7.3 km, and 150 mbar above 7.3 km. The residence time of the air inside the optical cavities is estimated to be 0.5 s.

The measured absorption spectrum is fit to a linear combination of literature or reference spectra of absorbing gas-phase species and a polynomial to account for drifts in the cavity stability or light source intensity, as detailed by Min et al. (2016), using a Levenberg-Marquardt least-squares fitting algorithm. For the 365 nm channel, those species are NO₂, HONO, O₄, and a 4th order polynomial. For the 455 nm channel, those species are NO₂, glyoxal, methylglyoxal, H₂O, and O₄, as well as a 0th order polynomial, though only NO₂ is presented here. The algorithm uses reference spectra for NO₂ and glyoxal, as measured in the field, scaled linearly to the literature spectra of Vandaele et al. (1998) at 296 K and Volkamer et al. (2005) at 294 K, respectively. The literature spectra from Stutz et al. (2000), Meller et al. (1991), Harder & Brault, (1997), and Keller-Rudek et al. (2013) are used for HONO, methylglyoxal, H₂O, and O₄, respectively. The fitting range was 438 – 467 nm for the 455 nm channel, and 362 – 387 nm for the 365 nm channel. No structure was observed in the fit residuals. Because the 455 nm channel has higher precision, only those NO₂ data are presented here, although the two channels agree to within 3%. The data are averaged to 1 s. The reported uncertainties are ± (9% + 0.6 ppbv) for HONO and ± (5% + 0.26 ppbv) for NO₂.

2.2.5 Iodide-Adduct Chemical Ionization Mass Spectrometry (HONO)

HONO was measured using a modified commercial time of flight chemical ionization mass spectrometer (TOF CIMS, Aerodyne Research, Inc.; Lee et al., 2014; Veres et al., 2020). Trace gases are ionized by mixing ambient air with reagent ions made in flight, and the resulting product ions are detected. Ions are separated by mass-to-charge ratio (m/z) using a time-of-flight mass spectrometer with a resolving power of 5000 m/Δm and a range of mass to charge ratio up to 494 m/z. Spectra were obtained at a 25 kHz repetition rate, and then averaged to 1 s. High resolution peak fitting was performed on the spectra, using over 500 known masses. Reagent ions were formed by flowing 1 slpm N₂ through a temperature controlled CH₃I permeation tube followed by a 20 mCi ²¹⁰Po radioactive source. Two reagent
ions are generated: Iodide ions (I\textsuperscript{−}) are formed in the radioactive source, and iodide-water clusters (I\textsuperscript{−}•H\textsubscript{2}O) are formed when I\textsuperscript{−} reacts with water in the ion-molecule reactor (IMR). In the IMR, the reagent ions cluster with analyte gases to form a stable iodide adduct. The IMR was controlled at 40 mbar pressure to reduce the effects of secondary ion chemistry that increase at higher pressures.

Ambient air was sampled through a mass flow controlled (6 slpm) heated perfluoroalkoxy (PFA) inlet (70 cm length, 0.64 cm inner diameter). A pressure control region upstream of a critical orifice at the entrance to the IMR was maintained at 140 mbar, so that a constant flow of 1.2 slpm ambient air entered the IMR to mix with the 1 slpm ion source flow. A small nitrogen flow of about 20 sccm containing water vapor was added directly into the IMR region and controlled to maintain a measured I\textsuperscript{−}•H\textsubscript{2}O:I\textsuperscript{−} cluster ratio of 50 ± 2%, in order to maintain constant detection sensitivity. The reagent ion signals during FIREX-AQ were typically 2 MHz for I\textsuperscript{−}•H\textsubscript{2}O and 4 MHz for I\textsuperscript{−}, and they were stable as a function of aircraft altitude. In the most concentrated fire plumes with CO over 7 ppm, the abundance of reactants reduced the reagent ion signals by up to 15%. The product cluster ions were normalized by the iodide signals to account for changes in reagent ions. The instrument background signal was determined in-flight by overflowing the inlet with scrubbed ambient air for 30 seconds every 10 minutes through a port located 2 cm downstream of the inlet entrance. Calibrations with Cl\textsubscript{2} and HNO\textsubscript{3} permeation sources were performed hourly in flight to diagnose the stability of instrument sensitivity.

HONO was detected as a cluster with I\textsuperscript{−} that has a mass to charge ratio of 173.90575 m/z. Contributions from the \textsuperscript{13}C isotope of formic acid at 173.91342 m/z are not completely mass resolved but are accounted for using high resolution peak fitting and isotope ratios based on the formic acid signal at its most abundant isotope. We know of no other contributions to the signal at the mass used for HONO detection, consistent with previous studies (Neuman et al., 2016). The background HONO signals were typically equivalent to a mixing ratio of 40 ppt, and these were subtracted from the total signal to determine ambient HONO. Sensitivity to HONO was determined in the laboratory, using a tunable, calibrated HONO source that uses HCl reactions on humid NaNO\textsubscript{2} to generate HONO (Lao et al., 2020). The output was calibrated spectroscopically using the NOAA ACES instrument (Min et al., 2016). The absolute sensitivity to HONO was 3.4 ion counts/s/pptv for typical conditions. Sensitivities normalized by the reagent ions are used to determine mixing ratios from the normalized product ion signals. The HONO measurement uncertainty at fixed temperature was ±(15% + 3 pptv), where the first term was from the laboratory calibrations and the second was the variability of the in-flight background determinations. The HONO measurement precision was ±2 pptv for 1 second data. Calibrations and field work conducted subsequent to FIREX-AQ identified a temperature dependence to the CIMS calibration. Section 3.3 below describes this sensitivity in more detail.

2.2.6 SNOy
To determine the extent of budget closure for reactive odd nitrogen species during FIREX-AQ, we compare measured NO$_x$ (see section 2.2.1) with ΣNO$_y$ defined as:

$$\Sigma\text{NO}_y = \text{NO}_x + \text{HONO} + \text{HNO}_3 + \text{pNO}_3 + \text{APNs} \quad (\text{Eq. 2})$$

Other nitrogen oxides 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%. These minor NO$_y$ species are alkene hydroxy nitrates, nitromethane (CH$_3$NO$_2$), N$_2$O$_5$, and C$_1$–C$_5$ alkyl nitrates. ClNO$_2$ was also measured by I-CIMS but not included in this work as its contribution to the NO$_y$ budget was negligible during FIREX-AQ.

- HNO$_3$ observations were made by the California Institute of Technology Chemical Ionization Mass Spectrometer (CIT-CIMS) compact time-of-flight (cToF, TofWerk/Caltech) sensor using CF$_3$O$^-$ ion chemistry (Crounse et al., 2006). In short, a large flow of ambient air 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$_3$O$^-$, and underwent subsequent product ion analysis by time-of-flight mass spectrometry. The HF•NO$_3^-$ (m/z 82) product ion is used to quantify HNO$_3$. The hydroxy nitrates produced from the oxidation of isoprene, ethene, propene, and butene are detected as cluster ions. In-flight instrumental zeros were performed every ~15 minutes using dry N$_2$ and ambient air passed through NaHCO$_3$-coated nylon wool. Laboratory-generated, water-dependent calibration curves were performed to produce ambient mixing ratios from raw signals. Continuous HNO$_3$ data, with the exception of zero and calibration periods, are reported with 1Hz frequency with an uncertainty of ± (30%+ 50 pptv).

- Particulate nitrate (pNO$_3$) was measured with a high-resolution time-of-flight AMS (HR-AMS, Aerodyne Research, Inc., Billerica, MA, USA). The HR-AMS measured submicron (PM$_{0.9}$; calibrated in the field as described in Guo et al., 2021) aerosol composition at high time resolution (0.1–1 s) by flash vaporization of the aerosol, 70 eV electron ionization of the volatilized gas phase and subsequent analysis by mass spectrometry (Canagaratna et al., 2007; DeCarlo et al., 2006). pNO$_3$ is detected in the HR-AMS as the sum of H$_x$NO$_y^+$ ions (mostly NO$^+$ and NO$_2^+$). Typical 1 s detection limits for pNO$_3$ were about 90 ng sm$^{-3}$ (30 pptv) for urban/background conditions. Given the size cut in the HR-AMS instrument, pNO$_3$ does not include coarse nitrate from the reaction of HNO$_3$ with sea salt or dust aerosol. It does include particulate organic nitrates (pRONO$_2$; Day et al., 2021; Farmer et al., 2010), which are speciated using the algorithm described in Fry et al. (2013) and Day et al. (2021). Likewise, particulate aryl nitrates such as nitrocatechol also contribute to the total pNO$_3$ signal (Guo et al., 2020). Nitrocatechol was also characterized by extractive electrospray ionization time-of-flight mass spectrometry (EESI-MS; Pagonis et al., 2021) and...
positive matrix factorization and tracer analysis suggests that total aryl nitrates could be 3–7 times the concentration of nitrocatechol.

- APNs were measured using a thermal dissociation – chemical ionization mass spectrometer (TD-CIMS) method. The CIMS instrument used during the FIREX-AQ campaign was similar to that described in Slusher et al. (2004) and Lee et al. (2020). Briefly, ambient air is sampled into the TD-CIMS through heated Teflon tubing at a temperature of approximately 150°C to thermally dissociate APNs. The thermal dissociation region was maintained at a constant pressure of 60 torr using a commercial pressure controller (MKS 640) to minimize negative interference due to NO, NO2 and radical-radical reactions. In-flight calibrations were performed by continuous addition of isotopically labeled peroxyacetyl nitrate (PAN) standard quantified as acetate ion (61 m/z; C13H3C13(O)O–) in the TD-CIMS. NO was periodically added to the inlet (~10 ppm) to react away peroxyacetyl radicals and thus to measure the instrument background signal.

- Nitromethane (CH3NO2), along with other volatile organic compounds (VOCs), was measured by proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS; Gkatzelis et al., in prep). The PTR-ToF-MS sampled VOCs at 5Hz through short (1 m) heated inlet. Periodically, instrument backgrounds were determined by passing ambient air through a platinum catalyst heated to 350°C. The instrument response to VOCs was calibrated by gravimetrically prepared standards or by liquid calibration, as described by Gkatzelis et al. (2021). CH3NO mixing ratios were determined by liquid calibration with an uncertainty of 30%.

- N2O5 was detected as a cluster with I– at mass 234.88574 m/z. Sensitivity was determined by standard addition laboratory calibrations, with N2O5 generated by reacting a NO2 calibration standard with O3 (Bertram et al., 2009), and quantified using cavity ring down NOy measurements (Womack et al., 2017). For typical operating conditions during FIREX-AQ, N2O5 sensitivity was 70 ion counts/s/ppt. N2O5 was measured with ±(15% ± 2 pptv) accuracy and 0.1 pptv precision for 1 second data. Iodide ions cluster with a DMS oxidation product, hydroperoxymethyl thioformate (HPMTF), that has a mass only 0.0074 amu greater than N2O5, and these two molecules cannot be completely resolved spectrometrically with the resolution (m/∆m = 5000) of this instrument (Veres et al., 2020). For these measurements over the continent, the contribution from HPMTF to the signal at the iodide N2O5 cluster is assumed to be negligible.

- C1–C5 alkyl nitrates were measured by the NOAA integrated whole air sampling system with off-line analysis by gas chromatography-mass spectrometry (iWAS/GC-MS as described in Lerner et al. (2017)). There were 142 iWAS samples collected over the LA Basin with an average fill time of 5.2 ± 0.7 seconds. There were 897 wildfire samples and 467 eastern fire samples with average fill times of 7.6 ± 1.1 and
4.5 ± 0.8 seconds, respectively. Due to the relatively fast fill times and targeted, on-demand sampling capabilities of the iWAS, 88% and 74% were “full smoke” samples for wildfire and eastern fire samples, respectively. All samples were analyzed in the NOAA Chemical Science Laboratory within 213 hours of sample collection with an average sample age of 87 ± 34 hours between sample collection and sample analysis for FIREX-AQ.

2.2.7 Integrated Cavity Output Spectroscopy (CO)

CO was measured using a modified commercial off-axis ICOS instrument (Los Gatos Research (LGR) N$_2$O/CO-30-EP; Baer et al., 2002) at approximately 4.6 µm. The commercial instrument has two flow paths, a slow flow path with cavity pressure controlled by an internal proportional valve, and a parallel high flow path with a needle valve to control pressure. The instrument was modified to use only the high flow path, but with an automatic cavity pressure controller. The needle valve was removed from the flow path in favor of a Piezo proportional valve (Horiba Stec UR-Z732M) located near the inlet.

Air was sampled from a ram-air intake inlet through 0.64 cm (outside diameter) stainless steel tubing. Cavity pressure was maintained at 85.0 ± 0.2 Torr in flight. Immediately inside the fuselage, two CO (and N$_2$O) calibration gas standards known to within ±0.4 ppb CO were regularly delivered to the inlet line during flight to evaluate instrument sensitivity between 58.4 and 993.3 ppb CO (all ICOS-CO mixing ratios are reported as dry air mole fractions). The calibration standards were added to displace ambient air and overflow the inlet, and were calibrated before and after the project using standard tanks tied to the World Meteorological Organization CO$_{X2014A}$ scale from the NOAA Global Monitoring Laboratory (Hall et al., 2007; Novelli et al., 1991). The 1-sigma variability of the slope and intercept of all in-flight calibrations was 0.6% and 0.9 ppb, respectively. A third calibration standard, referred to as a “target” (Peischl et al., 2010), was regularly introduced to the inlet between calibrations and treated as an unknown to evaluate long-term instrument performance. The retrieved value of 109 in-flight targets during FIREX-AQ was 301.6 ± 1.0 ppb CO compared with the calibrated value of 301.1 ± 0.4 ppb. The precision of the measurement in flight is estimated to be 0.4 ppb.

After the campaign, the H$_2$O measurement was calibrated using a MBW 373LX chilled-mirror hygrometer (MBW Calibration AG; Rollins et al., 2020). The H$_2$O measurement is estimated to have an uncertainty of ± (50 ppmv + 4%), and was used to convert the CO measurement to a dry air mole fraction. The uncertainty of the dry air mole fraction of CO is estimated to be ± (2.0 ppb + 2%) for mixing ratios below 1 ppm.

2.2.8 Tunable Diode Laser Absorption Spectroscopy (CO)

Carbon Monoxide (CO) was measured by tunable diode laser absorption spectroscopy (TDLAS) using the DACOM (Differential Absorption Carbon monOxide Measurement) instrument (Sachse et al., 1987). The TDLAS instrument configuration used during FIREX-AQ also included channels for measurements of methane (CH$_4$) and carbon dioxide isotopes ($^{12}$CO$_2$ and $^{13}$CO$_2$). This instrument utilizes three single-mode tunable diode lasers, with CO
measured using a quantum cascade laser (QCL) at approximately 4.7 µm. The three individual mid-infrared laser beams were combined by the use of dichroic filters and directed through a small volume (0.3 liter) Herriott cell enclosing a 36-meter optical path. After exiting the Herriott cell, the beams were spectrally separated and directed to individual HgCdTe (MCT) detectors.

The lasers were operated in a wavelength-modulated mode, each at an independent frequency, and line-locked to the centers of the species’ selected absorption lines. Lines were selected to provide both good sensitivity and good isolation from any potential spectral interferences. Detector signals were demodulated at twice the lasers’ modulation frequencies (2F detection), and normalized by average detected laser intensity.

Ambient air was sampled through an inlet probe, compressed, and passed through a permeable membrane dryer to remove water vapor prior to being introduced into the Herriott cell. Due to the need for very fast time response during FIREX-AQ, the instrument was operated with a flow of approximately 14 slpm with the Herriott cell at a pressure of approximately 67 mbar. The resulting time response, verified with a fast-acting valve, was faster than 0.2 s. Data were reported at both 0.2 s and 1 s timesteps.

The TDLAS instrument was calibrated using the same gas standards as for the ICOS instrument, nominally with a 4-minute period, but often advanced or delayed in time to avoid calibrating during fire plume encounters. Calibrations provided both slope and intercept values tying signals to species concentrations. The very large CO concentrations encountered necessitated post-campaign correction calibrations to account for response nonlinearity.

Post-campaign analysis of the TDLAS CO data indicated that measurement precision (1σ) was approximately 0.1% at 1 s and 0.14% at 0.2 s. Accuracy was dependent on CO mixing ratio, and varied from 2% to 7%.

### 2.2.9 H₂O

H₂O was measured using the NASA diode laser hygrometer, an open-path infrared absorption spectrometer that uses a laser locked to one of three water vapor absorption features near 1.395 µm, depending on the abundance of water vapor (Diskin et al., 2002; Podolske et al., 2003). H₂O mixing ratios were determined with an uncertainty of 5%.

### 2.2.10 Smoke age

The age of smoke from emission to sampling by the aircraft was determined from an ensemble of upwind trajectories from the aircraft (Holmes et al., 2020). Trajectories were computed with HYSPLIT (Stein et al., 2015) using three meteorological datasets (HRRR, NAM CONUS Nest, and GFS 0.25°). In each of the three trajectories, the advection time was determined from the point where the trajectory most closely approached the source fire. The age also includes plume rise time from the surface to trajectory altitude, which was estimated with a mean rise time of 7 ± 4 m s⁻¹ (Lareau et al., 2018). Trajectories and ages that were grossly inconsistent with smoke transport patterns seen in geostationary satellite images were
2.3 Methodology

This study focuses on comparing the different techniques used for the measurements of one or several reactive nitrogen species as well as CO during FIREX-AQ. Here we compare both archived 1 s data (https://www-air.larc.nasa.gov/missions/firex-aq/index.html) and the plume-integrated data. Plume-integrated data are obtained from integrating the 1Hz data of a given measurement over a smoke plume transect. A smoke plume transect was identified using the time period between a CO and/or black carbon (BC) increase above a local background value (beginning of the plume transect) and the CO and/or BC decrease back to a background value (end of the plume transect). Background values on either side of a plume were different for some fires in spatially heterogeneous source regions. Note that any 10 s period of background air, even if experienced during a single smoke plume transect, was sufficient to mark the end of one transect and the start of the next. All 1Hz data were time-aligned prior to comparison by synchronizing features in the time series of each species. Time shifts were typically less than 4 seconds. Some disagreement between measurement techniques is expected due to the rapid variations sampled during FIREX-AQ, particularly when those variations occur faster than the measurement period and/or with greater spatial heterogeneity than the distance between the sampling locations on a large aircraft that can reach 25m in some cases.

We first calculated the slope of the linear least-squares (LLS) orthogonal distance regression (ODR) to characterize the percent difference between measurements of a pair of instruments weighted by the inverse of the instrument precision. Here, we used a mixing ratio-independent instrument precision that corresponded to the 1σ precision in clean air. Weighting the fit by this term, rather than a more accurate but labor-intensive mixing-ratio-dependent precision, tend to overweight the highest measured mixing ratios. The slope and intercept resulting from the ODR regression analysis provide a measure of systematic or species-dependent instrumental biases. Additionally, we calculated the difference between a given pair of measurements. The difference, noted ΔY_{X1,X2} where X1 and X2 are the two measurement techniques for detection of the Y species, provides an understanding of the temporal evolution and environmental dependency of instrumental discrepancies. Note that the regression analysis yields slightly different information than the calculation of the difference: while the former is weighted more by fire plumes, where mixing ratios were greatest, the latter is weighted more by background conditions, where most of the measurements took place. Unless specified otherwise, all data available (i.e., both background and fire smoke data) were included in the following comparisons. We also calculated the fractional error (FE = ΔY_{X1,X2}/Y_{avg} where Y_{avg} = (Y_{X1} + Y_{X2})/2) between pair of instruments using specifically fire smoke data to minimize measurements below instrument detection limits (Figures S1 and S2).
3.1.1 Campaign-wide comparison

The 1Hz data comparison between the CL and LIF instruments is shown in Figure 2. The overall comparison slope (± combined instrument uncertainties) is $0.98 \pm 0.08$ ($R^2 = 0.93$) with an intercept of $-2 \pm 0$ pptv (Figure 2a). Figures 3a and 4a show the two instruments’ response in smoke from a wildfire and an eastern fire, respectively. While the NO signals track each other remarkably well, there is a difference in time response that is typical of the entire campaign. Figure S3 shows an expanded view of 10Hz NO and CO measurements in a partial smoke plume transect, including the transition from smoke to background air sampling. The NO signal in the CL instrument exhibits less structure than in the LIF instrument and a tail following the plume-to-ambient air transition. These tails were commonly observed during this transition. This effect in the CL instrument may partly explain the elevated scatter below the 1:1 line in Figure 2b. Integrating the NO signal across plume passes reduces the scatter due to different instrument time response: the regression analysis of smoke plume-integrated NO mixing ratios yields a slope of $0.99$ ($R^2 = 0.95$) for the whole dataset (Figure 2c).

A histogram of the absolute difference between LIF and CL ($\Delta NO_{\text{LIF-CL}}$) is shown in Figure 5a. 90% of the values were between $-44$ and $43$ pptv, and the whole dataset is normally distributed around $0 \pm 0$ pptv (central value of the Gaussian fit and standard deviation). $\Delta NO_{\text{LIF-CL}}$ exhibits no significant correlation with NO and H$_2$O mixing ratios, which suggests that there was no systematic bias between the two instruments over a wide range of NO mixing ratios and environmental conditions (Figures S4a and 6a). Similar slopes and intercepts were obtained when separately comparing NO measurements during the wildfire, eastern fire, and LA Basin sampling periods (Figures 2b and S5).

3.1.2 Literature aircraft NO measurement comparisons

Overall, the comparison between the two NO instruments shows an agreement within stated uncertainties. While the single-photon LIF detection of NO is a new technique that was evaluated for the first time during FIREX-AQ (Rollins et al., 2020), there are several studies that compared CL detection of NO to other measurement techniques during airborne field campaigns. The Global Tropospheric Experiment Chemical Instrumentation Test and Evaluation (GTE-CITE) was designed in the 1990’s to intercompare airborne measurement techniques for trace species including NO, NO$_2$ and CO. Comparison of two CL instruments and a two-photon LIF instrument showed agreement when NO mixing ratios were higher than 50 pptv, but pointed out periods of disagreement when NO mixing ratios were lower than 20 pptv (Gregory et al., 1990; Hoell et al., 1987). The Deep Convective Clouds & Chemistry (DC3) experiment in 2012 allowed for side-by-side comparison of instruments aboard two aircrafts at two level flight legs (7 and 12 km) for flight periods spanning 20–30 minutes. Pollack et al. (2016) showed that these NO measurements from two CL instruments agreed within 2% for NO mixing ratios up to 1 ppbv. More recently, Sparks et al. (2019) reported an intercomparison of several NO$_x$ species measurements, including NO, from the Wintertime Investigation of Transport, Emissions, and Reactivity (WINTER) airborne experiment over the Northeast US in 2015. During WINTER, NO measured by CRDS and CL differed on average by 16% across all flights, which is outside of the combined
instrument uncertainties. CL measurements were more consistent with an independent calculation of NO based on a photostationary state assumption.

3.2 NO$_2$

3.2.1 Campaign-wide comparison

Three instruments measured NO$_2$ mixing ratios during FIREX-AQ using CL, CES and LIF detection techniques. The 1Hz data comparison between all three instruments is shown in Figure 7. We find that the LIF and CES overall comparison yields a slope ($\pm$ combined instrument uncertainties) of 1.03 $\pm$ 0.08 ($R^2 = 0.98$), well within the combined instrument uncertainties of 8% (Figure 7c). However, we find that comparing either the LIF or CES instruments to the CL instrument results in correlation slopes ($\pm$ combined instrument uncertainties) ranging from 0.88 $\pm$ 0.12 to 0.90 $\pm$ 0.11 ($R^2 = 0.97$), comparable to the 8–11% combined uncertainties for each pair of instruments (Figures 7a and b). The higher NO$_2$ mixing ratios measured by the CL instrument are further illustrated in the time series in Figures 3b and 4b, and is consistent with a calibration error in one or all instruments, or an interference from another species in the CL instrument. HONO is a known source of interference in measured NO$_2$ by instruments that use photolysis in the near-UV region (Pollack et al., 2011). However, this interference was determined to be low (less than 5% of HONO concentration) following laboratory tests using a HONO calibration source (Lao et al., 2020), and the NO$_2$ measurement by CL was corrected for it. Additionally, we did not find a correlation between either $\Delta$NO$_2$CES–CL or $\Delta$NO$_2$LIF–CL and HONO mixing ratios. There was better agreement between the CL and the other two instruments when sampling the wildfires (slopes of 0.91) than the eastern fires (slopes of 0.75 and 0.87 for the LIF and CES, respectively) (Figures 7d and e). Similarly, the agreement between the CES and the LIF instruments was near perfect during the first period (slope of 1.00), but worse during the latter period (slope of 1.13; Figure 7f). Note that the LIF instrument did not report data for three flights out of seven during the eastern fires sampling period. The increased difference may be caused by the physical distance between instrument inlets combined with higher spatial heterogeneity of trace gases in the smaller and thinner eastern fire plumes, although higher mixing ratios of a potential interferent may still exist. Non-acyl peroxy nitrate species such as pernitric acid (HO$_2$NO$_2$) and methyl peroxy nitrate (MPN) can be abundant in smoke plumes and interfere with NO$_2$ measurements (Browne et al., 2011; Nault et al., 2015). This interference is the result of the thermal dissociation of HO$_2$NO$_2$ and MPN in heated inlets and sampling lines, and impact differently each instrument depending on their flush time. During FIREX-AQ, the CES and CL instruments had similar flush time of about 750ms meaning that the thermal decomposition of non-acyl peroxy nitrates is unlikely to explain the 10–12% higher NO$_2$ signal in the CL instrument. Nitrated phenolic compounds can be abundant in aged smoke (Decker et al., 2021), and have large UV cross sections (Chen et al., 2011). They are unlikely to contribute to the interference as their NO$_2$ photolysis quantum yields are very low. Nevertheless, further laboratory work on the NO$_2$ interference of such species in photolytic converters is of interest. The agreement between all three instruments for individual flights was generally within combined instrument uncertainties, but with some variability (Figures S6–S8).
Histograms of the absolute difference between CES, LIF and CL ($\Delta$NO$_{2\text{LIF-CL}}$, $\Delta$NO$_{2\text{CES-CL}}$ and $\Delta$NO$_{2\text{CES-LIF}}$) are shown in Figures 5b–d. 90% of $\Delta$NO$_{2\text{LIF-CL}}$, $\Delta$NO$_{2\text{CES-CL}}$ and $\Delta$NO$_{2\text{CES-LIF}}$ values were between −298 and 338 pptv, −469 and 302, and −576 and 393 pptv, respectively, and all are normally distributed around the central value of the Gaussian fit of 0.038 ± 0.001, −0.052 ± 0.001, and −0.071 ± 0.001, respectively. $\Delta$NO$_{2\text{LIF-CL}}$, $\Delta$NO$_{2\text{CES-CL}}$ and $\Delta$NO$_{2\text{CES-LIF}}$ exhibit no significant trend with H$_2$O mixing ratios (Figures 6b–d), yet $\Delta$NO$_{2\text{LIF-CL}}$ and $\Delta$NO$_{2\text{CES-CL}}$ were weakly (R$^2$ = 0.36 and 0.31, respectively) correlated with the absolute NO$_2$ mixing ratio (Figures S4b and d).

### 3.2.2 Literature aircraft NO$_2$ measurement comparisons

Previous comparisons of NO$_2$ airborne measurements often show periods of disagreement between instruments, although there were some occasions where instruments agreed within stated uncertainties. During the GTE-CITE experiment, the comparison of NO$_2$ measurements using a two-photon NO LIF system with laser photolysis of NO$_2$ to NO with a CL detector equipped with a xenon arc lamp for NO$_2$ photolysis into NO showed agreement within 30–40% (Gregory et al., 1990). Pollack et al. (2016) showed that two NO$_2$ measurements, both using CL but each in a different aircraft, agreed within 28% during the DC3 campaign. During WINTER, NO$_2$ measurements by CRDS and LIF agreed with an average proportional bias of 2% across all flights – well within combined uncertainties (Sparks et al., 2019). During SENEX, three techniques were used to measure NO$_2$: a CRDS instrument, a CES instrument and a CL instrument. The agreement between CRDS and CES measurements with the CL technique was on average 6 and 10% (Warneke et al., 2016).

### 3.3 HONO

#### 3.3.1 Campaign-wide comparison

The 1Hz data comparison between the CES and the CIMS instruments is shown in Figure 8, and timeseries of HONO measurements in wildfires and eastern fires are shown in Figures 3c and 4c, respectively. The correlation between the CES and CIMS was very high in each plume transect (Figures 3c and 4c), but the overall comparison yielded a slope (± combined instrument uncertainties) of 1.80 ± 0.16 (R$^2$ = 0.77) and an intercept of −0.12 ± 1.10 ppbv (Figure 8a). Integrating across plume transects yielded a slope of 1.34 ± 0.16 (Figure 8c). The CIMS consistently reported less HONO than the CES in smoke plumes, and the average slope between the two measurements was considerably greater during the eastern fires compared to the wildfires (Figures 8b and S9). However, flight averages of the absolute difference between the two measurements ($\Delta$HONO$_{\text{CES-CIMS}}$) ranged between −332 and 245 pptv throughout the campaign and were similarly scattered around zero during the two different time periods (Figure S9). A histogram of $\Delta$HONO$_{\text{CES-CIMS}}$ is shown in Figure 5e. 90% of the values were between −965 and 880 pptv, and the whole dataset is normally distributed around the central value of the Gaussian fit (± standard deviation) of −119 ± 2 pptv. $\Delta$HONO$_{\text{CES-CIMS}}$ exhibits no significant slope with HONO (Figure S4e). While the deployment out of Salina was operated under noticeably more humid conditions (H$_2$O ranged from 0.002 to 2.944%) than out of Boise (H$_2$O ranged from 0.004 to 1.479%), we find no significant correlation between $\Delta$HONO$_{\text{CES-CIMS}}$ and H$_2$O mixing ratios (Figure 6e).
However, further laboratory studies, field measurements, and examination of this comparison has revealed that the CIMS sensitivity to HONO is reduced when the instrument reaches temperatures greater than 30°C (Figure S10). This sensitivity dependence on temperature does not affect all compounds measured by the CIMS, and the sensitivity to Cl₂ and HNO₃ used for in-flight calibrations was independent of instrument temperature. The aircraft cabin temperature was greatest during the eastern agricultural flights, when the CIMS instrument temperatures were often 40°C and far greater than the typical 25°C instrument temperatures in the laboratory when the CIMS HONO sensitivity was determined. As a consequence, the reported CIMS HONO values were spuriously low, especially during the eastern fires, and particularly later in flights when the aircraft temperatures were greatest. This intercomparison has yielded new insights into the CIMS HONO detection sensitivity, and future work will identify and implement appropriate corrections to this measurement.

3.3.2 Literature aircraft and ground HONO measurement comparisons

HONO measurements are notoriously difficult due to the potential for artifacts associated with inlet surfaces as well as interferences associated with some methods (e.g., Kleffmann et al., 2006; Xu et al., 2019). Past ground-based intercomparisons often revealed significant discrepancies in HONO measurements. For example, six ground-based HONO measurement techniques including a CIMS instrument were compared during the Study of Houston Atmospheric Radical Precursors (SHARP) campaign in 2009 (Pinto et al., 2014). While three out of six of these techniques agreed within 20%, larger deviations were found when the other three instruments were considered and attributed to the physical separation of these instruments. Three different techniques, including a CIMS instrument, were used to measure HONO in the urban area of Shanghai, China (Bernard et al., 2016). The percent difference between these measurements ranged from 27 to 46%. In 2019, six HONO measurement techniques were again compared in a Chinese urban area, this time in Beijing, and included a CIMS instrument as well as two broadband cavity enhanced absorption spectrometers (BBCEAS) (Crilley et al., 2019). Percent differences up to 39% were observed during this intercomparison and again attributed to the physical distance separating inlets coupled to high spatial heterogeneity of HONO mixing ratios. Airborne measurements of HONO by CIMS and CES were made during the Southeast Nexus Experiment (SENEX), and the CES instrument was approximatively 25% higher than the CIMS instrument (Neuman et al., 2016).

3.4 NOₓ

3.4.1 Campaign-wide comparison

The 1Hz data comparison between the total NOₓ measurement by CL and ∑NOₓ is shown in Figure 9. ∑NOₓ definition is given by Eq. 2 (see section 2.2.8). C₁–C₅ alkyl nitrates and other minor NOₓ species (including N₂O₅, CH₃NO₂, and alkene hydroxy nitrates) contributed less than 7% of the NOₓ budget on average (Figure 10). The overall comparison yielded a slope (± combined instrument uncertainties) of 1.00 ± 0.25 (R² =0.98) and an intercept of −0.52 ± 0.01 ppbv (Figure 9a). The regression analysis of smoke plume-integrated NOₓ mixing ratios yields a slope of 1.00 (R² = 0.99) for the whole dataset (Figure 9c). Comparison of CL NOₓ...
to $\Sigma$NO$_y$ in fresh (<1h since emission) and aged (>1h since emission) smoke during the wildfires sampling period showed similar agreement (slopes of 0.98 and 1.05, respectively) despite the chemical evolution of NO$_x$ species, highlighted by the different proportion of those species to the NO$_x$ balance (Figure S11). Measurements used in Eq. 2 are CL NO$_x$, CIMS HONO, CIMS HNO$_3$, HR-AMS pNO$_3$ and CIMS APNs. These measurements were primarily used because they had better precision. Using LIF NO, CES NO$_2$ and CES HONO as primary measurements changed the correlation slope between measured NO$_y$ and $\Sigma$NO$_y$ by less than 5% (Figure S12).

Despite this correlation, two modes are apparent in the overall distribution of the absolute difference ($\Delta$NO$_y$$_{CL}$–Sum) between $\Sigma$NO$_y$ and the total NO$_y$ measurement (Figure 5f). The first mode is distributed around $-0.068 \pm 0.001$ ppbv (central value of the first mode of the Gaussian fit), while the second is distributed around an average value of $0.158 \pm 0.009$ ppbv (central value of the second mode of the Gaussian fit). Separating the comparison into three time periods reveals that this two-mode distribution of $\Delta$NO$_y$$_{CL}$–Sum comes from the eastern fires sampling period as well as from the LA Basin flights whereas during the wildfires sampling period $\Delta$NO$_y$$_{CL}$–Sum distribution is unimodal (Figure 11).

Higher $\Sigma$NO$_y$ compared to NO$_y$ (first mode) could be explained by (i) a lower conversion efficiency of one or more NO$_y$ species in the CL instrument than estimated in the laboratory, (ii) sampling loss of pNO$_3$ through the NO$_y$ inlet, and (iii) inaccuracy in one of the individual NO$_y$ species measurement techniques. Here, we further investigated the sampling loss of pNO$_3$ through the CL instrument NO$_y$ inlet using a multistage flow model following the template of the Particle Loss Calculator (von der Weiden et al., 2009). The model calculates aerodynamic losses at each stage of the NO$_y$ inlet and provides the resulting total pNO$_3$ sampling efficiency (See Section S1 and Figure SA). We find that the main aerosol sampling loss occurs at the NO$_y$ inlet tip orifice (1.0 mm in diameter) due to the inlet orientation (perpendicular to the aircraft flight direction). Additional loss was calculated to be negligible once pNO$_3$ penetrated the NO$_y$ inlet, meaning that pNO$_3$ is fully volatilized into NO inside the heated gold catalyst (See Section S1 and Figure SA). Particle sampling through the NO$_y$ inlet is highly dependent on altitude, air speed (see section S1 and Figure SB) and pNO$_3$ mass size distribution (Figure 12a). Figure 12b shows the average modelled particle sampling fraction through the NO$_y$ inlet, given as a ratio where a value of 1 means the total pNO$_3$ is sampled, for each flight during FIREX-AQ. Particle sampling fraction was calculated for three different air speeds for each flight: 40%, 65%, and 100% of the aircraft speed. An assumed sampled air speed of 65% that of the aircraft improved the correlation between $\Delta$NO$_y$$_{CL}$–Sum and the modelled pNO$_3$ loss in the inlet (see Section S1 and Figure SB). At that speed, the calculated average particle sampling fraction varied between 0.36 and 0.99 for each flight (Figure 12b). Consequently, 0–24% of the measured NO$_y$ in smoke (assuming a sampled air speed 65% that of the aircraft) initially attributed to pNO$_3$ may result from other reactive nitrogen species than those included in the $\Sigma$NO$_y$ (Figure 12b). This additional contribution has a large uncertainty because the model may underestimate pNO$_3$ sampling through the NO$_y$ inlet due to the large uncertainty when the losses are calculated at high air
Further, we used bulk aerosol volume size distributions measured with a Laser Aerosol Spectrometer (LAS; Moore et al., 2021) to derive pNO$_3$ sampling fractions in Figure 12a as pNO$_3$ mass size distribution measurements were not available for all flights during FIREX-AQ. At a typical FIREX-AQ sampling altitude of 5 km, the LAS and HR-AMS size distributions can differ by about 10% (See Section S1 and Figure SC), which adds to the uncertainty of the pNO$_3$ sampling fraction through the NO$_y$ inlet. Correcting for particle sampling through the NO$_y$ inlet still yields an agreement between measured NO$_x$ and ΣNO$_y$ that is within the combined instrument uncertainties of 25%. On the other hand, the positive ∆NO$_y$CL–Sum mode (second mode) may indicate either an inaccuracy in one of the individual NO$_y$ species measurement techniques or an NO$_y$ species not measured. Further, we find that positive ∆NO$_y$CL–Sum occurred both in smoke (Figure 11d) and in background air (Figure 11c) when sampling the eastern fires and that ∆NO$_y$CL–Sum exponentially decreased with altitude, a pattern also observed during the LA Basin flights but not during the wildfires sampling period (Figure 13b). Note that flight altitude when sampling the wildfires was 4.6 km on average, higher the altitude average of 0.6 and 1.1 km during the eastern fires and the LA Basin flights, respectively. Both water vapor and C$_1$–C$_5$ alkyl nitrates (not included in ΣNO$_y$ thus far) were enhanced at lower altitude and may be possible causes for the positive ∆NO$_y$CL–Sum mode. Alkyl nitrates have been shown to account for a significant fraction of the NO$_y$ budget in past studies (e.g., Fisher et al., 2016; Hayden et al., 2003; Horii et al., 2005). However, we find only a weak correlation between ∆NO$_y$CL–Sum and C$_1$–C$_5$ alkyl nitrates during both the wildfires (R$^2 = 0.07$) and eastern fires (R$^2 = 0.08$) sampling periods (Figure 13c). The correlation is stronger (R$^2 = 0.44$) during the LA Basin flights (Figure 13c). Further, we find that C$_1$–C$_5$ alkyl nitrates contributed similarly to the NO$_y$ budget when smoke from the wildfires (1.1% on average) and the eastern fires (0.8% on average) was sampled (Figure 10a), while the positive mode in the ∆NO$_y$CL–Sum distribution is present in the latter period only. H$_2$O is a known source of interference in most instruments, and its impact on measurements is minimized when an accurate correction can be applied. Increasing ∆NO$_y$CL–Sum is associated with increasing H$_2$O mixing ratios in the eastern fires, although the correlation is weak (R$^2 = 0.05$) due to the elevated scatter of the data (Figure 13a). Similar slopes and intercepts were obtained when separately comparing NO$_y$ measurements in smoke from the wildfires and eastern fires (Figures 9b and S13). The slope of 0.81 during the LA Basin flights, may be caused by the lower precision of ΣNO$_y$ than that of the CL NO$_y$ (Figure 9b). Overall, the agreement between the total NO$_y$ measured by the CL instrument and the ΣNO$_y$ is within instrument uncertainties. Budget closure implies that the historical definition of NO$_y$ (i.e., NO$_x$ and its oxidation products, excluding reduced nitrogen species such as NH$_3$ and HCN) is adequate even in extremely reactive conditions that foster rapid changes in NO$_y$ speciation. Reduced nitrogen species such as hydrogen cyanide (HCN) or ammonia (NH$_3$) represent a large fraction of the total nitrogen emission from biomass burning (Roberts et al., 2020) and have been shown to cause a small interference in CL instruments in dry air (Fahey...
et al., 1985, 1986). This interference is often neglected because of either the low atmospheric abundance of these species or sampling in humid air where such an interference is thought to be negligible. Here, we find no evidence for a potential interference of HCN or NH₃, despite their high abundance (tens of ppbv) in smoke plumes (Figure S14). Altogether, our findings show that the NOₓ instrument provides an accurate and conservative measurement of total reactive nitrogen species, although further work is needed to empirically characterize pNO₃ sampling through the NOₓ inlet.

There are a few studies that recently examined the NOₓ budget closure from aircraft measurements. Calahorrano et al. (2020) presented reactive odd nitrogen partitioning during the Western wildfire Experiment for Cloud chemistry, Aerosol absorption and Nitrogen (WE-CAN) that sampled western American wildfires during the summer 2018. The authors found significant (15–26%) contribution of organic N species other than APNs and alkyl nitrates to \( \Sigma \text{NO}_\text{x} \). However, there was no total NOₓ measurement during WE-CAN, and the conclusion is based on summed individual reactive nitrogen species. The FIREX-AQ comparison of \( \Sigma \text{NO}_\text{x} \) to total NOₓ finds 2-13% of the total NOₓ unaccounted for, smaller than the estimate of a 15-26% contribution from multifunctional organic nitrates from WE-CAN. While the FIREX-AQ NOₓ difference suggests a smaller contribution from organic nitrates, the WE-CAN estimate is within the uncertainty of the FIREX-AQ analysis. During the WINTER campaign, budget closure of NOₓ (\( \text{NO}_\text{x} = \text{NO}_\text{y} - \text{NO}_\text{z} \)) was demonstrated to occur within 20% for all flights following the comparison of \( \Sigma \text{NO}_\text{z} \) with total NOₓ from three different measurement techniques, including a CL instrument (Sparks et al., 2019). A recent ground-based study in New York State in the US found that the sum of the individual reactive odd nitrogen species accounted for 95% of the total NOₓ, well within measurement uncertainties (Ninneman et al., 2021). These recent studies contrast with somewhat older literature that often reported a significant shortfall in the NOₓ balance, where measured NOₓ was higher than \( \Sigma \text{NO}_\text{x} \) (Hayden et al., 2003; Horii et al., 2005; Williams et al., 1997; Zhang et al., 2008). This shortfall has often been attributed to unmeasured organic N species and more specifically alkyl nitrates (Day et al., 2003; Horii et al., 2005). During FIREX-AQ, C₁–C₅ alkyl nitrates accounted for less than 7% on average of the NOₓ budget (Figure 10), consistent with findings from other regions in the US (Benedict et al., 2018; Russo et al., 2010). However, FIREX-AQ did not include a measurement of total alkyl nitrates.

3.5 CO

3.5.1 Campaign-wide comparison

The 1Hz data comparison between the ICOS and the TDLAS instruments is shown in Figure 14. The overall comparison yielded a slope (± combined instrument uncertainties) of 0.98 ± 0.03 (R² = 0.99) and an intercept of −1.06 ± 0.01 ppbv (Figure 14a). The regression analysis of smoke plume-integrated CO mixing ratios yields a slope of 0.99 (R² = 1) for the whole dataset (Figure 14c). A histogram of the absolute difference between CO measurements (\( \Delta \text{CO}_{\text{ICOS-TDLAS}} \)) is shown in Figure 5g. 90% of the values were between −6.05 and 2.35 ppbv, and the whole dataset is normally distributed around the central value of the Gaussian fit of −2.87 ± 0.02 ppbv. This is indicative of an offset between the two CO instruments, with the
TDLAS systematically higher than the ICOS instrument. This average 2.87 ppbv offset was consistent throughout the campaign regardless of the type of fires that were sampled. Therefore, it cannot explain the significantly lower agreement of the instruments during the eastern fires compared to the wildfires sampling period (Figures 14b and S12). During the first period, the overall slope was 0.99 and ranged from 0.97 to 1.02 (average of 0.99) for individual flights, well within the combined instrument uncertainties of 3% (Figures 14b and S12). However, all individual flight measurements during the eastern fires sampling period exhibit slopes reduced by about 10% (range = 0.86–0.91 with an average of 0.89) and largely positive intercepts (range 6.75–19.04 with an average of 11.51) (Figure S15). As observed for other species, the second period proved to be a more challenging environment for CO measurements. This may be attributed to a spectral issue with one or the other of these two instruments, although we could not identify the source of the discrepancy. ∆CO\textsubscript{ICOS–TDLAS} exhibit no significant slope with CO (Figure S4g) and H\textsubscript{2}O (Figure 6g) mixing ratios.

3.5.2 Literature aircraft CO measurement comparisons

Overall, the comparison between the two CO instruments shows an agreement well within stated uncertainties. We find that the agreement between the two CO instruments used during FIREX-AQ is well in line with past intercomparisons. During the GTE-CITE experiment, the comparison of a TDLAS technique with two grab sample/gas chromatograph methods for detection of CO showed agreement across the instruments – within the combined instrument uncertainties and strong correlations (R\textsuperscript{2} = 0.85–0.98) for CO ranging from 60 to 140 ppbv (Hoell et al., 1987). During the North Atlantic Regional Experiment (NARE 97) CO was measured by TDLAS and vacuum ultra-violet fluorescence with agreement to within 11% and systematic offsets of less than 1 ppbv (Holloway et al., 2000). CO was also more recently measured by TDLAS and vacuum ultra-violet fluorescence during the side-by-side comparison of instruments aboard two aircraft during the DC3 experiment. There, CO measurements agreed within 5% during flight periods typically ranging from 20 to 30 minutes (Pollack et al., 2016).

4 Conclusion

In this study, we compare airborne measurements of NO, \textsubscript{NO}\textsubscript{2}, HONO, NO\textsubscript{y} and CO conducted during the FIREX-AQ campaign in the summer 2019. This dataset offers the opportunity to assess the accuracy of a large suite of detection techniques in a challenging environment where species mixing ratios increased by tens of ppbv in seconds between background air and fire smoke. For NO, \textsubscript{NO}\textsubscript{2} (CES and LIF), NO\textsubscript{y} and CO, correlations agree better than the combined instrument uncertainties, indicating that the stated individual uncertainties are conservative estimates. For \textsubscript{NO}\textsubscript{2} (CL) and HONO, the percent difference between measurements is higher than the combined instrument uncertainties, indicating potential interferences or calibration inaccuracies that are not identified at this time. Based on the analysis above, we make the following recommendations, which are specific to the FIREX-AQ campaign.

1) Comparison of NO measurements by LIF and CL showed an overall agreement well within instrument uncertainties. Flight-to-flight agreement was generally more variable.
during the eastern fires sampling period than during the wildfires sampling period, which was attributed to the heterogeneous nature of smoke plumes combined with the physical separation of inlets. Both measurements are considered reliable for FIREX-AQ, although the LIF instrument has better 1Hz precision (1 pptv) than the CL instrument (6 pptv), and the CL instrument exhibited slower time response.

2) Comparison of NO$_2$ measurements by LIF and CES showed an overall agreement well within the stated instrument uncertainties. However, NO$_2$ measured by CL is on average 10% higher than that measured by the other two techniques. The agreement worsens for all instruments when comparing NO$_2$ measured during the eastern fires sampling period, likely for similar reasons as indicated for the NO measurements.

3) The CES and CIMS HONO measurements were highly correlated in each fire plume transect, but the correlation slope of CES vs. CIMS for all 1 Hz data from the entire campaign was 1.8. The HONO measured by CIMS was on average 74% of that measured by CES during the wildfires sampling period, and on average 40% of CES during the eastern fires sampling period. The higher precision data from the CIMS are most useful for analysis of HONO when mixing ratios are lower. The redundancy of HONO measurements during FIREX-AQ led to the discovery that the CIMS sensitivity to HONO was reduced in a high temperature environment. This intercomparison has initiated further studies of the CIMS sensitivity to HONO and other compounds.

4) Closure of the NO$_y$ budget between the total NO$_y$ measurement by CL and $\Sigma$NO$_y$ was achieved for all flights and correlation slopes were usually much better than the combined instrument uncertainties of 25%. NO$_x$, HNO$_3$, HONO, APNs and pNO$_3$ are the main contributors to the NO$_y$ budget, with the other reactive N species contributing less than 10% on average. We find that the modelled pNO$_3$ sampling fraction through the NO$_y$ inlet is highly dependent on altitude, air speed and pNO$_3$ mass size distribution, and varied on average between 0.36 and 0.99 during FIREX-AQ. Therefore, approximately 0–24% on average of the total measured NO$_y$ by CL may be unaccounted for and possibly explained by other species such as multifunctional organic nitrates. The reason for the secondary positive mode of 0.4 ppbv in the $\Delta$NO$_y$$_{CL-Sum}$ distribution in the eastern fires and LA Basin flights could not be clearly identified. Potential explanations include the contribution of gas-phase organic nitrates, not included in the $\Sigma$NO$_y$, and/or a water vapor interference in one or more instruments. Regardless, we conclude that the total NO$_y$ measurement by CL provides a robust quantification of the reactive nitrogen species in background air as well as in smoke plumes, and that the total NO$_y$ measurement is not sensitive to interference from reduced nitrogen species in fire plumes. Further laboratory and field work will be needed to fully characterize pNO$_3$ sampling through the NO$_y$ inlet.

5) Comparison of CO measurements by TDLAS and ICOS showed an agreement well within the combined instrument uncertainties. An offset of ~2 ppbv between the two instruments was identified but has little impact on the correlation. There was a clear difference in the
agreement between the wildfires sampling period and the eastern fires sampling period, where the correlation slopes were about 10% lower.

6) Integrating data across smoke plume transects generally improved the correlation between independent measurements and may be necessary for fire-science related analyses, especially for smaller plumes with greater spatial heterogeneity compared to the distance between the sampling locations on a large aircraft.

Data availability
All data used in this manuscript are archived online and available at https://www-air.larc.nasa.gov/cgi-bin/ArcView/firexaq.

Author contribution
I.B. and T.B.R. designed research. All authors performed FIREX-AQ measurements. P.C.-J., H. G., and J.L.J performed the flow modelling analysis. All authors analyzed data. I.B., J.P., J.A.N., and S.S.B. wrote the original draft and all authors edited and revised the paper.

Competing interests
The authors declare they have no conflict of interest.

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Figure 1 Examples DC-8 flight tracks from western wildfires and eastern agricultural fires. Panel a) shows the DC-8 flight track (black line) during the sampling of the Williams Flat fire (03/08/2019) smoke plume, colored by NO$_y$ mixing ratios (only data in smoke are colored here). Panel b) shows the DC-8 flight track during the sampling of multiple agricultural burns (21/08/2019), also colored by NO, mixing ratios (only data in smoke are colored here).
Figure 2 NO measurements by LIF versus CL with a) 1 s data on a linear scale, b) 1 s data on a log scale, and c) integrals of 330 crosswind smoke plume transects. N is the number of independent 1 s observations or smoke plume transects that are compared. In panel b, the three sampling periods are shown in different colors with the wildfires sampling period in red, the eastern fires sampling period in mustard, and the Los Angeles (LA) Basin flights in grey. The red lines indicate the fit of the data. The dotted black line is the 1:1 line.
Figure 3 1 s measurements of a) NO, b) NO\textsubscript{2}, c) HONO, d) NO\textsubscript{y}, and e) CO 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. Note that in panel b) the NO\textsubscript{2} trace from the CES instrument is hidden behind the NO\textsubscript{2} trace from the LIF instrument.
Figure 4 1 s measurements of a) NO, b) NO$_2$, c) HONO, d) NO$_y$, and e) CO during crosswind plume transects of smoke from crop burning in southeastern US on 30/08/2019.
Figure 5. Histograms of the absolute difference of 1 s measurements of a) NO, b)–d) NO₂, e) HONO, f) NO₃, g) CO for the entire campaign. Parameters of the gaussian fit to the histogram is indicated in each panel with $x_0$ and $w_0$ being the central value and the width of the fit, respectively. Note that in panel f) a double gaussian was fitted to the histogram and that the parameters for the second mode are given by $x_1$ and $w_1$. 
Figure 6 Measurement difference (1 s data) of a) NO, b)–d) NO$_2$, e) HONO, f) NO$_y$, g) CO as a function of water vapor for the entire campaign.
Figure 7 NO2 measurements by LIF, CES and CL with a)–c) 1 s data on a linear scale, d)–f) 1 s data on a log scale, and g)–i) integrals of 208–320 crosswind smoke plume transects. N is the number of independent 1 s observations or smoke plume transects that are compared. In the panels d)–f), the three sampling periods are shown in different colors with the wildfires sampling period in red, the eastern fires sampling period in mustard, and the Los Angeles (LA) Basin flights in grey. The red lines indicate the fit of the data. The dotted black lines are the 1:1 line.
Figure 8 Same as Figure 2 but comparing HONO measurements by CES and CIMS. No slope is given for the Los Angeles (LA) flights in panel as most of the HONO signal at that time was below the instruments’ detection limits.
Figure 9 Same as Figure 2 but comparing the sum of individually measured NO$_y$ species (= NO$_x$ + HONO + HNO$_3$ + APNs + pNO$_3$) with the total NO$_y$ measurement by CL.
Figure 10 Contribution of individually measured reactive odd nitrogen species to the total NO\textsubscript{y} budget during FIREX-AQ. The campaign is separated in three periods (wildfires sampling period in red, eastern fires sampling period in yellow, and Los Angeles (LA) Basin flights in grey). The panel a) show the NO\textsubscript{y} budget in smoke plumes, while the panel b) shows that in background air. C\textsubscript{1}–C\textsubscript{5} alkyl nitrates are referred to as C\textsubscript{1}–C\textsubscript{5} ANs. Other nitrogen species include N\textsubscript{2}O\textsubscript{5}, CH\textsubscript{3}NO\textsubscript{2}, and alkene hydroxy nitrates.

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Figure 11 Histograms of $\Delta NO_y$CL-Sum for three sampling periods during FIREX-AQ with the wildfires sampling period in red, the eastern fires sampling period in yellow, and the Los Angeles (LA) Basin flights in grey. Further separation was made between in smoke measurements (panels b and d) and background air measurements (panels a, c, and e). Parameters of the gaussian fit to the histogram is indicated in each panel with $x_0$ and $w_0$ being the central value and the width of the fit, respectively. Note that in the panels c) and e) a double gaussian was fitted to the histogram and that the parameters for the second mode are given by $x_1$ and $w_1$. 

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Figure 12 Panel a): The modelled pNO$_3$ sampling fraction through the NO$_y$ inlet as a function of altitude and pNO$_3$ mass size distribution (SD) is shown with a gradient of color from green (low sampling fraction) to yellow (high sampling fraction). The average pNO$_3$ mass size distribution measured in the Williams Flat fire smoke on 07/08/2019 by HR-AMS is shown in red. The modelled pNO$_3$ size distribution sampled in the NO$_y$ inlet assuming an altitude of 5km and a sampled air speed 65% that of the aircraft is shown in blue. In this example case, the sampled pNO$_3$ mass fraction is ~50%. Panel b): The average modelled particle sampling fraction in the NO$_y$ inlet (in black) and the corresponding percentage of measured NO$_y$ that may be unaccounted for (in red) are shown for each flight assuming a sampled air speed of 40% (bottom bars), 65% (markers) and 100% (top bars) that of the aircraft speed. The sampling fractions were calculated using bulk aerosol volume distributions measured by a Laser Aerosol Spectrometer (see Section S1 and Figure S5). The missing NO$_y$ corresponds here to the percentage of measured NO$_y$ that pNO$_3$ not sampled through the NO$_y$ inlet represents. Data shown in the panel b) are from air in smoke only.
Figure 13 Scatterplots of a) $\Delta$NO$_{y\text{CL-Sum}}$ vs H$_2$O, b) $\Delta$NO$_{y\text{CL-Sum}}$ vs altitude and c) $\Delta$NO$_{y\text{CL-Sum}}$ vs C$_1$–C$_5$ alkyl nitrates measured by the iWAS instrument for three sampling periods during FIREX-AQ (wildfires sampling period in red, eastern fires sampling period in yellow, and Los Angeles (LA) Basin flights in grey). The box and whisker plots show the 10$^{th}$, 25$^{th}$, 50$^{th}$, 75$^{th}$, and 90$^{th}$ percentiles of $\Delta$NO$_{y\text{CL-Sum}}$ distributions in each bin. The dots are the 1Hz data in panels a) and b), and 1Hz data averaged to match the iWAS sampling time in panel c).
Figure 14 Same as Figure 2 but comparing CO measurements by TDLAS and ICOS.