

Influence of Solar Irradiation on Nitrous Acid Production in Western U.S. Wildfire Smoke

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Abstract

Biomass burning is a primary emission source for a host of gas- and aerosol-phase compounds, which can damage environmental and human health. During the FIREX-AQ campaign in July and August of 2019, we measured reactive nitrogen species (NO_x, NO₂, HONO, HNO₃ and p-NO₃-), in wildfire plumes aboard NASA Langley's Mobile Aerosol Characterization Laboratory (MACH-2). Nitrous acid (HONO) and nitric acid (HNO₃) mixing ratios were measured at nominal 5-minute resolution using a dual mist chamber-ion chromatograph from five separate areas of fire in the western US and are the primary focus of this paper. Average HONO mixing ratios were significantly higher in young daytime smoke compared to young nighttime smoke, while no statistical differences were observed between young versus aged smoke during the day or night. In the largest fire sampled during the day, UV-A irradiation was highly correlated ($R^2 = 0.91$) with HONO to nitrogen dioxide (NO₂) ratios indicating that photo-enhanced heterogeneous NO₂ to HONO conversion, likely facilitated by ground surfaces (e.g. soil, foliage, and dust), more than compensated for rapid photolytic loss of HONO.

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Key Points:

- Strong evidence for substantial daytime and nocturnal secondary production of nitrous acid in biomass burning plumes.
- Daytime conversion of nitrogen dioxide to nitrous acid more than compensated for rapid photolytic losses of HONO in Williams Flats fire.
- Ground surfaces likely provide the dominant surface area for the heterogeneous secondary production of HONO.

Abstract

Biomass burning is a primary emission source for a host of gas- and aerosol-phase compounds, which can damage environmental and human health. During the FIREX-AQ campaign in July and August of 2019, we measured reactive nitrogen species (NO_x , NO_2 , HONO, HNO_3 and p-NO_3^-), in wildfire plumes aboard NASA Langley's Mobile Aerosol Characterization Laboratory (MACH-2). Nitrous acid (HONO) and nitric acid (HNO_3) mixing ratios were measured at nominal 5-minute resolution using a dual mist chamber-ion chromatograph from five separate areas of fire in the western US and are the primary focus of this paper. Average HONO mixing ratios were significantly higher in young daytime smoke compared to young nighttime smoke, while no statistical differences were observed between young versus aged smoke during the day or night. In the largest fire sampled during the day, UV-A irradiation was highly correlated ($R^2 = 0.91$) with HONO to nitrogen dioxide (NO_2) ratios indicating that photo-enhanced heterogeneous NO_2 to HONO conversion, likely facilitated by ground surfaces (e.g. soil, foliage, and dust), more than compensated for rapid photolytic loss of HONO.

Plain Language Summary

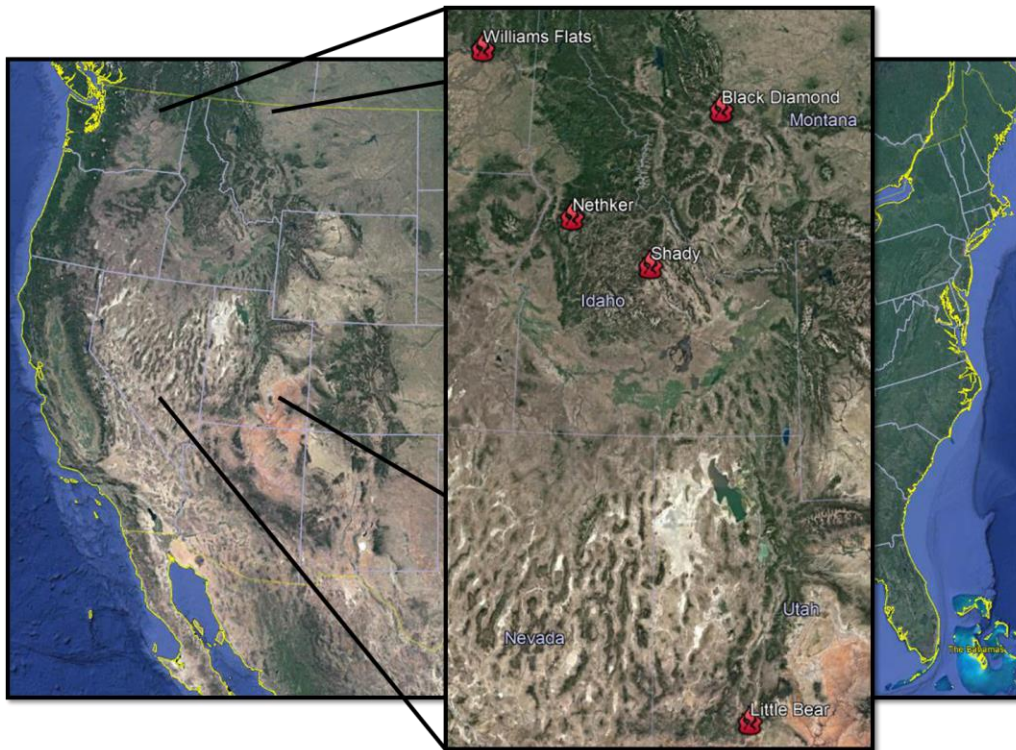
Wildfires negatively impact environmental and human health. Reactive nitrogen pathways are complex and research questions still remain regarding the formation of nitrous acid (HONO) in wildfire plumes. Our observations show that HONO can be made in a smoke plume, even as that smoke plume ages and mixes with surrounding air in both the daytime and nighttime. During the day sunlight rapidly destroys HONO but our data suggests that HONO is being made faster than it is lost in smoke close to the land surface. Moreover, the HONO is being produced by the combination of nitrogen dioxide (NO_2) on surfaces such as soil, leaf foliage and dust.

1. Introduction

Biomass burning (BB) is a primary emission source for a multitude of gas- and aerosol-phase compounds that impact environmental and human health (Grutzen & Andreae, 1990). Climate change induced global temperature increases have resulted in rises in the total acreage burned in the Western United States (Hoover & Hanson, 2019). A single degree centigrade of warming is predicted to result in a two to four times increase in burned areas (Warneke et al., 2015). The pressing need to better understand BB impacts on air quality and climate has motivated a number of recent collaborative field campaigns including the Studies of Emissions, Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC⁴RS); the fourth Fire Lab at Missoula Experiment (FLAME-4); the Fire Influence on Regional to Global Environments Experiment Fire Lab (FIREX-FIRELAB); Western wildfire Experiment for Cloud chemistry, Aerosol absorption and Nitrogen (WE-CAN); and the Fire Influence on Regional to Global Environments Experiment-Air Quality Campaign (FIREX-AQ) during which the data for this paper were collected. FIREX-AQ addressed four main research topics: the dependence of emissions on fuel sources, the difference in emissions between flaming and smoldering fires, the mode of atmospheric transport of smoke plumes, and how plumes compositionally change as they age (ESRL Chemical Sciences Division, 2019).

During FIREX-AQ collaborators from UNH, NASA Langley Aerosol Research Group Experiment (LARGE), and Brown University deployed NASA Langley's Mobile Aerosol Characterization Laboratory (MACH-2) during July and August of 2019 to measure the compositional and microphysical properties of smoke in the vicinity of active forest fires. Daytime and nighttime measurements were taken at the Shady, Black Diamond, Williams Flats, Nethker and Little Bear fires which spanned four states (Idaho, Montana, Washington and Utah) in the western U.S (Figure 1). Access to these fires varied depending on the availability of roads as well as safety concerns, but in all cases, sampling was performed at the closest allowable locations. MACH-2 is capable of stationary and mobile sampling, with stationary sampling preferred as it limited issues with instrumentation caused by rough road conditions as well as potential interference from sampling anthropogenic roadway emissions. However, the lofted nature of most wildfire smoke plumes during the daytime required sampling while driving to locations where smoke from the Williams Flats and Nethker fires was mixed down to the ground. Most nighttime sampling was conducted while MACH-2 was parked in locations where it was

85 anticipated that smoke would settle into nearby valleys as fire intensity was lower than during
 86 late afternoon peak fire activity.



87
 88 Figure 1. Locations of fires sampled by MACH-2 during FIREX-AQ.

89 This work examines the observed mixing ratios of nitrous acid (HONO), nitric acid
 90 (HNO_3), and particulate nitrate to establish the daytime and nighttime formation pathways and
 91 oxidative products of nitrogen oxides (NO_x). HONO and NO_x are of particular importance
 92 because their reactivity with other atmospheric species result in a net production of ozone (O_3) in
 93 the troposphere (Platt et al., 1980). Tropospheric O_3 is an oxidant and potent greenhouse gas that
 94 negatively impacts environmental and human health (Seinfeld & Pandis, 2016.). Enhanced O_3
 95 results in reduced photosynthesis and growth of vegetation, impairing the resiliency of
 96 ecosystems (Ainsworth et al., 2012). In humans, O_3 can cause muscle constrictions in airways
 97 leading to trapped air in the alveoli. Limited exposure thus makes breathing more difficult and
 98 results in inflammation and potential damage to airways. Prolonged exposure may result in more
 99 serious conditions such as lung disease, chronic obstructive pulmonary disease and aggravation
 100 of asthma (Nuvolone, Petri, & Voller, 2018).

101 Daytime reactions of HONO and HNO_3 are summarized in Figure 2. Hydroxyl radicals (OH)
 102 initially produced from the photolysis of HONO and O_3 (not shown) play a central role in the

photocyclization of HONO and formation of HNO₃. Isotopic results from the 2016 FIREX-FIRELAB study show that at moderate combustion temperatures (~700 °C) the most preferable nitrogen reaction pathway post NO formation from BB is NO to NO₂ to HONO shown in light blue in Figure 2 (Chai et al., 2019). This reaction pathway is initiated via the reaction of NO with O₃ to form NO₂. NO₂ can then participate in a surface catalyzed heterogeneous reaction to form HONO which then is photolyzed back to NO. These surface catalyzed reactions, such as those fostered by quinone species in soil, occur regardless of the presense of solar radiation but are enhanced during solar flux periods (Scharko et al., 2017). While NO_x cyclization occurs, NO also reacts with OH forming HONO which rapidly photolyzes back to NO and OH (George et al., 2015). Peroxy radicals (HO₂ and RO₂) formed from the oxidation of volatile organic compounds form NO₂ from NO without consuming O₃ and thus lead to a net production of O₃ (George et al., 2015). HNO₃ is formed when NO₂ reacts with OH and serves as a major sink for NO_x as it is removed from the atmosphere by wet and dry deposition relatively rapidly (Adon et al., 2013; Ossohou et al., 2019).

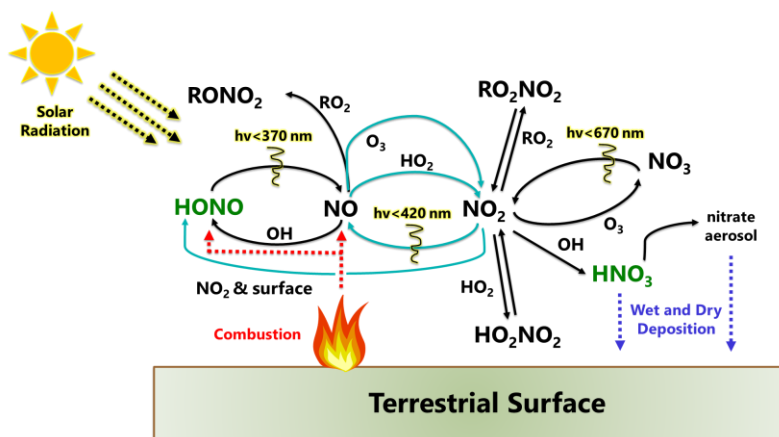


Figure 2. Summary of daytime pathways for reactive nitrogen in smoke plumes. Light blue arrows indicate the preferred pathway for HONO production under moderate combustion temperatures.

Less is known about nighttime reactions involving HONO and HNO₃. At night, plumes settle down into the boundary layer and have major impacts on air quality close to the terrestrial surface. This provides a chance for ground-based mobile lab measurements to collect data inaccessible to airborne platforms due to nighttime flight restrictions and proximity of the plume to the ground. At night the lack of solar radiation ceases photolysis and therefore halts the NO_x cycling between NO and NO₂ (Figure 3). This generally leads to increasing concentrations of HONO until dawn when photolysis starts back up (Stutz et al., 2004). As the nighttime NO_x sink

occurs again via wet and dry deposition, these nitrate aerosols stem from the formation of NO_3 radicals via reaction of NO_2 with O_3 , which can further react with NO_2 forming dinitrogen pentoxide (N_2O_5) (Brown & Stutz, 2012). Water on the surface of aerosol reacts with N_2O_5 to form gaseous HNO_3 as well as nitrate aerosol (Brown & Stutz, 2012).

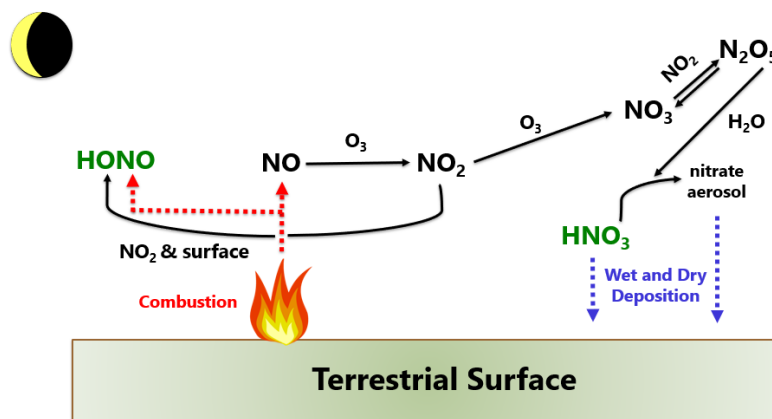


Figure 3. Summary of nocturnal pathways for reactive nitrogen in smoke plumes.

Here we present evidence for the secondary production of HONO in biomass burning plumes and explore the surface-based pathways responsible for that production. Results are reported for the Western U.S. wildfires sampled during FIREX-AQ (Figure 1) and a case study is presented for the most prominent of those fires (William Flats Fire). Observations from this work are crucial to understanding the evolution of wildfire-sourced reactive nitrogen, the implications for air quality in the human breathing zone and highlight the importance of ground-based research platforms.

2. Methodology

2.1 Mobile Aerosol Characterization (MACH-2) Laboratory and Sampling Logistics

The NASA mobile laboratory known as MACH-2 was equipped with a variety of aerosol and gas phase sensors, as well as a dual mist chamber-ion chromatograph (MC/IC) system and denuder collections for measurements of reactive nitrogen species. Further descriptions of the MACH-2 data set are included in section 3.1. MACH-2 was initially deployed to the Boise, Idaho area to sample surface level biomass burning plumes from target fires identified by FIREX-AQ campaign leadership. The majority of collections were conducted at the Williams Flats and Nethker fires, accounting for approximately 54% and 21% of MC/IC sampling, respectively. The Williams Flats fire was by far the largest, growing to a maximum of 44,446

acres (Table 1). Each fire presented distinct conditions resulting from available fuels, fire state (smoldering versus flaming) and sampling access. In this work the Williams Flats fire is used as a case study due to the duration and continuity of sampling. Comparisons between Williams Flats, Nethker and Little Bear fires are also made. Data for these fires are available in the Ecosystems Burned Analysis files in the FIREX-AQ data archive (see data acknowledgment below). The NASA DC-8 research aircraft, as part of FIREX-AQ, also sampled the Williams Flats fire which allowed for data set comparisons between the two platforms during overlap periods.

Table 1. MC/IC Sampling Dates, Fire Names, Approximate Locations and Maximum Burned Acreage.

Sampling Dates	Fire	Approximate Location	Max Burned Acreage
7/26 – 7/28	Shady	Challis, ID	6,286
8/2	Black Diamond	Lincoln, MT	36
8/3 – 8/7	Williams Flats	Fort Spokane, WA	44,446
8/9 – 8/16	Nethker	Burgdorf, ID	2,360
8/20 – 8/21	Little Bear	Bryce Canyon, UT	2,350

2.2 Nitrous and Nitric Acid Sampling Technique

HONO and HNO₃ concentrations were measured, in near real time, using a dual mist chamber-ion chromatograph (MC/IC) system resulting in approximately 1,200 total samples. The MC/IC sampling/analysis technique has been previously described in detail by Talbot et al. (1997). The MC/IC was shock mounted within the NASA mobile laboratory to reduce the potential for malfunctions during transits. The automated custom-built MC/IC is composed of Dionex analytical components and utilizes automated syringe pumps to inject samples and standards (Scheuer et al., 2003). The system is closed minimizing the potential for contamination. Injection volumes were fixed at 5 mL to allow for enough sensitivity to detect the targeted analytes. The use of electronic suppression via a Dionex Anion Self-Regenerating Suppressor minimized the background signal. Trifluoroacetate (TFA) added to the ultrapure sampling water filling the MC served as an internal tracer for sample solution volumes. The TFA concentration increased 10-20% due to evaporation caused by the sample air flow over a 300 second sample period, allowing the final sample solution volume to be amended within $\pm$ 3%. Between the 300 second samples there are 100 second gaps during which samples are injected into the IC and the MC is refilled before the next run. The IC was calibrated on a daily basis utilizing a series of eight known standards of aqueous NO₂⁻ and NO₃⁻. Eluents are

maintained under a pressurized helium environment. These solutions were replenished after two calibration runs. This system was utilized during the initial phase of FIREX-AQ to analyze smoke during controlled laboratory studies at the FIREX-FIRELAB in the fall of 2016 (Chai et al., 2019) and more recently during the 2018 collaborative WE-CAN Campaign (Chai et al., 2020).

The mist chambers collected gas soluble samples. The sample flow was pulled into parallel streams through an externally mounted Fluoropore filter by use of a scroll pump at a controlled nominal rate of 35 L/min. These filters were retained for the aerosol analysis described in section 2.3. Samples from one mist chamber were injected into one channel of the IC for HNO_3 and HONO concentration measurements. Samples from the second mist chamber were transferred via a syringe pump to an amber polyethylene sample bottle to be analyzed by Brown University for isotopic analysis of HNO_3 if >10 nmol of nitrate was collected.

2.3 Filter Sampling and Extractions

A total of 37 Fluoropore filter samples were collected and extracted in the field to determine the relative concentrations of aerosol associated ions (Cl^- , NO_3^- , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}). Collection times per sample ranged from 0.5 – 15 hours depending on factors such as the thickness of the plume, duration of the plume and MC/IC run time. Upon removal, filters were stored in a freezer for preservation until extraction in batches of 16 filters. Due to the hydrophobic nature of the filters, methanol (500 μL) was used to wet the filter allowing for the contents to be dissolved in deionized water (20 mL). The solutions were then transferred to sample bottles and preserved via the addition of chloroform (100 μL). Concentrations of the ionic species were determined using a benchtop IC at the University of New Hampshire.

3. Ancillary Data Sets

3.1 MACH-2

All real time 1 Hz data collected on MACH-2 were averaged and merged to MC/IC run times accounting for the 100 second sample breaks. Gas phase data includes mixing ratios for CO and NO_2 . Aerosol data includes $\text{PM}_{2.5}$ mass loading and aerosol optical scattering coefficients at 450 nm. Furthermore, an AirMar sensor logged GPS coordinates. A full list of utilized merged variables, units and the instruments used for measurements relevant to this analysis are included in Table 2.

Table 2. Variables, associated units and instruments used for measurements on MACH-2.

Variable	Units	Instrument
CO	ppmv	Los Gatos Research iCOS Spectrometer
NO ₂	ppbv	Los Gatos Research NO ₂ Spectrometer
PM _{2.5}	μg/m ³	Teledyne T640 PM Mass Monitor
AerOpt. Scat.	Mm ⁻¹	Air Photon Nephelometer (450 nm)
Lat. and Long.	Deg.	AirMar G2183 GPS Sensor

3.2 Physical Distances

The Fire to Fuels group at NASA Langley provided the position of the maximum fire radiative potential (FRP) for the Williams Flats fire at the midpoint of each MC/IC sample, straight-line physical distances were determined between MACH-2 logged GPS coordinates and these locations of maximum FRP. FRP detections were combined from the Moderate Resolution Imaging Spectroradiometer (MODIS) and Visible Infrared Imaging Radiometer Suite (VIIRS) instruments. MODIS is a key instrument onboard NASA's Terra and Aqua satellites while VIIRS is housed onboard the Suomi National Polar-Orbiting Partnership spacecraft.

3.3 UV-A Irradiance

In situ calibrated UV-A irradiance measured by an Ultraviolet Multifilter Rotating Shadowband Radiometer located in Pullman, WA approximately 65 miles from the Williams Flats fire was used to determine correlations between total UV-A irradiation and HONO/NO₂. Irradiance at 368 nm was used as a proxy for the full UV-A range (315 – 400 nm) which is known to drive heterogeneous reactions of NO₂ resulting in the production of HONO. These UV-A data is publicly available as part of the Colorado State University UV-B Monitoring and Research Program (Colorado State University, 2020)

4. Results and Discussion

4.1 HONO and HNO₃ Variations

Across the campaign HONO mixing ratios ranged from a minimum recorded concentration of 0.03 ppbv to a maximum of 6.6 ppbv with an average value of 0.9 ppbv (Figure 4a). The most continuous and robust sampling was conducted at the Williams Flats fire (Figure 4b). HONO and HNO₃ exhibited corresponding diurnal variability (Figure 4b). Average mixing ratios were enhanced during the daytime compared to nocturnal levels at all fires where diurnal sampling was conducted. Both species display greater mixing ratio variability in the daytime as a result of

photolytic processes and the turbidity of the convective mixed layer. The lack of photolysis and convection produced much smaller and more constant mixing ratios at night. Daytime HONO mixing ratios were generally an order of magnitude greater than those measured for HNO_3 . This matches the pathways presented in Figure 2, as HONO is directly emitted and has two expected formation pathways, while BB emissions of HNO_3 are minimal and its single production pathway in the atmosphere from NO_2 is outcompeted by HONO formation as the plume ages. Furthermore, HNO_3 undergoes wet and dry deposition and contributes to the formation of nitrate aerosol (p-NO_3^-). Analysis of filter collected NO_3^- indicates that HNO_3 partitioning favored p-NO_3^- over the gas phase HNO_3 60% of the time (Figure S1). The photolysis of p-NO_3^- presents another potential pathway for secondary HONO production (Ye et al., 2017). However, isotopic modeling conducted by collaborators at Brown University indicates that this pathway is a minor contributor to the overall HONO budget (Chai et al., 2020), thus we focus on other mechanisms to explain the observations.

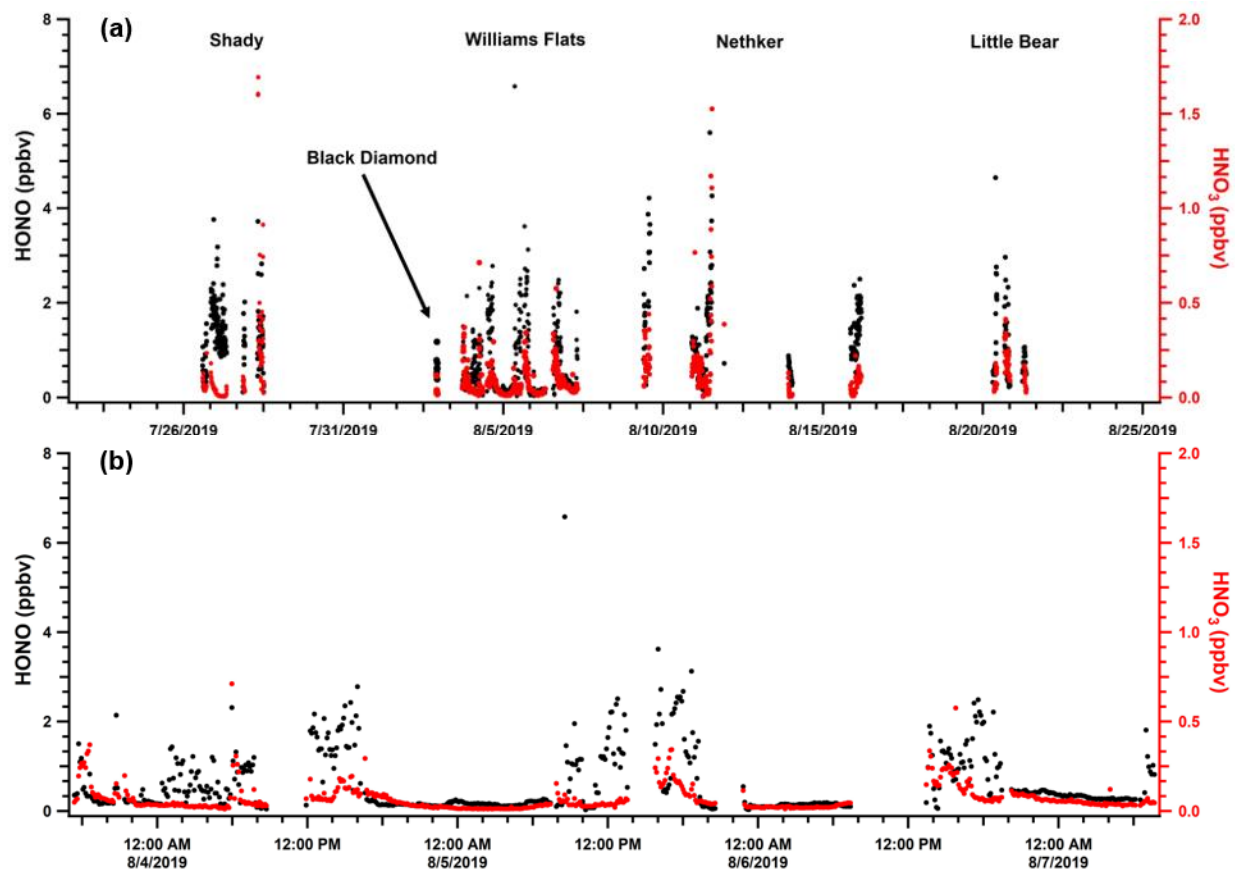


Figure 4. Timeseries of HONO and HNO_3 across the five fires sampled by the MACH-2 mobile laboratory platform during the 2019 FIREX-AQ campaign (a) and expanded plot for the Williams Flats fire (b).

4.2 Young vs. Aged Smoke

A major FIREX-AQ goal was to quantify compositional differences between young and aged smoke plumes. In these classifications, young plumes are more freshly emitted and aged plumes correspond to a greater extent of chemical processing. A recently published paper by Selimovic et al. (2020) suggests use of enhancement ratios between PM_{2.5} and CO as a valid method to bin wildfire plume age. Applying that approach here, scatter plots of PM_{2.5} versus CO exhibit two distinct highly linear populations for the Williams Flats, Nethker and Little Bear fires (Figure 5). These differing fire conditions resulted in distinct ratios used to separate the populations. Of the two, the population with the steeper slope (i.e., more PM_{2.5} (y-axis) loading per CO (x-axis) levels) corresponds to young smoke while the other population is representative of aged smoke (Figure 5a-c). The Shady fire proved to be a useful example for comparing background to smoke impacts (Figure 5d). The plume from the Shady fire was very well defined and thus allowed for a clean assessment of background levels which exhibit no correlation ($R^2 = 0.004$) between PM_{2.5} and CO. Once the plume front moved into the valley where we were sampling, PM_{2.5} was elevated and is tightly correlated with CO ($R^2 = 0.90$). This divergence in correlations highlights that virtually all samples taken at the Williams Flats, Nethker and Little Bear fires were smoke impacted. In each case $\Delta\text{PM}_{2.5}$ (enhancement from background PM_{2.5}) to ΔCO (enhancement from background CO) ratios prove to be powerful metrics allowing the categorization and thus quantification of differences present between younger and more processed plumes.

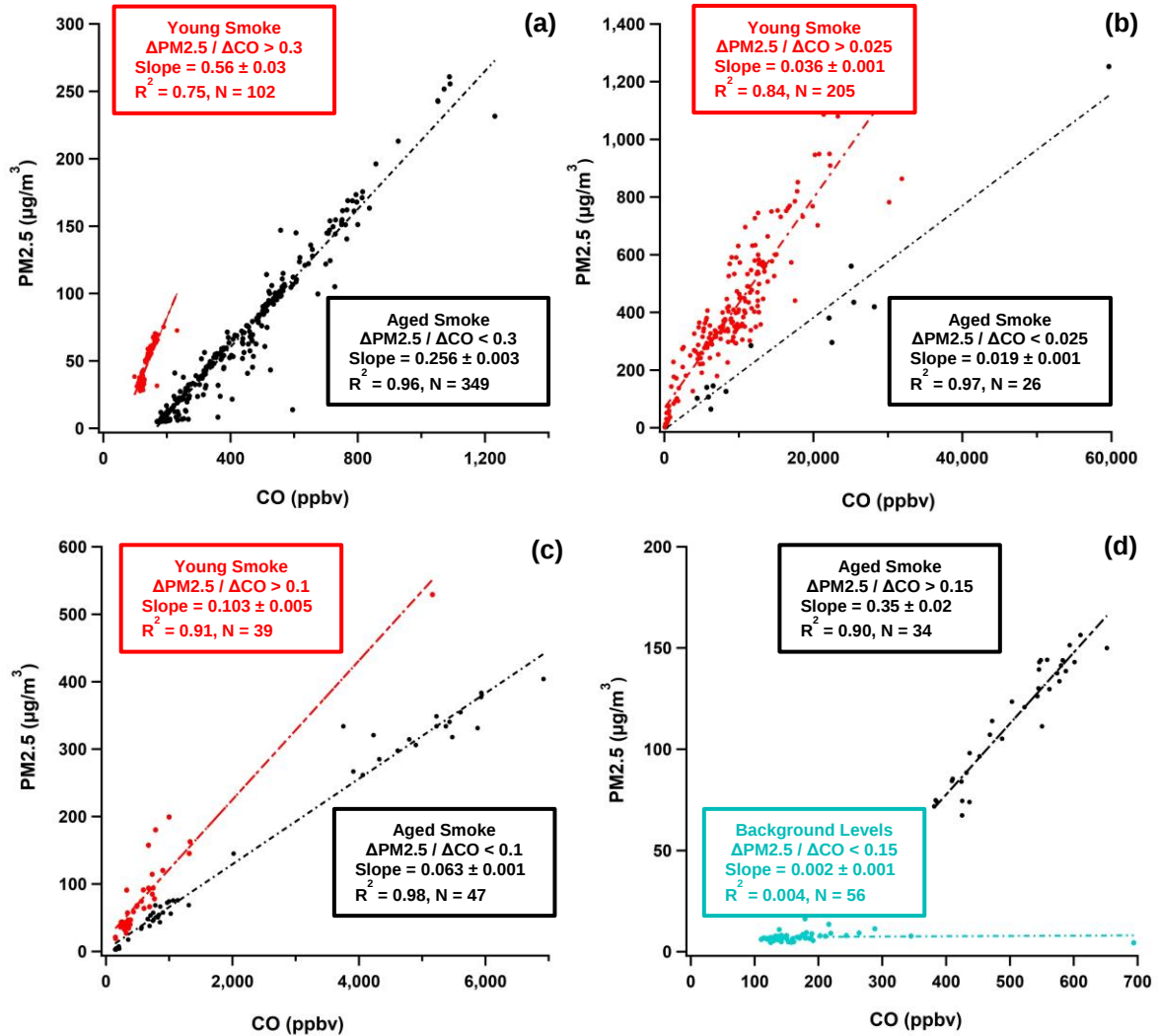


Figure 5. Young vs.aged $\Delta PM_{2.5} / \Delta CO$ binning for Williams Flats (a), Nethker (b), Little Bear (c) and Shady (d) fires. Williams Flats, Nethker and Little Bear all exhibit two strongly correlated populations (with the red dashed line indicative of “young” smoke and the black dashed line indicative of “aged” smoke). The Shady fire is included as an example of background levels.

To validate the $\Delta PM_{2.5}$ to ΔCO ratio as an indicator of processing, all values of the ratio measured in the Williams Flats smoke plume are plotted as a function of the physical distance between MACH-2 and the maximum FRP measured by MODIS and VIIRS (Figure S2). The red dashed line indicates the $\Delta PM_{2.5}$ to ΔCO ratio of 0.3 used to distinguish young from aged smoke for the Williams Flats data herein. All ratios categorized as being young were measured at a straight-line distance of 8 km while those categorized as aged exceeded 10 km spanning out towards 70 km at maximum. Note, the categorization between young and aged smoke is relative, hence the ratio applied for this distinction varies from one fire data set to the next (Figure 5).

4.3 Implications of Secondary HONO Production

It is well established that the diurnal cycle impacts BB-sourced HONO concentrations. Surprisingly our results indicate that for Williams Flats and Nethker young daytime smoke contained significantly higher concentrations of HONO than young nighttime smoke (Figure 6a-b). Higher nighttime concentrations were expected due to a lack of nocturnal HONO loss pathways and the stability of the shallow nocturnal boundary layer. At Nethker, enhanced HONO in young daytime smoke can be attributed to differences in fire state between day and night. More flaming during the day results in proportionally greater primary HONO production. This primary production was accessible to MACH-2 at the Nethker fire, as sampling occurred where vegetation was actively flaming within 15 m of the mobile lab. Day/night differences for the Williams Flats smoke were less obvious. In the presence of solar irradiation, primary HONO has a lifetime ranging between 10 – 20 minutes (Spataro & Ianniello, 2014). At a straight-line distance of 8 km the average windspeed would need to exceed 24 km/hr for primary HONO to be measurable by MACH-2. Real-time weather data for the region indicates a maximum recorded windspeed of 24 km/hr during the sampling period. Therefore, it is unlikely that enhanced daytime primary HONO emission caused the difference at the Williams Flats fire. CO observations suggest that plume thickness was the dominant factor causing the statistical difference in HONO loading, as much higher CO was measured during the daytime (daytime average = 368 ppbv, nighttime average = 285 ppbv).

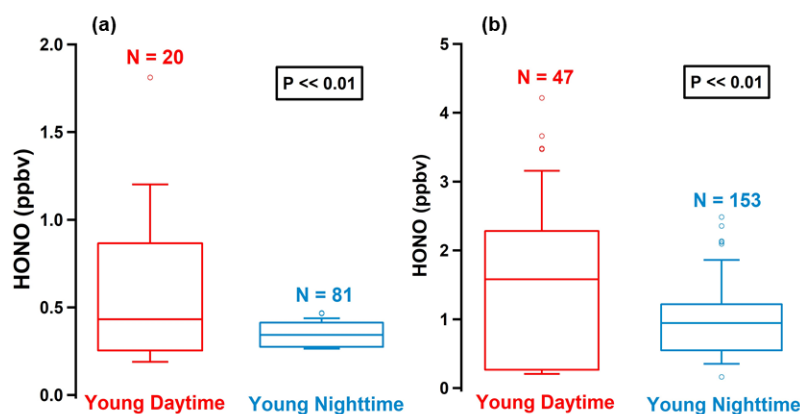


Figure 6. The impact of diurnal cycle on average HONO concentrations in young smoke plumes for the Williams Flats (a) and Nethker (b) fires. Statistical P values are based off a 95% confidence interval and N values represent population sizes.

The lack of statistical differences between average HONO mixing ratios in young and aged smoke from a given fire is a strong indicator of substantial secondary HONO production under daytime and nocturnal conditions as shown by examples from the Williams Flats and Little Bear fires, given the short lifetime of HONO during both day (10-20 min) and night (1-2 hr) (Figure 7a-c). This ground-based observation contrasts with previous findings from airborne platforms.

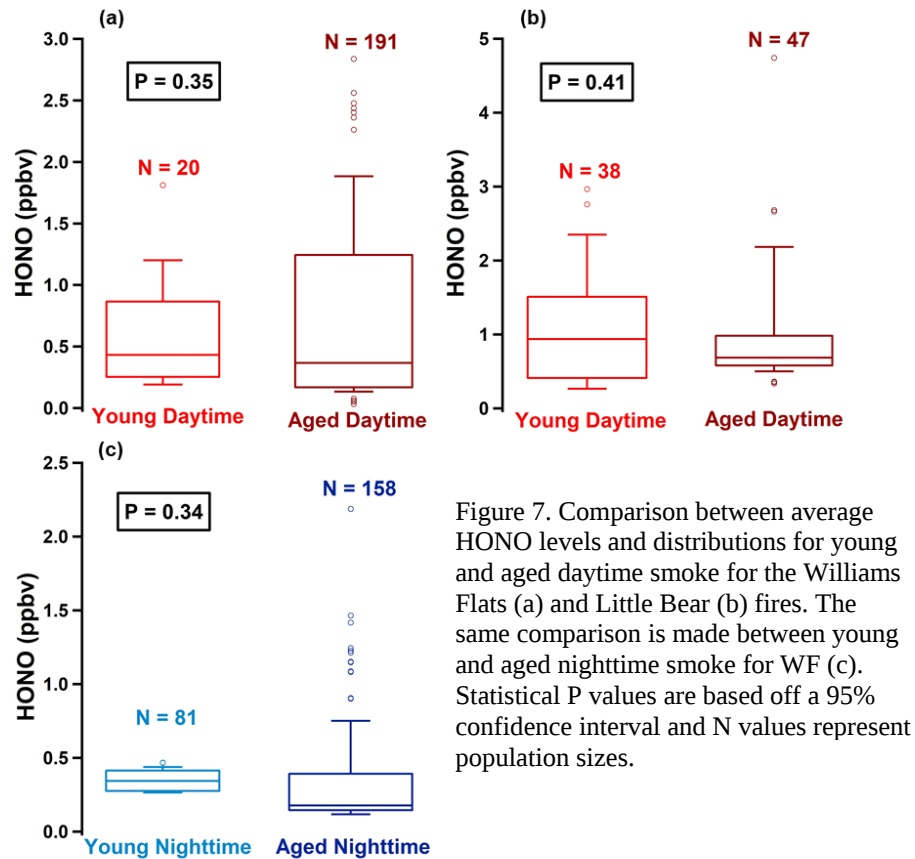


Figure 7. Comparison between average HONO levels and distributions for young and aged daytime smoke for the Williams Flats (a) and Little Bear (b) fires. The same comparison is made between young and aged nighttime smoke for WF (c). Statistical P values are based off a 95% confidence interval and N values represent population sizes.

No substantial evidence was found for secondary HONO production in BB plumes sampled from the NOAA P3 aircraft during the Southeast Nexus Experiment (Neuman et al., 2016). Interestingly, results from NASA's DC-8, which took measurements of the Williams Flats fire at higher altitudes, also provide no clear evidence for substantial secondary production of HONO. However, there are several factors which could contribute to the differences in the budget and cycling of HONO between the ground-based MACH-2 mobile laboratory and the DC-8.

The atmospheric environment could be a substantial factor. In near-source plumes, which the DC-8 had better access to, the conditions are NO_x limited due to a large quantity of VOCs and SVOCs that store reactive nitrogen as temporary sinks. The secondary production of HONO is very limited in these NO_x deficient environments and could explain why DC-8 results do not

indicate secondary HONO production. Stark differences in measured NO₂ mixing ratios support this hypothesis (Figure S3). Furthermore, heterogenous conversion on ground surfaces (soil, foliage and dust) are also suggested as dominant pathways for the secondary production of HONO (see section 4.4 below). These ground-based conversions would enhance HONO levels in the boundary layer airmasses sampled by MACH-2. Overall, the divergent results indicate the importance of ground-based studies and present an argument for mobile laboratories to collaborate with aircraft during future campaigns.

4.4 Influence of UV-A Solar Irradiation and Aerosol Surface Area on Heterogenous NO₂ to HONO Conversions

Heterogenous conversion of NO₂ to HONO has been represented in the literature by use of HONO/NO₂ ratios (Li et al., 2012; Nie et al., 2015). The diurnal variation of these ratios exhibit alignment with daily changes in UV-A solar flux across five days for the Williams Flats fire. HONO/NO₂ declines in magnitude along the falling edge of UV-A on August 3rd and can be seen increasing along the rising edge on the morning of August 7th with maxima aligning with peak solar flux on August 5th (Figure 8a). This dependency was further probed by averaging ratios for approximately 30-minute intervals across each day. The maximum 30-minute HONO/NO₂ average each day, which occurred at different times due to the MC/IC duty cycle, show a clear dependency ($R^2 = 0.91$) on corresponding averaged UV-A flux (Figure 8b). This relationship indicates that heterogenous conversions of NO₂ to HONO more than compensate for rapid photolytic losses of HONO even when UV-A flux is at its highest intensity. A similar observation was made in an urban setting by Wong et al. (2012) during the 2009 Study of Houston Atmospheric Radical Precursor (SHARP) experiment. The resulting net HONO production supports the lack of statistical differences in mean HONO mixing ratios between young and aged daytime smoke for the William's Flats and Little Bear fires (Figure 7a-b).

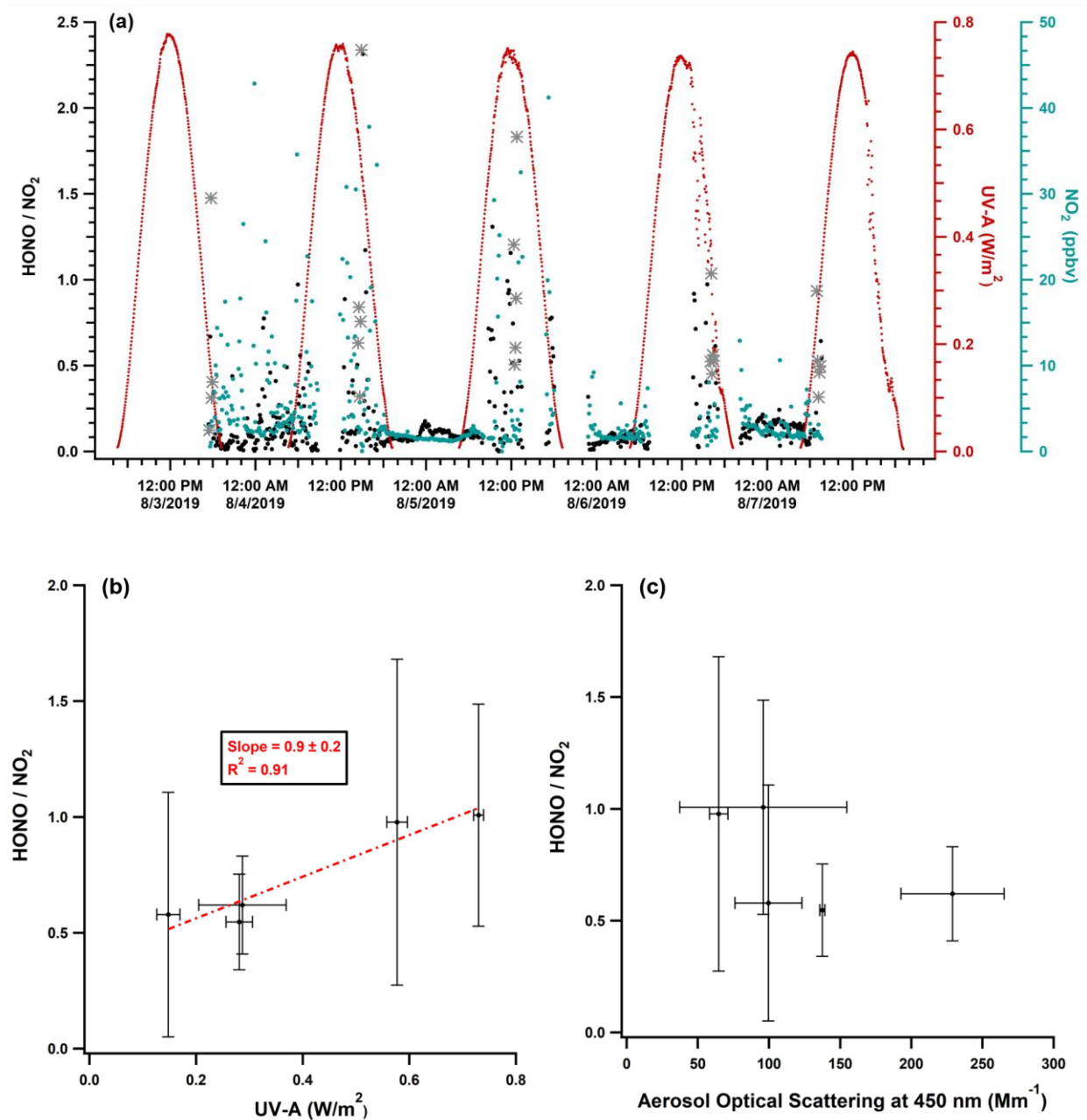


Figure 8. Time series HONO to NO₂ ratios (left), UV-A irradiation and NO₂ mixing ratios (right) (a), as well as the dependence of those HONO to NO₂ ratios on UV-A irradiation across five daytime collection periods at the Williams Flats fire (b). The same NO₂ to HONO conversion efficiencies are also included as a function of aerosol optical scattering at 450 nm (c). The gray stars in panel (a) indicate the HONO/NO₂ data points utilized for the averaging based analysis in panels (b) and (c). Error bars represent the standard deviations (1 σ) over the averaged intervals.

A comprehensive review of HONO sources notes that aerosols can significantly contribute to the secondary production of HONO if the aerosol loading is substantial, however ground sources were found to overshadow aerosol impacts in urban and forest studies (Spataro & Ianniello, 2014). These conversions include those from redox chemistry facilitated by quinone species present in humic acid (Han et al., 2016; Scharko et al., 2017), surface reactions promoted by mineral dust (Ma et al., 2013; Ndour et al., 2008; Chai et al., 2020), as well as the photolysis of adsorbed nitric acid on the surface of foliage (Zhou et al., 2011). Anthropogenic surfaces could also be a contributor, but those surface site reactions have not been well constrained. In contrast to urban and forest environments the aerosol loading and corresponding surface area in biomass burning plumes is considerably higher. Thus, the contribution of aerosol to secondary HONO production was explored using the same averaging method as was done for Figure 8b. No clear relationship is present between HONO/NO₂ and aerosol optical scattering at 450 nm, which is used here as a proxy for mass loading (Figure 8c). In fact, the highest HONO/NO₂ ratios correspond with the lowest two scattering averages. This indicates that the terrestrial surface provides the vast majority of available sites facilitating the daytime heterogeneous HONO production. Under higher aerosol loading conditions there may be a dampening effect where aerosol optical extinction limits the UV-A flux reaching the terrestrial surface, potentially inhibiting the extent to which heterogeneous reactions occur there. It is possible that aerosol surface sites also contribute to secondary HONO production although our data did not provide evidence for this. More work is required to further assess the quantitative impact of aerosol loading on ground-based secondary HONO formation.

5. Conclusions

Over the course of FIREX-AQ, MC/IC samples collected on board NASA's MACH-2 provided near-real time concentrations of HONO and HNO₃ for five distinct fires in the Western U.S. This variety of fires offered a chance for high-level comparisons between the aforementioned species. Relative plume age was determined by use of enhancement ratios between PM_{2.5} and CO. Average HONO concentrations were significantly higher in young daytime than young nighttime smoke while no statistical differences were observed upon comparing young and aged smoke. The lack of statistical differences between young and aged smoke under both daytime and nocturnal conditions is evidence that substantial secondary HONO production is associated with ground-level smoke plumes.

The Williams Flats fire presented a unique opportunity for a case study given the fire's size, the extent of sampling and overlap with the DC-8 platform. Across five days, heterogeneous conversions of NO₂ to HONO are strongly correlated with UV-A flux indicating that these conversions, likely occurring on the ground, more than compensate for rapid photolytic losses of HONO.

Overall, this work presents strong evidence for secondary production of HONO occurring through heterogeneous NO₂ surface site reactions. However, more studies utilizing ground-based platforms are needed to verify whether the results from the Williams Flats fire case study are universal to all wildfires. Furthermore, future collaborations between mobile laboratories such as MACH-2 and aircraft will be essential for a comprehensive understanding of reactive nitrogen evolution in smoke plumes and their implications for air quality.

6. Data Availability Statement

All data used for this analysis, except for UV-A solar irradiation, is publicly available at the NASA Airborne Science Data for Atmospheric Composition database ([doi:10.5067/SUBORBITAL/FIREXQAQ2019/DATA001](https://doi.org/10.5067/SUBORBITAL/FIREXQAQ2019/DATA001)). The UV-A data is publicly available at the Colorado State UV-B Monitoring and Research Program.

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**Influence of Solar Irradiation on Nitrous Acid Production in
Western U.S. Wildfire Smoke**

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Figures S1 to S3

Introduction

Figure S1 highlights the nitrate partitioning between the gas and particle phase for the Williams Flats, Nethker and Little Bear fires. Figure S2 provides verification for chemical ageing classifications for the Williams Flats fire. Figure S3 serves as a comparison between measured distributions in NO₂ mixing ratios for the MACH-2 and DC-8 platforms. These data are from a sampling overlap period that occurred on August 6th, 2019 at the Williams Flats fire. Differences in reported N values are a result of a slight shift in the overlap period by four minutes. Special thanks to Carrie Womack for collecting the DC-8 data sets used in this analysis.

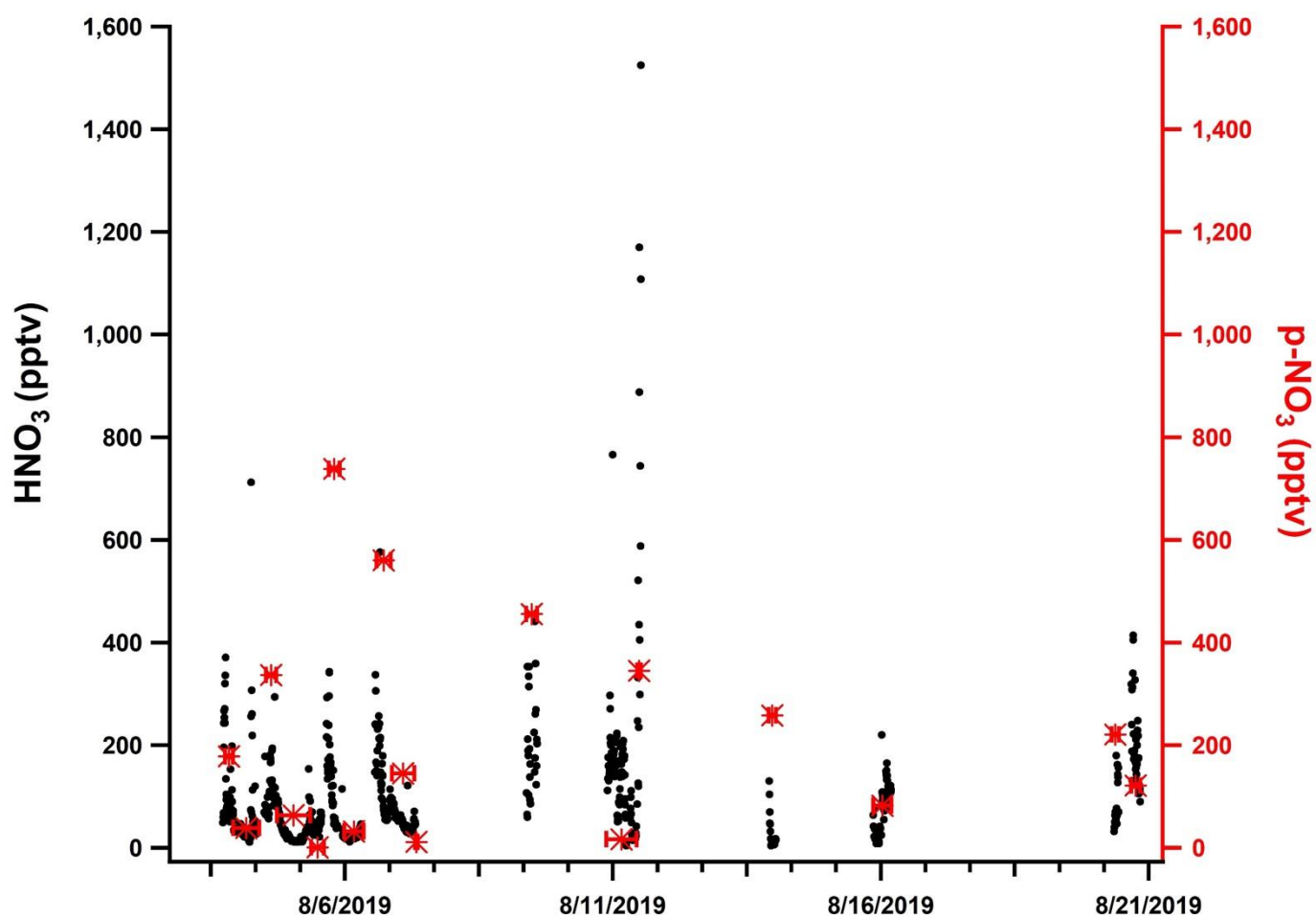


Figure S1. Gas and particle phase (p-NO_3) partitioning for HNO_3 for the Williams Flats, Nethker and Little Bear fires. HNO_3 favored p-NO_3 approximately 60% of the time over the course of these fires. For p-NO_3 stars indicate local midpoint-times while horizontal bars indicate the start and stop times for each filter.

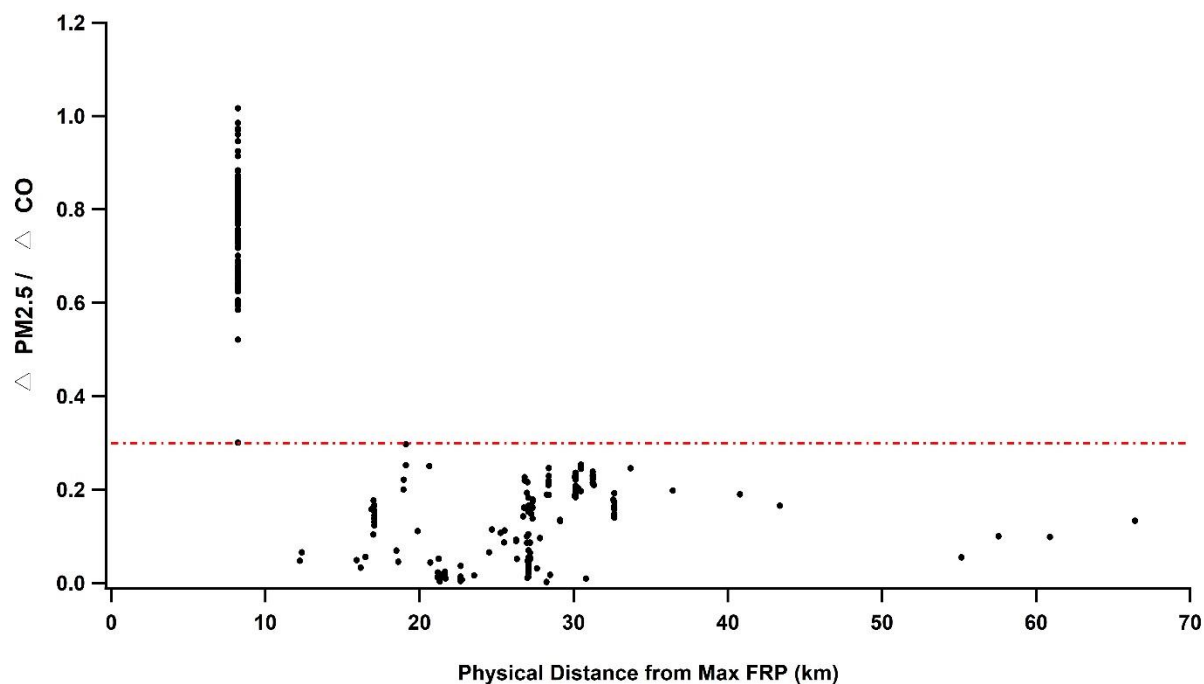


Figure S2. Physical distance verification of young vs. aged $\Delta\text{PM}_{2.5} / \Delta\text{CO}$ binning for the Williams Flats fire. The red dashed line indicates the $\Delta\text{PM}_{2.5}$ to ΔCO ratio of 0.3 used to distinguish young from aged smoke. The red dashed line indicates the $\Delta\text{PM}_{2.5}$ to ΔCO ratio of 0.3 used to distinguish young from aged smoke for the Williams Flats data.

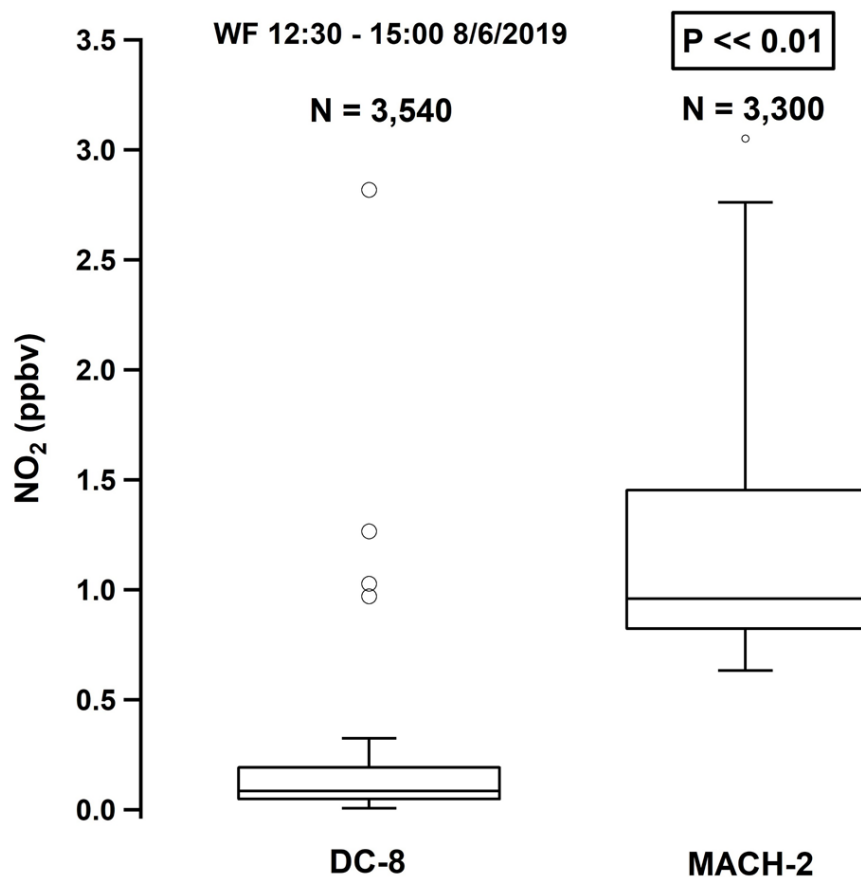


Figure S3. Comparisons between NO_2 average mixing ratios and distributions. Statistical P values were determined using a 95% confidence interval and N values represent population sizes. The average NO_2 mixing ratio measured by MACH-2 is approximately 6.5x that which was measured by the DC-8 during the August 6th overlap of the Williams Flats fire.