

Nitrous Acid Formation in Wildfire Plumes: Implications for Atmospheric Oxidation and Ozone Pollution

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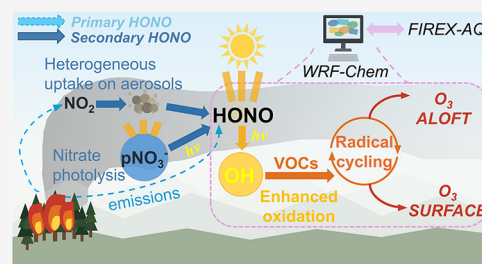
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ABSTRACT: Nitrous acid (HONO) is a vital precursor for hydroxyl (OH) radicals in wildfire plumes, yet chemical transport models often underrepresent observed in-plume HONO levels. We implemented wildfire HONO emissions and literature-based secondary formation pathways in the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) and evaluated simulations against airborne measurements from the Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ) campaign during 2019 summer wildfires in the northwestern United States. The revised model substantially improves in-plume HONO representation. Source attribution revealed that emissions contributed up to 40% of HONO in near-source smoke, while heterogeneous NO_2 uptake on aerosol surfaces acted as the dominant pathway (47%–74%) due to the dense reactive surface area of smoke aerosols. HONO photolysis accounted for approximately 80% of the primary OH production in the near-field smoke, identifying HONO as the leading primary radical-initiation pathway during this stage of plume evolution. HONO-initiated radical production further accelerated radical cycling, yielding a net increase in O_3 concentrations both near the surface and at the plume transport altitude. Our findings underscore the pivotal role of HONO in driving smoke-plume chemical evolution and highlight its importance for assessing regional air pollution and tropospheric O_3 burdens.

KEYWORDS: nitrous acid, wildfire events, hydroxyl radicals, ozone, WRF-Chem simulations



1. INTRODUCTION

In recent years, increasingly frequent and severe wildfires have intensified smoke-related risks to air quality, climate, and human health.^{1–5} By injecting substantial amounts of gases and aerosols into the atmosphere, wildfires profoundly alter atmospheric composition and the radiative balance.^{6–8} Wildfire emissions are dominated by carbon dioxide (CO_2), which accounts for approximately 90% of the total emitted mass.^{9,10} Concurrently, the incomplete combustion of carbon- and nitrogen-containing biomass releases large quantities of chemically reactive species, including total reactive oxidized nitrogen (NO_y) and volatile organic compounds (VOCs).^{11–13} Although these reactive species have much lower emission factors than CO_2 , they exhibit high chemical reactivity.

In addition to directly emitting primary air pollutants, wildfires drive complex secondary chemistry within their plumes. Smoke chemistry is governed by interactions among oxidants and reactive species, with NO_y playing a pivotal role. Among fire-emitted NO_y , nitrogen oxides (NO_x , including NO and NO_2) constitute a major fraction and serve as important catalysts in atmospheric oxidation reactions.^{14–16} By modulating radical cycling in the presence of VOCs,^{17,18} NO_x can accelerate the photochemical formation of secondary pollutants, including ozone (O_3) and secondary organic aerosol (SOA).^{19–21} This chemical process exacerbates air pollution

and increases exposure risks in downwind regions.²² Wildfire plumes also provide a favorable environment for multiphase reactions because high concentrations of reactive gases coexist with dense smoke aerosols.^{23,24} This feature distinguishes wildfire plumes from typical urban or remote environments.²⁵ Their large aerosol surface area offers a distinct medium for heterogeneous reactions and alters the lifetimes of reactive species.^{26–28}

Nitrous acid (HONO) is another key NO_y species emitted from biomass burning, although its direct emission rate is lower than that of NO_x .⁹ HONO can also be rapidly produced through secondary reactions involving NO_x .²⁹ First, NO reacts with hydroxyl (OH) radicals to form HONO through homogeneous oxidation. More importantly, the heterogeneous uptake of NO_2 on aerosol surfaces is favored in smoke plumes, where elevated NO_2 concentrations and large reactive surface areas promote HONO production.^{26,29} Furthermore, NO_2 is oxidized by OH to form HNO_3 , which can partition into the

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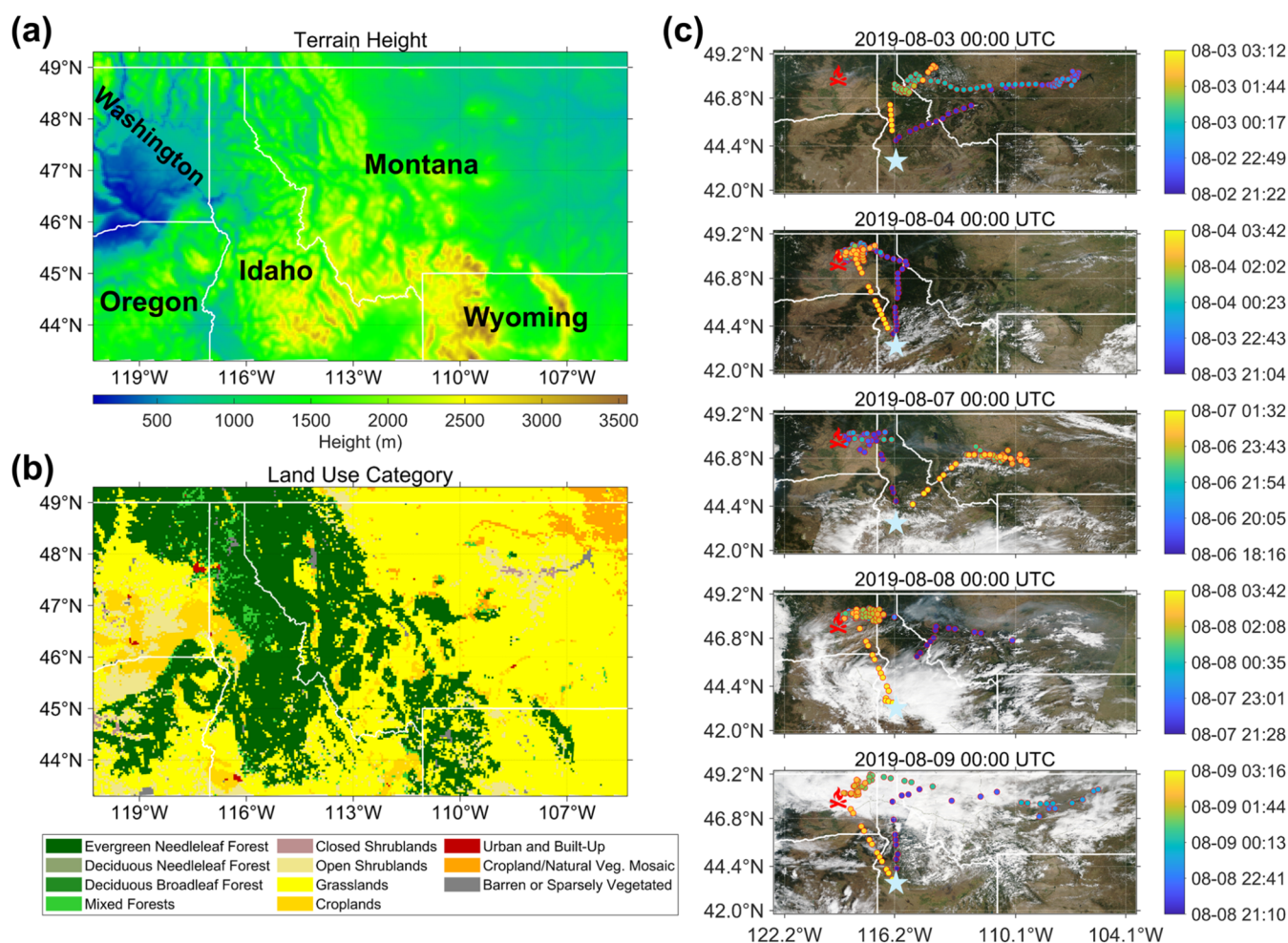


Figure 1. Overview of the study region, land-use characteristics, and airborne measurements. (a–b) Spatial distributions of terrain height and land-use categories across the study region. (c) MODIS true-color corrected-reflectance imagery for selected sampling days. The colored dots represent the flight tracks, with color indicating the time of day (UTC). The red fire icon marks the location of the Williams Flats Fire, and the blue star indicates Boise.

particle phase as nitrate and subsequently provide an additional HONO source through photolysis.^{30–32} Under sunlight, HONO typically has a lifetime of ~ 20 min and photolyzes to yield OH radicals.^{33,34} Aerosol attenuation within wildfire plumes can reduce its photolysis frequency and extend its lifetime.³⁵ HONO photolysis can contribute approximately 20%–80% of primary OH production,^{36–38} making it particularly important in fresh wildfire plumes, where elevated HONO can enhance OH concentrations and atmospheric oxidizing capacity (AOC), thereby accelerating secondary pollutant formation.^{18,39}

Recent field measurements and satellite retrievals have detected elevated HONO concentrations in wildfire plumes.^{40–43} For instance, Bourgeois et al. reported HONO mixing ratios of up to 20 ppbv in wildfire smoke over the northwestern United States,⁴⁰ approximately 1–2 orders of magnitude higher than typical observations in urban areas.^{44–46} The HONO budget in wildfire plumes is complex, involving both direct emissions and poorly constrained secondary formation, especially on dense smoke aerosol surfaces.^{26,39} Despite the recognized environmental importance of HONO, chemical transport model (CTM) evaluations have shown substantial underestimation of HONO in smoke plumes.⁴⁷ Previous efforts to improve HONO

chemistry in CTMs have largely focused on urban and regional air pollution, where direct emissions and heterogeneous or multiphase HONO formation pathways have been incorporated and evaluated.^{48–50} However, these advances have not fully addressed the wildfire-specific combination of direct emissions and complex plume chemistry. Several wildfire studies have used aircraft observations and box-model analyses to characterize HONO sources and chemical evolution along sampled plume trajectories.^{29,39,51} The regional three-dimensional evolution of wildfire HONO source contributions across altitude and downwind transport, together with their links to primary radical initiation and O₃ formation, remains insufficiently quantified.

To address these gaps, this study integrates measurements from the Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ) campaign with the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem). The model represents direct wildfire HONO emissions and literature-based secondary formation pathways, while FIREX-AQ observations are used to evaluate the simulated plume structure, reactive-nitrogen partitioning, and HONO abundance. Overall, we quantify how the contributions of individual HONO sources vary across altitude and

downwind transport and assess their implications for primary OH production and the modeled O₃ response.

2. MATERIALS AND METHODS

2.1. Measurements of Wildfire Smoke Pollution

The FIREX-AQ campaign was conducted from July to September of 2019 under the joint leadership of the National Aeronautics and Space Administration (NASA) and the National Oceanic and Atmospheric Administration (NOAA).⁵² In this study, we utilized data collected aboard the NASA DC-8 aircraft, a flying laboratory equipped with a comprehensive suite of instruments for gas and aerosol measurements.⁵³ HONO mixing ratios were quantified using an iodide-adduct chemical ionization mass spectrometer (I-CIMS). NO and O₃ were measured using chemiluminescence. NO₂ was converted to NO by a UV-LED photolytic converter operating at 385 nm before chemiluminescence detection.⁴⁰ The NO₂ data were further corrected for interference from HONO photolysis at 385 nm, quantified as 5% of the HONO mixing ratio. Aerosol chemical composition and mass concentrations were determined using an Aerosol Mass Spectrometer (AMS). Navigational and meteorological parameters, including latitude, longitude, altitude, temperature, pressure, water vapor mixing ratio, and wind speed, were recorded simultaneously aboard the DC-8.

To align the observations with the model results, we used the 1 min averaged merged dataset obtained from the NASA public archive. As shown in Figure 1, the analysis focused on five flights conducted over the northwestern United States on 3–4 and 7–9 August 2019 (UTC). During this period, the DC-8 was based in Boise, Idaho, and primarily sampled smoke plumes from the Williams Flats Fire (118.62° W, 47.94° N) in eastern Washington State. The fire was ignited by lightning on 2 August 2019 near the Colville Indian Reservation. The burned biomass fuels included short grass, timber, and tall brush, and the total burned area was approximately 18,000 ha. The Williams Flats Fire was the largest wildfire sampled during FIREX-AQ and has been extensively investigated as a representative case in previous studies.^{14,54,55} Supplementing the airborne measurements, we collected ground-level PM_{2.5} and O₃ observations from the U.S. Environmental Protection Agency (EPA) monitoring network. We also utilized aerosol optical depth (AOD) at 1 km resolution retrieved using the Multi-Angle Implementation of Atmospheric Correction (MAIAC) algorithm from the combined Level-2 MODIS products from the Terra and Aqua satellites. Following the methodology of Ye et al.,⁵⁴ we processed the original MAIAC data to derive the spatial distribution of smoke AOD associated with the Williams Flats Fire.

2.2. Configurations of WRF-Chem Modeling

The regional WRF-Chem model (version 4.1.5) was employed to simulate the chemical evolution of the wildfire plumes. The modeling domain had a horizontal resolution of 4 × 4 km², encompassing Washington, Oregon, Montana, Idaho, and Wyoming (Figure 1). The vertical grid consisted of 71 layers extending from the surface to 50 hPa. Meteorological initial and boundary conditions were derived from the National Centers for Environmental Prediction (NCEP) 1° Final Operational Global Analysis data available at 6-hour intervals. Four-dimensional data assimilation (FDDA) was applied to nudge the simulated meteorological fields towards observations. The simulation period extended from 1 to 10 August 2019 and covered all selected FIREX-AQ flights. The major physical parameterizations are summarized in Table S1. Gas-phase chemistry was represented using the Statewide Air Pollution Research Center (SAPRC99) mechanism, coupled with the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) for aerosol thermodynamics and chemistry.^{56,57} Photolysis frequencies were calculated using the FAST-J scheme.⁵⁸ Chemical initial and boundary conditions were obtained from global simulations of the Community Earth System Model (CESM, version 2.1).⁵⁹

Anthropogenic emissions were derived from the Emissions Database for Global Atmospheric Research (EDGAR, version

8.1).⁶⁰ Biogenic emissions were calculated online using the Model of Emissions of Gases and Aerosols from Nature (MEGAN, version 2.0).⁶¹ Biomass-burning emissions were obtained from the Fire Inventory from NCAR (FINN, version 2.5).⁹ As shown in Figure S1, biomass-burning emissions were distributed among scattered fire locations, with the Williams Flats Fire exhibiting the highest pyrogenic emission intensity. Total emissions of organic carbon (OC) and black carbon (BC) from wildfires were 47 and 5 times those from anthropogenic sources, respectively, highlighting the dominance of wildfire emissions during the study period. The ungridded FINNv2.5 fire-level emission records were processed using the NCAR fire_emis utility. Each fire record was assigned according to its geographic coordinates, and the emissions were aggregated directly onto the 4 km model grid. Wildfire emissions were vertically allocated online using the plume-rise algorithm developed by Freitas et al.⁶²

2.3. Implementation of Multiple HONO Sources in the Model

We expanded the model representation of HONO by incorporating primary emissions and additional secondary formation pathways. Anthropogenic HONO emissions were parameterized using a fixed HONO/NO_x ratio of 0.8% to represent traffic-related direct emissions.⁶³ This parameterization does not include other potential anthropogenic or terrestrial HONO sources, such as coal combustion, soils, and livestock activities.^{46,64–67} Accordingly, the anthropogenic HONO source represented here should be regarded as a traffic-related background source rather than a complete representation of all non-fire HONO emissions. Although the omission of these sources may affect background HONO levels and the absolute HONO budget, it is less likely to influence the attribution of HONO sources in wildfire-affected regions, which is the primary focus of this study. Wildfire HONO emissions were represented through the FINNv2.5 MOZART-T1 species-mapping framework rather than a standalone HONO entry in the principal emission-factor table.⁹ HONO emission factors (EF_{HONO}) were calculated from vegetation-dependent total non-methane organic gas (NMOG) emission factors using the corresponding species-mapping coefficients. The resulting effective EF_{HONO} values ranged from 0.395 to 2.442 g kg⁻¹ dry biomass across the FINNv2.5 vegetation classes. As shown in Figure S1, total HONO emissions from biomass burning within the modeling domain were approximately 10 times those from anthropogenic activities, indicating the dominant contribution of wildfire emissions.

Three additional secondary HONO formation pathways were implemented (Table S2). The first pathway was heterogeneous uptake of NO₂ on ground and aerosol surfaces. The heterogeneous reaction rates are governed primarily by two parameters, the reactive uptake coefficient (γ) and the available surface area density (S/V). For ground surfaces, a baseline γ of 4 × 10⁻⁶ was used at night.⁴⁹ To represent photo-enhanced uptake, this value was linearly scaled with solar radiation to a maximum of 6 × 10⁻⁵ at noon.^{68,69} For NO₂ uptake on aerosol surfaces, we adopted a reference γ of 4.9 × 10⁻⁴ presented by Peng et al. on the basis of airborne measurements of wildfire smoke during the Western Wildfire Experiment for Cloud chemistry, Aerosol absorption and Nitrogen (WE-CAN) campaign.²⁶ A diurnal maximum γ of 1.0 × 10⁻³ was prescribed to represent photo-enhanced aerosol uptake, following previous studies.^{49,69} The aerosol surface area density (S_a/V) was computed online within the MOSAIC aerosol module.⁵⁷ The ground surface area density (S_g/V) was determined from the underlying land-use category. Over vegetated regions, S_g/V was parameterized as twice the leaf area index divided by the height of the first model layer. Over urban regions, S_g/V was assumed to range from 0.1 to 0.3 m² m⁻³.⁴⁸ This parameter was calculated as a linear function of the urban-area fraction, such that more highly urbanized grid cells were assigned larger reactive surface areas.^{68,70} The second additional pathway was the photolysis of particulate nitrate (pNO₃⁻).³¹ The photolysis frequency of pNO₃⁻ (J_{NO₃⁻}) was set to 63 times that of gas-phase nitric acid (J_{HNO₃}), based on WE-CAN airborne measurements.²⁶ The third pathway represented potential HONO production through

gaseous photo- and dark-oxidation reactions of NO_x following the laboratory kinetics reported by Song et al.⁷¹

All HONO parameterizations were adopted from previous field, laboratory, or modeling studies. No reaction parameter was derived, fitted, or optimized using FIREX-AQ measurements. Instead, the FIREX-AQ measurements served as observational benchmarks for evaluating the combined model representation of emissions, transport, photolysis, and chemical production and loss within smoke plumes.

2.4. Sensitivity Experiment Design for HONO Source Apportionment

The baseline simulation (BASE) included all HONO sources described in Section 2.3. Nine additional sensitivity experiments, collectively referred to as CTRL simulations, were conducted to quantify HONO formation mechanisms within smoke plumes. As summarized in Table 1, the CTRL simulations used the same

Table 1. Design of the Sensitivity Experiments

simulations	biomass burning emissions except for HONO	biomass burning emissions of HONO	HONO chemical sources
BASE	ON	ON	ON
CTRL _{OFF_BB}	OFF	OFF	ON
CTRL _{OFF_BB_HONO}	ON	OFF	OFF except for NO+OH
CTRL _{OFF_BB_HONO_Emis}	ON	OFF	ON
CTRL _{OFF_BB_HONO_Chem}	ON	ON	OFF except for NO+OH
CTRL _{OFF_BB_HONO_HOMO}	ON	ON	OFF _{NO+OH}
CTRL _{OFF_BB_HONO_NOxOxi}	ON	ON	OFF _{NOxOxi}
CTRL _{OFF_BB_HONO_HET_AERO}	ON	ON	OFF _{HET_AERO}
CTRL _{OFF_BB_HONO_HET_LAND}	ON	ON	OFF _{HET_LAND}
CTRL _{OFF_BB_HONO_NIT_PHOT}	ON	ON	OFF _{NIT_PHOT}

anthropogenic and biogenic emissions as BASE. Their meteorological and chemical initial and boundary conditions were also identical. They differed only in the inclusion of wildfire emissions or selected HONO formation pathways. The CTRL_{OFF_BB} simulation excluded all biomass-burning emissions. The wildfire-induced CO enhancement (ΔCO) was calculated from the difference in CO mixing ratios between BASE and CTRL_{OFF_BB} and was used to identify grid cells affected by wildfire emissions. Figure S2 shows the statistical distribution of ΔCO across the modeling domain. The ΔCO values followed an approximately log-normal distribution, with most values ranging from 1 to 100 ppbv.

To evaluate the robustness of the ΔCO threshold used for plume identification, we examined how the diagnosed HONO source contributions varied across different thresholds. Direct wildfire HONO emissions were disabled in CTRL_{OFF_BB_HONO_Emis}, the additionally implemented HONO formation pathways were disabled in CTRL_{OFF_BB_HONO_Chem} and both direct wildfire HONO emissions and additional secondary pathways were disabled in CTRL_{OFF_BB_HONO}. The resulting BASE-minus-CTRL differences quantified the contributions of direct emissions, secondary formation, and total wildfire-related HONO, respectively. The HONO differences derived using ΔCO thresholds of 1, 2, 5, 10, 15, 20, and 30 ppbv are listed in Table S3. The fraction of ambient HONO attributable to wildfire-related sources, calculated as BASE minus CTRL_{OFF_BB_HONO}, exceeded 97% across all tested ΔCO thresholds (Figure S3a). As the ΔCO threshold increased, the mean in-plume HONO concentrations derived from both sensitivity comparisons increased substantially (Figure S3b and Table S3). This trend reflects the progressive selection of the denser smoke-core grid cells, where precursor concentrations and chemical reactivity are higher. We further examined the additivity of the isolated source contributions to assess the reliability of the source-apportionment method. As shown in Figure S3c, the sum of the separately diagnosed direct and

secondary contributions was strongly correlated with the total simulated wildfire-related HONO enhancement. The regression slope of 1.06 indicates only a small positive deviation from perfect additivity, suggesting that nonlinear chemical coupling effects among HONO sources were minor. This result supports the use of paired simulation differences to quantify the individual source contributions. An intermediate threshold of $\Delta\text{CO} > 10$ ppbv was selected as the standard plume-identification criterion because it captured most smoke-affected grid cells while providing representative source attribution. The resulting plume boundaries were broadly consistent with the satellite-observed smoke pattern (Figure S4).

To quantify the contribution of each secondary pathway to HONO production, five specific source-removal experiments were conducted by separately disabling homogeneous HONO formation from NO + OH (CTRL_{OFF_BB_HONO_HOMO}), photo- and dark-oxidation of NO_x (CTRL_{OFF_BB_HONO_NOxOxi}), NO_2 heterogeneous uptake on aerosol surfaces (CTRL_{OFF_BB_HONO_HET_AERO}), NO_2 heterogeneous uptake on the ground surface (CTRL_{OFF_BB_HONO_HET_LAND}), and pNO_3 photolysis (CTRL_{OFF_BB_HONO_NIT_PHOT}).

2.5. Source-Oriented Analysis of OH Radicals

A source-oriented method (SOM) was used to quantify pathway-specific primary OH production within wildfire plumes. This approach tracks the contributions of individual chemical reactions to the production of a target species by introducing explicit diagnostic tracers into the WRF-Chem chemical module.^{68,72} For each pathway i , the OH production rate ($P_{\text{OH},i}$) was calculated from the change in OH concentration induced by that reaction during each chemical integration time step (Δt)

$$P_{\text{OH},i} = \frac{C_{\text{new},i} - C_{\text{old},i}}{\Delta t} \quad (1)$$

where $C_{\text{old},i}$ and $C_{\text{new},i}$ denote the OH concentrations before and after the calculation of chemical reaction i , respectively.⁷³ The instantaneous production rates were accumulated online and output as hourly mean production rates in ppbv h⁻¹ for subsequent analysis. Additional diagnostic variables were implemented to quantify primary OH production from four pathways, including the reaction of excited oxygen atoms [$\text{O}(^1\text{D})$] with water [$\text{O}(^1\text{D}) + \text{H}_2\text{O}$] following O_3 photolysis, HONO photolysis ($\text{HONO} + h\nu$), hydrogen peroxide (H_2O_2) photolysis ($\text{H}_2\text{O}_2 + h\nu$), and VOC ozonolysis ($\text{O}_3 + \text{VOCs}$).⁷⁰ It should be noted that the rapid HO_2 -to-OH recycling reaction ($\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$) was excluded from this diagnosis to isolate primary OH production pathways rather than total gross OH production.

3. RESULTS AND DISCUSSION

3.1. Smoke Pollution and Model Evaluation during the Williams Flats Fire

The Williams Flats Fire occurred under a persistent anti-cyclonic system over the western United States during 2–9 August 2019 (Figure S5). The associated subsidence, suppressed precipitation, anomalously high temperature, and low relative humidity favored fuel aridity and fire development. At the same time, prevailing westerly winds transported the smoke mainly eastward, affecting extensive downwind inland regions. This transport pattern was confirmed by MAIAC smoke AOD, which showed dense plumes extending eastward from the fire source, with near-source smoke AOD exceeding 1.0 on selected sampling days (Figure S6a). Consistently, EPA surface monitoring sites east of the fire recorded episodic $\text{PM}_{2.5}$ enhancements, with maximum hourly concentrations exceeding $100 \mu\text{g m}^{-3}$ within 100 km downwind of the ignition point (Figure S6b). These satellite and ground-based observations provide observational context for the smoke episode evaluated below.

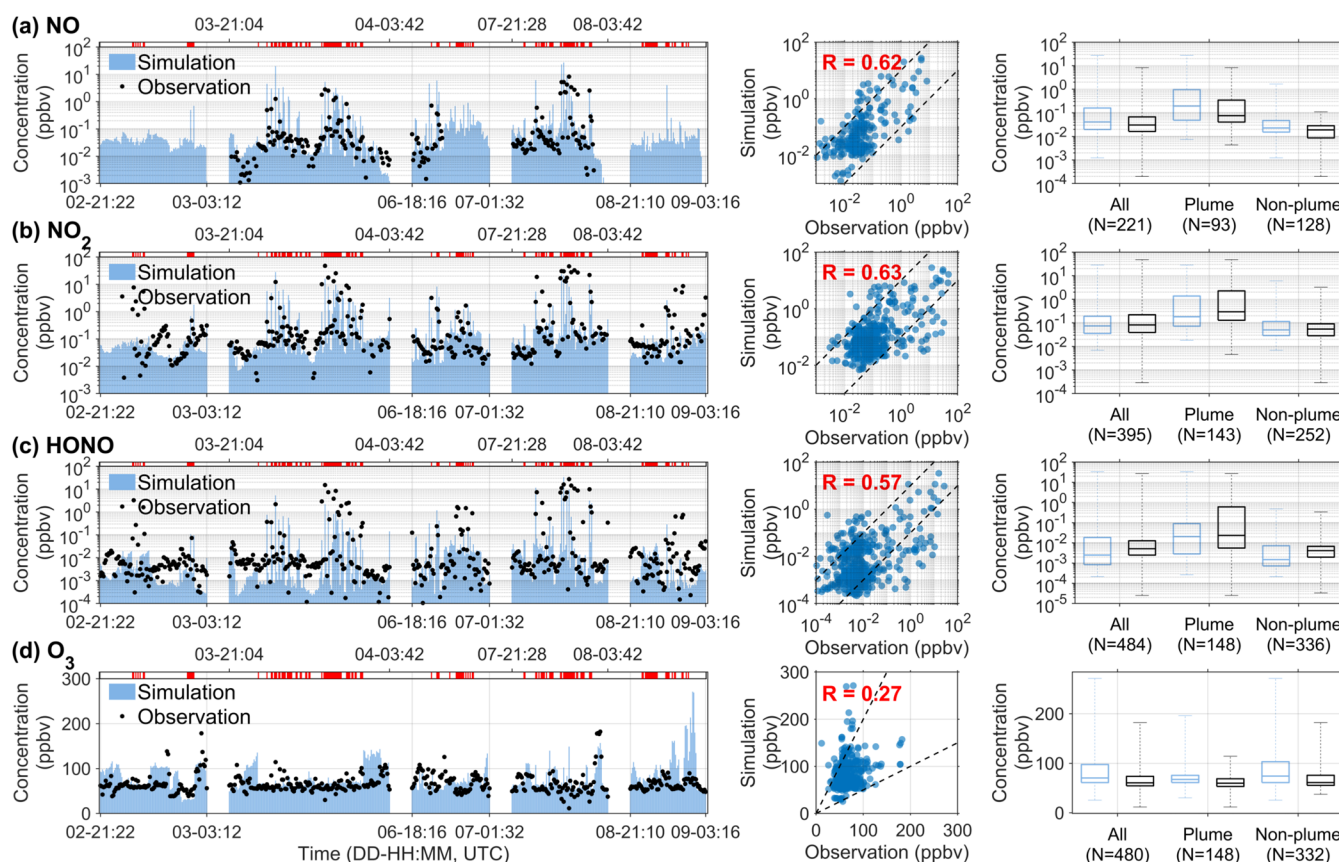


Figure 2. Comparison of observed and simulated gaseous species concentrations along the DC-8 flight tracks including (a) NO, (b) NO₂, (c) HONO, and (d) O₃. The panels are organized into time series, scatter plots, and box-and-whisker plots. The red bars at the top of the time-series panels indicate the time intervals when the aircraft sampled within the smoke. In the scatter plots in panels (a–c), the dashed lines indicate the 10:1 and 1:1 reference lines. In the scatter plot in panel (d), the dashed lines indicate the 2:1 and 1:2 reference lines. The correlation coefficients are labeled in red. The box-and-whisker plots compare the statistical distributions of simulated (blue) and observed (black) concentrations for all data, in-plume, and non-plume groups. The boxes represent the interquartile range (25th–75th percentiles), and the horizontal lines are the medians. The upper and lower caps show the maxima and minima, respectively.

To characterize the chemical fate of wildfire plumes, we used the three-dimensional WRF-Chem model for further investigation. We first compared the BASE simulation with measurements to assess the model performance in reproducing meteorological fields and chemical species. As shown in Figure S7, the model effectively captured the temporal variations in temperature, pressure, water vapor mixing ratio, and horizontal wind speed observed by the DC-8 aircraft, yielding correlation coefficients of 0.91, 0.99, 0.58, and 0.87, respectively. Results revealed that meteorological conditions were well represented, providing a reliable basis for simulating the evolution of chemical species.

In terms of aerosol concentrations, airborne measurements showed that PM_{2.5} within smoke plumes was dominated by carbonaceous components (Figure S8). Samples were categorized into in-plume and non-plume groups based on aircraft transects through the smoke. The in-plume aerosol concentrations were substantially higher than the non-plume concentrations. The model reproduced the dominance of organic aerosol in PM_{2.5} and the contrast between in-plume and non-plume samples, with correlation coefficients of 0.47–0.48. Quantitatively, the modeled peak concentrations of OA (1224.9 $\mu\text{g m}^{-3}$), BC (28.1 $\mu\text{g m}^{-3}$), and PM_{2.5} (1710.4 $\mu\text{g m}^{-3}$) were comparable in magnitude to the extreme values observed in smoke plumes. However, the present model underestimated the median in-plume aerosol concentrations by

a factor of 4–5. This discrepancy is likely attributed to the inherent large uncertainties in current biomass burning emission inventories.^{55,74} A previous intercomparison study for the Williams Flats Fire has noted that OA emission estimates can vary by a factor of 20 to 50.⁵⁴ Additionally, missing mechanisms for SOA formation in the model may further contribute to the underestimation of OA mass concentrations.^{20,75}

For NO and NO₂, the model showed good agreement with the airborne measurements, with correlation coefficients of 0.62–0.63. The simulation also reproduced the tens-of-ppbv enhancements observed within the high-NO_x smoke plume (Figure 2a–b). The reasonable NO_x representation supports the subsequent evaluation of secondary HONO production. Airborne measurements detected extremely high HONO concentrations up to 27.2 ppbv within the smoke plumes (Figure 2c). The CTRL_{OFF BB}_{HONO} simulation, which retained only the default HONO chemistry, underestimated the observed pyrogenic HONO levels by approximately two orders of magnitude (Figure S9a). By incorporating representations of additional sources, the revised model successfully reproduced the evident increase in HONO levels during wildfire events with a simulated maximum concentration of 33.5 ppbv. Simultaneously, the simulated median concentration of in-plume HONO (21 pptv) closely aligned with the measured level (24 pptv). Additionally, the model

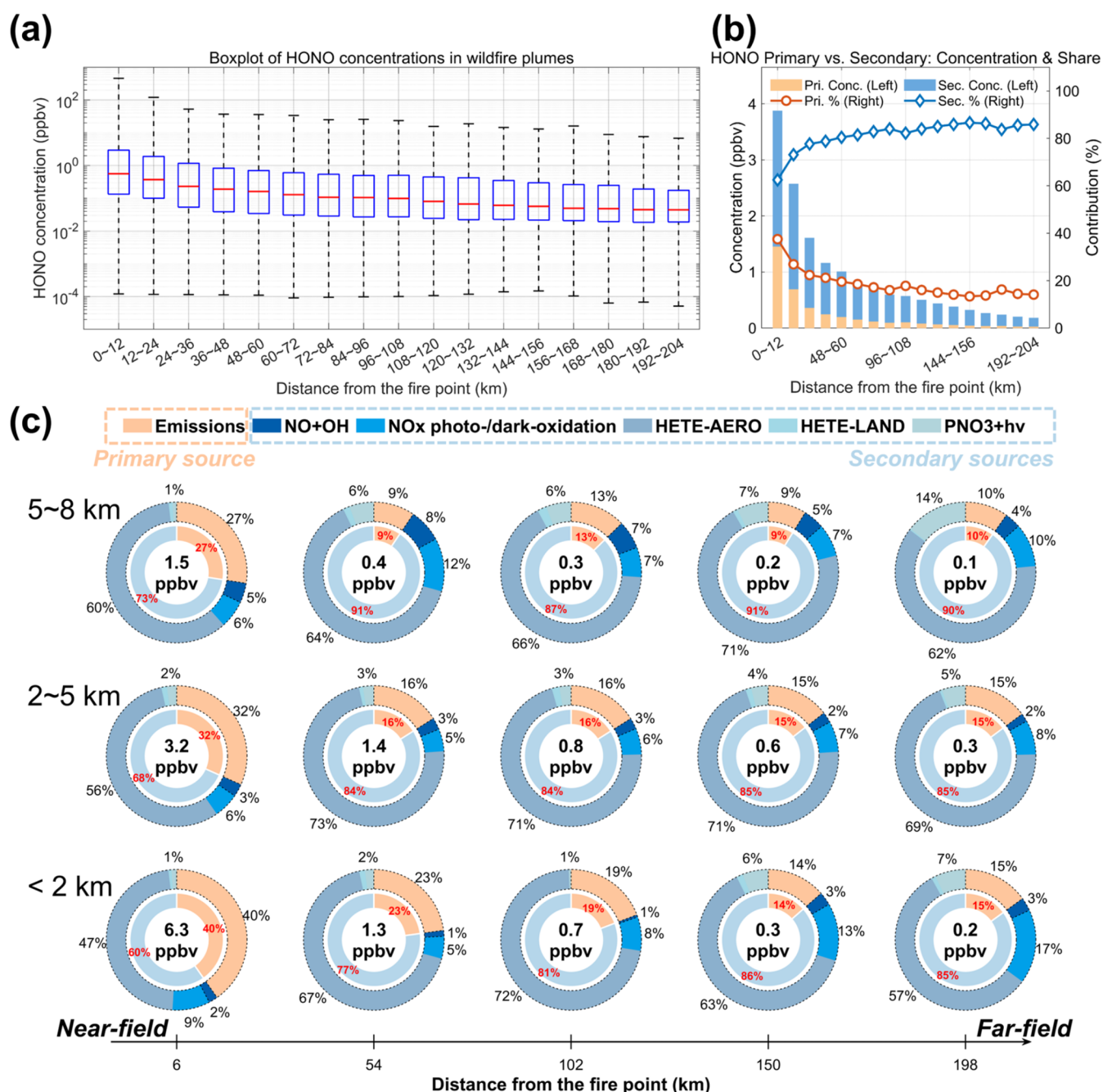


Figure 3. Evolution of HONO concentrations and source attribution in wildfire plumes as a function of distance from the Williams Flats Fire. (a) Box-and-whisker plots of simulated HONO concentrations at 12-km intervals. (b) Comparison of primary and secondary HONO contributions in terms of mixing ratios (bars) and percentage shares (lines). (c) Detailed source budgets for three altitude ranges (<2 km, 2–5 km, and 5–8 km). Numbers inside the circles indicate mean HONO concentrations (ppbv), and tick marks along the bottom arrow indicate distance from the fire (km).

demonstrated a robust capability in resolving the plume's vertical structure. Figure S10 presents simulated vertical profiles and airborne measurements of HONO mixing ratios along the flight tracks. The DC-8 aircraft cruised mainly at 7–10 km altitude and performed repeated transects through the smoke plumes at 3–5 km altitude. The model captured this vertical stratification and the higher HONO concentrations within the 3–5 km altitude range. This range corresponds to the main advection zone of the simulated plume rise, indicating that the model was capable of reasonably reproducing the injection heights and vertical dispersion of wildfire plumes.

Additional quantitative evaluation metrics, including mean bias (MB) and root mean square error (RMSE) for the simulated gaseous species along the DC-8 flight tracks are provided in Table S4.

Because HONO chemistry is closely coupled with the NO_x cycle, we further examined how the improved HONO representation affected NO_x and HONO/NO_x in those in-plume samples. As shown in Figure S9, the in-plume NO_x bias shifted from a positive value in CTRL_{OFF_BB_HONO} (MB = +3.7 ppbv) to a moderate negative value in BASE (MB = −1.8 ppbv), while the RMSE decreased from 22.4 to 10.0 ppbv. This

response reflects competing nitrogen processes, including HONO photolysis recycling to NO, NO₂ heterogeneous uptake, and OH-driven NO₂ oxidation to HNO₃. Meanwhile, the HONO/NO_x ratio was also better represented in BASE, with the MB reduced from −0.14 to −0.06 and the RMSE decreased from 0.20 to 0.16. These results indicate that the revised HONO representation improves HONO and HONO/NO_x simulations within wildfire plumes.

Unlike aerosols and NO_y, which peaked sharply within the plumes, observed O₃ levels were often higher in the non-plume background air due to the high-altitude cruising of the DC-8 in the upper troposphere around 7–10 km. The model captured the median O₃ level of 67.4 ppbv within smoke plumes, showing alignment with airborne measurements (60.0 ppbv). A systematic overestimation was evident in the non-plume group. This bias may be associated with uncertainties in chemical initial and boundary conditions and the representation of sharp vertical O₃ gradients in the upper free troposphere. Because it was most evident in high-altitude non-plume samples, it is more directly relevant to the absolute background O₃ level than to the paired modeled O₃ response attributed to wildfire HONO. These factors likely contributed to the lower statistical correlation for O₃ compared with other pollutants.

3.2. Source Attribution of HONO within Wildfire Plumes

Spatially, the highest simulated daily mean HONO vertical columns occurred near the fire source, exceeding 1.0×10^{16} molecules cm^{−2} (Figure S11). Driven by westerly winds, HONO showed a pronounced eastward transport pattern. To examine wildfire HONO evolution from the source to downwind regions, we analyzed the temporally averaged simulation results from 12:00 on 2 August to 12:00 on 9 August (UTC). Plume-affected grid cells were identified using the ΔCO fire-influence criterion introduced in Section 2.4. Distance from the fire source was not used to define the plume but was applied afterward to organize the identified plume cells into downwind spatial bins. The downwind plumes were segmented into 17 distance bins at 12-km intervals relative to the fire point. The distance bins provide a spatial coordinate for diagnosing downwind plume evolution and are not assumed to correspond to unique plume ages. Variations in wind speed, recirculation, and plume accumulation can produce a range of transport histories within each distance bin. Therefore, the distance-resolved results should be interpreted as spatial patterns of downwind source evolution rather than as a unique chemical-age trajectory.

As illustrated in Figure S12, extremely high PM_{2.5} loadings were concentrated at an altitude of 3–5 km in the near-field region. This pattern reflects smoke injection into this altitude range. As the distance from the fire point increased, PM_{2.5} levels decreased due to plume dilution. However, concentrations remained in the tens of μg m^{−3} after 150 km of transport in the plume injection layer, indicating substantial downwind transport within the free troposphere. At the same time, the high PM_{2.5} concentrations offered considerable reactive aerosol surface area for the heterogeneous uptake of NO₂, with the peak surface area density reaching approximately 1×10^{-2} m² m^{−3}.

The vertical distribution of HONO showed a similar pattern (Figure S13). From the fire to 200 km downwind, mean in-plume HONO declined from 3.87 to 0.18 ppbv as the plume diluted (Figure 3a–b), consistent with the large eddy

simulation (LES) and airborne measurements of the same fire presented by Wang et al.³⁵ In the near-field, HONO was concentrated near the surface (0–2 km), with an average concentration of 6.3 ppbv, surpassing levels in the middle and upper troposphere. However, as the distance to the fire increased, the concentration gradient reversed. The 2–5 km plume transport layer emerged as a persistent reservoir of HONO, maintaining higher levels than both the near-surface and upper layers. Source attribution indicates an evident shift in HONO formation with downwind plume transport. In the 0–12 km distance bin, direct emissions and secondary reactions jointly elevated HONO levels, with contributions of approximately 40% and 60% (Figure 3b). With downwind transport, the direct-emission contribution rapidly decreased, whereas secondary reactions accounted for more than 85% of the total in-plume HONO source budget. Among all secondary sources, heterogeneous uptake of NO₂ on aerosol surfaces (HETE-AERO) was the dominant pathway, accounting for 47%–74% of the total in-plume HONO budget (Figure 3c), consistent with previous isotopic and box-model studies.^{26,29} This dominance of HETE-AERO reflects the abundant reactive surface area provided by smoke aerosols, particularly within the 2–5 km smoke plume injection layer (Figures S12–S13). Despite its large absolute contribution, the fractional contribution of HETE-AERO was lower in aerosol-rich near-source plumes because direct emissions increased the total HONO budget and thereby reduced the fractional contribution of HETE-AERO. At higher altitudes, where direct smoke injection was weaker, HONO formation was mainly sustained by HETE-AERO. With continued downwind transport, dilution reduced the influence of direct emissions, while the 2–5 km smoke injection layer retained sufficient aerosol surface area to support continued HONO production through HETE-AERO. Consequently, HETE-AERO remained the dominant source, accounting for approximately 70% of the total in-plume HONO budget in this layer. Source-apportionment differences between Eulerian CTMs and observation-constrained box models exist. Box models can capture the immediate dominance of primary emissions near the fire,²⁶ whereas WRF-Chem may smooth near-source concentration peaks because of grid-averaging. Nevertheless, the predicted transition to secondary-dominated HONO downwind is consistent with 0.1-km-resolution LES modeling,³⁵ suggesting that sustained HETE-AERO can become dominant as plume dilution reduces the contribution from direct emissions. The exact timing of this transition may still depend on model resolution, dilution, and fire-specific combustion conditions.²⁶

It should also be noted that the source apportionment is not equally constrained across altitudes. The DC-8 aircraft measurements provide direct HONO constraints mainly in the elevated plume transport layer. By contrast, independent near-surface HONO observations were not available for the Williams Flats Fire. Thus, the HONO source partitioning below 2 km should be interpreted as a model-based estimate with uncertainties, whereas the dominance of HETE-AERO is most robustly supported for the elevated smoke plume transport layer. Overall, these results indicate that HONO persistence in downwind smoke is maintained by sustained secondary formation within aerosol-rich plumes after the influence of direct emissions declines. This process can extend the chemical influence of wildfire HONO beyond the immediate fire source.

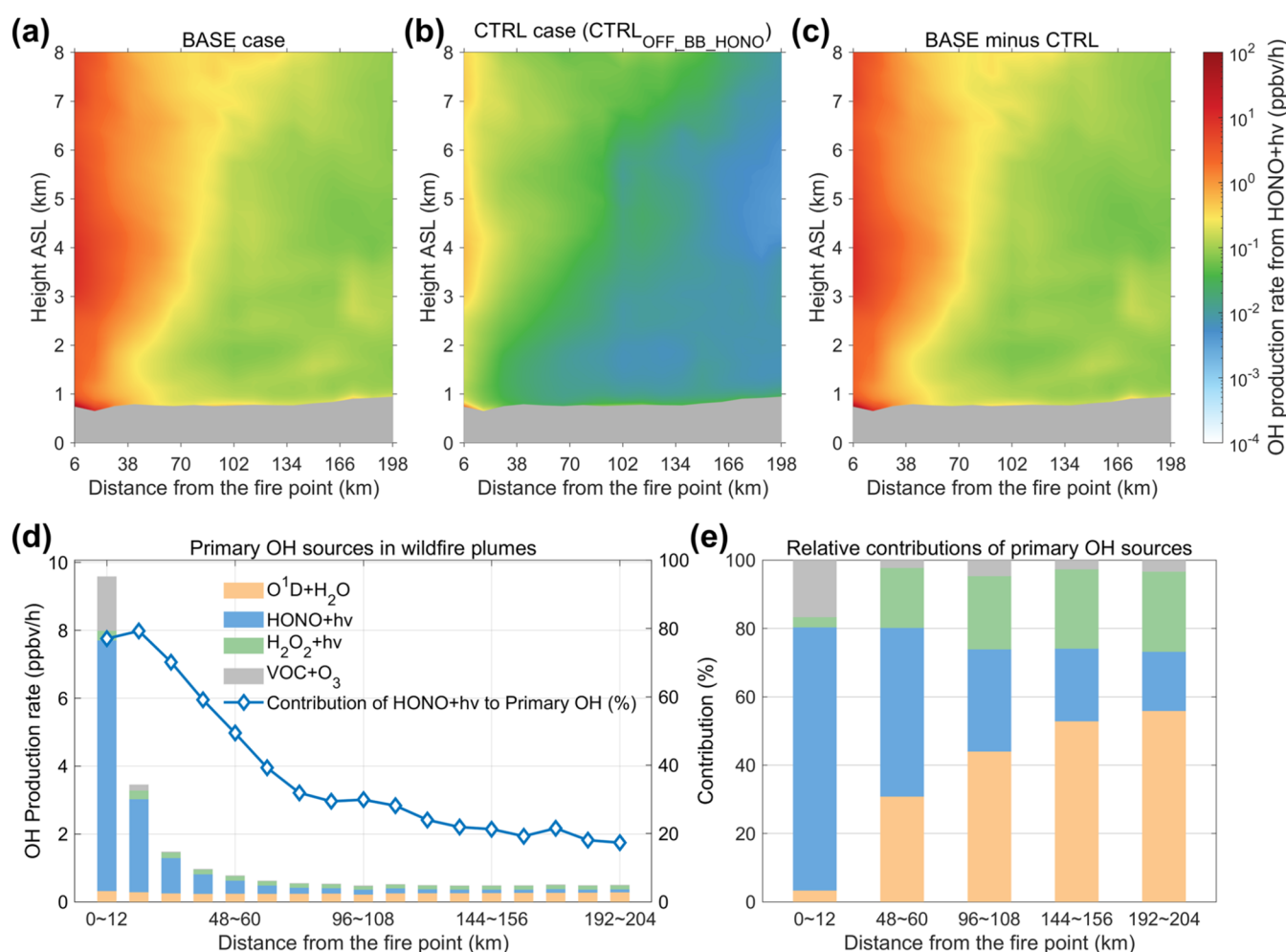


Figure 4. Impact of HONO photolysis on primary OH radical production within wildfire plumes. (a–c) Vertical cross sections of OH production rates along the plume transport path for (a) BASE, (b) CTRL_{OFF_BB_HONO}, and (c) BASE minus CTRL_{OFF_BB_HONO}. (d) Variations of primary OH production rates and the relative contribution of HONO photolysis as a function of distance from the fire. (e) Relative contributions of different primary OH sources across five distance intervals.

3.3. Impacts of Wildfire HONO on OH Radicals and Ozone

Wildfire-derived HONO can enhance primary OH radical production through photolysis. Using sensitivity experiments and SOM analysis, we show the temporally averaged impact of HONO on in-plume primary OH production rates in Figure 4. Wildfire HONO enhanced primary OH radical production by orders of magnitude within the plume core. Generally, the vertical distribution of the HONO-induced enhancement in primary OH production corresponded well to the vertical structure of in-plume HONO described in Section 3.2. In the near-field region, the elevated primary OH production extended from the surface to approximately 8 km altitude. As the plume transport distance increased, the HONO-induced enhancement in primary OH production became more pronounced within the smoke injection layer (2–5 km). This indicates that secondary HONO production aloft enhanced primary radical initiation within the 2–5 km plume transport layer, where background radical sources were limited.

Specifically, the total primary OH production peaked in the near-field region of the fire, with a maximum value reaching 9.6 ppbv h⁻¹ (Figure 4d). As illustrated in Figure 4e, the SOM diagnosis indicates that HONO photolysis supplied approximately 80% of the primary OH production in near-field

smoke. Because $HO_2 + NO$ recycling was excluded from this diagnosis, this percentage describes primary radical initiation rather than total gross OH production or the total AOC. FAST-J explicitly represented the modeled attenuation of photolysis within wildfire smoke. During daytime at 2–5 km altitude, in-plume J_{HONO} was 21%–26% lower than nearby non-plume values within 0–60 km of the source, and this reduction weakened to approximately 6% in the far-field region as the plume diluted (Figure S14). This attenuation reduced HONO photolysis and extended its photolytic lifetime relative to nearby non-plume conditions. Nevertheless, near-field HONO concentrations were more than two orders of magnitude higher inside the plume than in nearby non-plume air. This large enhancement in HONO abundance outweighed the moderate reduction in J_{HONO} , so $J_{HONO} \times [HONO]$ remained sufficiently large for HONO photolysis to be the leading diagnosed primary OH source.

The contribution from this pathway substantially exceeded that from the conventional pathway involving the reaction of $O(^1D)$ with H_2O following O_3 photolysis. The finding is consistent with previous wildfire-HONO studies reporting a strong contribution of HONO photolysis to primary radical initiation.^{18,39,51} Meanwhile, a distinct transition in the regime of radical initiation occurred with downwind plume transport

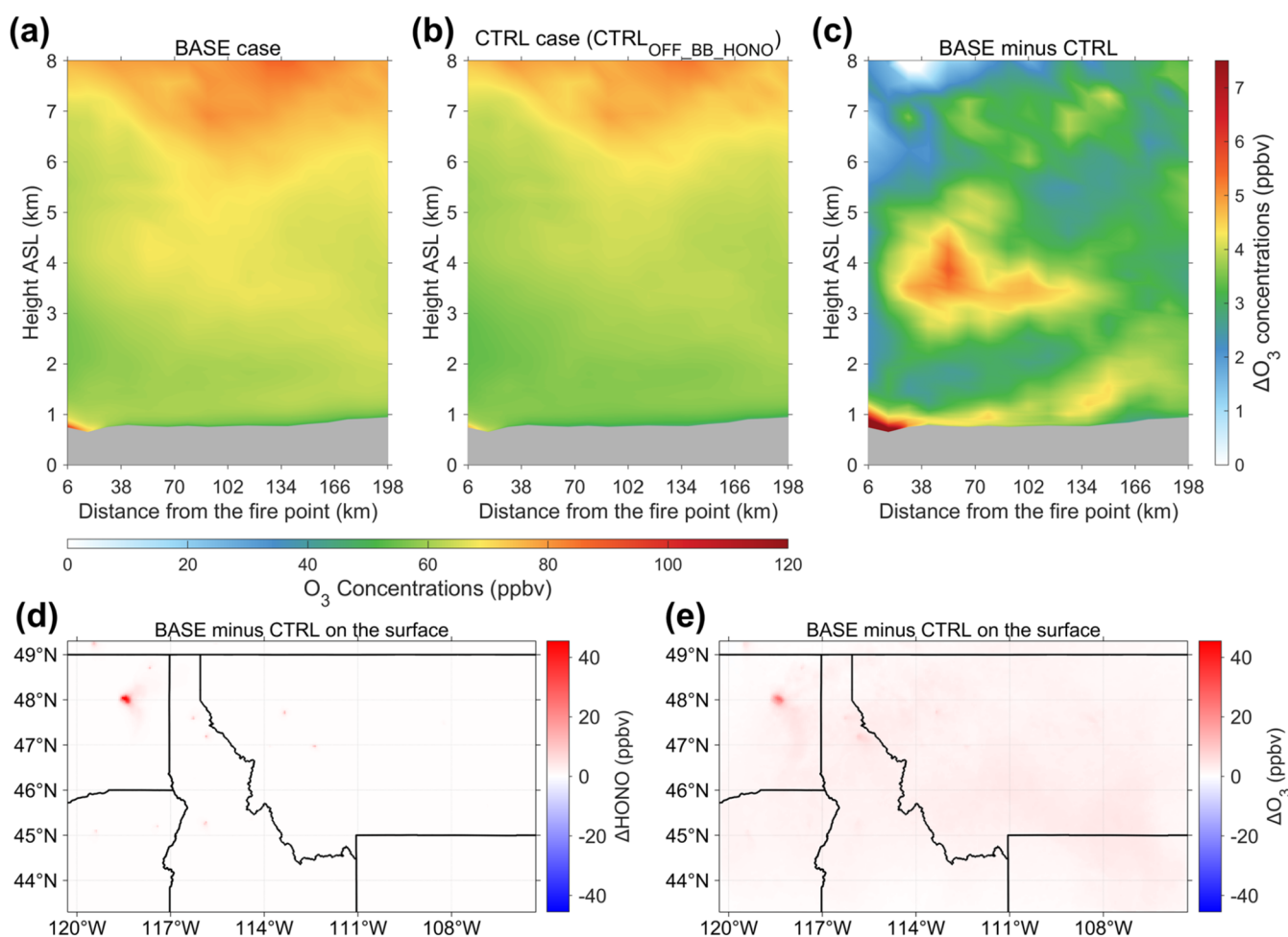


Figure 5. Impact of wildfire HONO on O_3 . Vertical cross sections of O_3 concentrations along the plume transport path for (a) BASE, (b) CTRL_{OFF_BB_HONO}, and (c) BASE minus CTRL_{OFF_BB_HONO}. Panels (d, e) show the BASE-minus-CTRL differences in mean surface HONO and O_3 concentrations, respectively.

(Figure 4d). The absolute production rate of primary OH resulting from HONO photolysis declined from 7.4 ppbv h^{-1} to 0.1 ppbv h^{-1} as the smoke moved from the near-field to the far-field region. This decrease was driven by the dilution of HONO concentrations (Figure S13). Thus, the contribution of HONO photolysis to the OH production budget dropped to 17%. Nevertheless, the relative contribution of the reaction between $O(^1D)$ and H_2O increased and eventually became the predominant source in the far-field region. These results demonstrate that HONO photolysis dominated the diagnosed primary OH production near the source, whereas conventional primary OH sources became predominant farther downwind.

The enhanced OH production from HONO photolysis can initiate VOC oxidation and RO_x cycling in smoke, providing a direct chemical linkage between HONO chemistry and O_3 formation. We therefore further investigated the temporally averaged impact of wildfire HONO on in-plume O_3 (Figure 5). Overall, the modeled O_3 responses to wildfire HONO varied strongly with altitude (Figure 5a–c). Near the surface, wildfire HONO increased O_3 by more than 15 ppbv near the fire. This large enhancement was associated with the coexistence of abundant precursors and enhanced OH production. The modeled near-surface O_3 increase suggests that wildfire HONO can play an important role in smoke-related surface air-quality impacts. Even in downwind regions hundreds of

kilometers away from the fire, HONO photolysis still sustained a net increase of O_3 by 3 to 4 ppbv.

Compared with the near-surface layer, a distinct pattern emerged within the plume injection layer at 3–5 km altitude. The maximum O_3 increase due to HONO chemistry occurred 50 km downwind rather than near the source, reaching approximately 5 ppbv, whereas the near-field enhancement at this altitude was less than 2 ppbv. The relatively weak near-source O_3 response likely reflects concurrent suppression pathways in high- NO_x smoke. The abundant OH radicals generated in near-source plumes rapidly react with NO_2 to form HNO_3 (Figure S15a–b), thereby removing both radicals and NO_2 and temporarily suppressing the O_3 formation cycle.⁷⁶ In parallel, rapid titration of O_3 by freshly emitted NO can further reduce net O_3 accumulation in the immediate near field. As the plume dilutes and NO is oxidized downwind, these suppressing effects weaken and a larger positive O_3 response emerges. Meanwhile, the O_3 formation regime also shifted with downwind plume transport. The ratio of HNO_3 to H_2O_2 indicated a transition from NO_x -saturated to NO_x -limited conditions with downwind plume transport, both at the surface and within the plume transport layer (Figure S15c). This finding is consistent with a recent study by Palmo et al.⁷⁷ Overall, the elevation of O_3 levels within the lower and middle

troposphere underscores an important influence of wildfire HONO in modulating the tropospheric O₃ burden.

We also show the impact of HONO on surface O₃ concentrations on a larger spatial scale, as presented in Figure 5d–e. While the elevation of HONO concentrations was spatially confined to the near-source region due to its rapid photolytic loss, the resulting O₃ enhancement exhibited a broader downwind footprint. HONO acted as a local source of OH radicals, inducing subsequent atmospheric oxidation reactions that led to the accumulation and transport of O₃. This highlights that wildfire HONO can modulate lower-tropospheric O₃ abundance and regional surface air quality. The inclusion of wildfire HONO also improved the simulation of surface MDA8 O₃ at EPA monitoring sites, increasing the regional average from 47.0 ppbv in CTRL_{OFF_BB_HONO} to 49.5 ppbv in BASE, closer to the observed value of 49.6 ppbv (Figure S16).

3.4. Uncertainties

The heterogeneous conversion of NO₂ on aerosol surfaces remains one of the largest uncertainties in the HONO budget. To assess the impact of varying $\gamma_{\text{NO}_2\text{-aero}}$ values, we conducted three fixed- γ sensitivity simulations with $\gamma_{\text{NO}_2\text{-aero}}$ values of 1.0×10^{-4} , 4.9×10^{-4} , and 1.0×10^{-3} , covering the range reported by previous studies. As shown in Figure S17, the γ perturbation experiments showed that simulated HONO was sensitive to the assumed uptake coefficient, but the response was nonlinear. The low- γ case consistently reduced HONO concentrations, especially within smoke plumes in the lower troposphere. In contrast, the intermediate and high- γ cases produced broadly comparable HONO distributions, and the high- γ case did not lead to a proportional enhancement relative to the intermediate case. This phenomenon is expected because $\gamma_{\text{NO}_2\text{-aero}}$ governs the pseudo-first-order uptake rate coefficient, whereas the ambient HONO reflects the net balance among heterogeneous production, NO₂ availability, and HONO loss within wildfire plumes. Despite this quantitative sensitivity, HETE-AERO remains a major contributor to HONO formation across the tested $\gamma_{\text{NO}_2\text{-aero}}$ range. Across the fixed $\gamma_{\text{NO}_2\text{-aero}}$ range from 1.0×10^{-4} to 1.0×10^{-3} , the mean HETE-AERO contribution remained substantial in all altitude layers, with values of 48%–69% in the 0–2 km layer, 62%–71% in the 2–5 km layer, and 54%–69% in the 5–8 km layer. These results indicate that the importance of HETE-AERO is not an artifact of selecting the upper-limit γ value. Nevertheless, the exact magnitude of HONO production and the fractional contribution of HETE-AERO should be interpreted as uncertain, and future studies combining laboratory kinetics with field observational constraints are still needed to derive more robust uptake parameterizations for biomass burning aerosols under different environmental conditions.

In addition, current chemical mechanisms in the WRF-Chem model require improvement to better characterize the complex chemical conversions within wildfire plumes. For example, our model lacks explicit treatment of furans and their subsequent oxidation chemistry, which are important contributors to both O₃ and SOA formation.⁷⁸ Moreover, standard biomass burning emission inventories often neglect emissions of semi- and intermediate-VOCs (S/IVOCs). Therefore, the related SOA formation potential from wildfires could be considerably underestimated. A recent development of full-volatility emission inventories of wildfire VOCs by Huang et al.

provides a useful foundation for future model updates.⁷⁹ The underestimation of SOA concentrations further affects the simulation of heterogeneous HONO production by limiting the available reaction surface area. In addition, the heterogeneous uptake of HO₂ radicals on smoke aerosol surfaces was not considered in this study, potentially introducing uncertainty to the assessment of HONO's impact on the radical budget and O₃ formation.^{80,81} Moreover, the modeled aerosol-shielding effect depends on aerosol abundance, optical properties, and vertical distribution. Because aerosol abundance was underestimated relative to the aircraft measurements, the smoke-induced reduction in J_{HONO} may also be underestimated. However, the magnitude of this bias depends on the represented aerosol optical properties and vertical distribution.

Wildfire EF_{HONO} represents an additional uncertainty in this study. The FINNV2.5-derived EF_{HONO} values are static, vegetation-dependent means, whereas actual biomass-burning emissions can vary dynamically with combustion conditions, including modified combustion efficiency (MCE), fuel type, and fuel moisture. Previous studies have shown that these factors can substantially affect emission factors for biomass-burning species.^{82,83} However, compared with those available for major fire-emitted constituents such as CO₂, CO, CH₄, NO_x, and PM_{2.5}, direct measurements of wildfire EF_{HONO} remain sparse, and no robust fuel- and MCE-dependent EF_{HONO} parameterization is currently available for implementation in regional chemical transport models. Therefore, the estimated near-field contribution of direct HONO emissions should be interpreted as conditional on the static FINNV2.5-derived EF_{HONO} values. Because the FIREX-AQ measurements reflect the combined effects of direct emissions and rapid secondary chemistry, they cannot independently constrain EF_{HONO}. This uncertainty therefore primarily affects the quantitative near-field partitioning between direct and secondary HONO sources. Further laboratory and field measurements across different fuel types and combustion conditions are required to better constrain wildfire HONO emissions.

3.5. Atmospheric Implications

This study integrated the revised WRF-Chem model with FIREX-AQ airborne measurements and used sensitivity experiments and SOM diagnostics to quantify HONO formation and its chemical impacts in wildfire plumes. Results indicate that the revised model reasonably reproduced the magnitude and evolution of in-plume HONO concentrations. The model revealed that direct emissions accounted for up to 40% of the total HONO budget in the near-field region. However, across both near-source and downwind smoke, the heterogeneous uptake of NO₂ on aerosol surfaces emerged as the predominant HONO formation pathway in wildfire plumes. This source regime differs from many previous urban HONO studies, where ground-surface uptake is often emphasized,^{49,68,84} though recent studies recognize aerosol-surface uptake as a major or even dominant HONO source during severe urban haze events.^{85–88} In wildfire plumes, the dominance of aerosol-surface uptake is amplified by the exceptionally large smoke aerosol surface area and by plume transport aloft.

HONO photolysis was the largest diagnosed primary OH source in the near-field region, accounting for approximately 80% of primary OH production. This result is consistent with

previous aircraft observations and box-model studies,^{39,51} while the present analysis further resolves how the three-dimensional evolution of direct and secondary HONO sources is linked to primary radical initiation and the altitude-dependent modeled O₃ response. HONO-initiated radical production increased modeled O₃ near the surface and within the elevated plume transport layer. While this study focused on plumes transported at 3–5 km altitude in the northwestern United States, larger wildfires globally with higher injection heights could influence radical chemistry in the upper troposphere, potentially altering O₃ distributions on a much broader spatial scale. Therefore, the impact of wildfire HONO on the global tropospheric O₃ budget needs further assessment.

To reduce model uncertainties in simulating HONO production, future studies should focus on two priorities: (1) constraining NO₂ uptake coefficients on biomass-burning aerosols through dedicated laboratory kinetic studies and field measurements; and (2) improving modeled aerosol concentrations by refining direct wildfire emissions and SOA formation parameterizations.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.6c12013>.

List of WRF-Chem modeling configurations; quantitative evaluation of simulated gaseous species along the DC-8 flight tracks; comparison of the simulated and observed spatial pattern of the wildfire plume; comparison of modeled and observed HONO mixing ratios along the flight tracks (PDF)

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Notes

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