Airborne Observations Constrain Heterogeneous Nitrogen and Halogen Chemistry on Tropospheric and Stratospheric Biomass Burning Aerosol

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Abstract

Heterogeneous chemical cycles of pyrogenic nitrogen and halides influence tropospheric ozone and affect the stratosphere during extreme pyrocumulonimbus (PyroCB) events. We report field-derived N2O5 uptake coefficients, γ(N2O5), and ClNO2 yields, φ(ClNO2), from two aircraft campaigns observing fresh smoke in the lower and mid troposphere and processed/aged smoke in the upper troposphere and lower stratosphere (UTLS). Derived φ(ClNO2) varied across the full 0–1 range but was typically < 0.5 and smallest in a PyroCB (< 0.05). Derived γ(N2O5) was low in agricultural smoke (0.2–3.6 ×10-3), extremely low in mid-tropospheric wildfire smoke (0.1 × 10-3), but larger in PyroCB processed smoke (0.7–5.0 × 10–3). Aged BB aerosol in the UTLS had a higher median γ(N2O5) of 17 × 10–3 that increased with sulfate and liquid water, but that was nevertheless 1–2 orders of magnitude lower than values for aqueous sulfuric aerosol used in stratospheric models.

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Key Points:

- N_2O_5 uptake coefficients are low on young biomass burning smoke and increase with transport through a PyroCB and UTLS aging
- $ClNO_2$ formation is active on biomass burning particles, but decreases with transport to the UTLS
- N_2O_5 uptake coefficients on aged biomass burning particles in the UTLS are significantly lower than those used in model parameterizations

Abstract

Heterogeneous chemical cycles of pyrogenic nitrogen and halides influence tropospheric ozone and affect the stratosphere during extreme pyrocumulonimbus (PyroCB) events. We report field-derived N_2O_5 uptake coefficients, $\gamma(N_2O_5)$, and $ClNO_2$ yields, $\varphi(ClNO_2)$, from two aircraft campaigns observing fresh smoke in the lower and mid troposphere and processed/aged smoke in the upper troposphere and lower stratosphere (UTLS). Derived $\varphi(ClNO_2)$ varied across the full 0–1 range but was typically < 0.5 and smallest in a PyroCB (< 0.05). Derived $\gamma(N_2O_5)$ was low in agricultural smoke ($0.2–3.6 \times 10^{-3}$), extremely low in mid-tropospheric wildfire smoke (0.1×10^{-3}), but larger in PyroCB processed smoke ($0.7–5.0 \times 10^{-3}$). Aged BB aerosol in the UTLS had a higher median $\gamma(N_2O_5)$ of 17×10^{-3} that increased with sulfate and liquid water, but that was nevertheless 1–2 orders of magnitude lower than values for aqueous sulfuric aerosol used in stratospheric models.

Plain Language Summary

The injection of reactive material into Earth's atmosphere from fires affects atmospheric composition at regional and hemispheric scales. Reported stratospheric ozone depletion during extreme events, such as the 2020 Australian wildfires, illustrates one example of fire impacts and the role of heterogeneous (gas-particle) processes. We report field quantification of rates and product yields from airborne observations of smoke. Extremely slow heterogeneous reaction rates on young smoke increase with transport and aging, but upper atmospheric values are still a factor of 10 slower than parameterizations used in stratospheric models. Heterogeneous production of $ClNO_2$, a major lower atmospheric chlorine activation pathway, may be active on biomass burning aerosol in the upper atmosphere.

1 Introduction

Biomass burning (BB) impacts global atmospheric chemical processes and is increasing regionally due to climate-change-induced trends in fire weather [*Jones et al.*, 2022]. Fires emit nitrogen oxides ($NO + NO_2 = NO_x$), volatile organic compounds (VOCs) and aerosol that affect tropospheric oxidants [*Koss et al.*, 2018]. Roughly 10% of global inorganic chloride enters the atmosphere by BB [*Wang et al.*, 2019], and a small fraction may be subsequently activated to inorganic chlorine radicals. The co-emission of NO_x and VOCs enhances tropospheric O_3 globally on a scale comparable to, or greater than, urban pollution [*Bourgeois et al.*, 2021; *Xu et al.*, 2021].

Large wildfires can form pyrocumulonimbus (PyroCB) towers [*Peterson et al.*, 2021; *Peterson et al.*, 2022] that loft pyrogenic emissions to the upper troposphere / lower stratosphere (UTLS). Aerosol injection from the 2019–2020 Australian New Year fires altered the partitioning of total reactive chlorine (Cl_y) and nitrogen (NO_y) species and led to stratospheric O_3 loss through heterogeneous reactions [*Bernath et al.*, 2022; *Solomon et al.*, 2022; *Solomon et al.*, 2023; *Strahan et al.*, 2022]. One of the major heterogeneous reactions is uptake of N_2O_5, which in stratospheric models produces exclusively nitric acid, HNO_3 [*Küll et al.*, 2002; *Zambri et al.*, 2019].

$$N_2O_{5(g)} + H_2O_{(l)} \rightarrow 2HNO_{3(g)} \qquad (R1, \gamma)$$

Here, γ is the reactive uptake coefficient [*Ravishankara*, 1997]. Reaction (1) influences NO_x and O_3 in both the stratosphere and troposphere by altering the partitioning of reactive nitrogen and the availability of NO_x [*Dentener and Crutzen*, 1993; *Solomon*, 1999].

Tropospheric observations have shown substantial yields of nitryl chloride, $ClNO_2$, from chloride-containing aerosol [*McDuffie et al.*, 2018a], represented below as reaction with HCl.

$$N_2O_{5(g)} + HCl_{(aq)} \rightarrow ClNO_{2(g)} + HNO_{3(g)} \qquad (R2, \phi)$$

Photolysis of $ClNO_2$ produces Cl. The yield, ϕ, for R2 is the molar ratio of $ClNO_2$ produced per N_2O_5 reacted. Due in part to the lack of chloride partitioning to highly-acidic stratospheric aerosol, R2 has been considered an unimportant contribution to stratospheric halogen activation [*Solomon*, 1999] despite its prevalence in the troposphere. Figure 1 illustrates biomass burning emissions to and heterogeneous chemistry in different regions of the atmosphere.

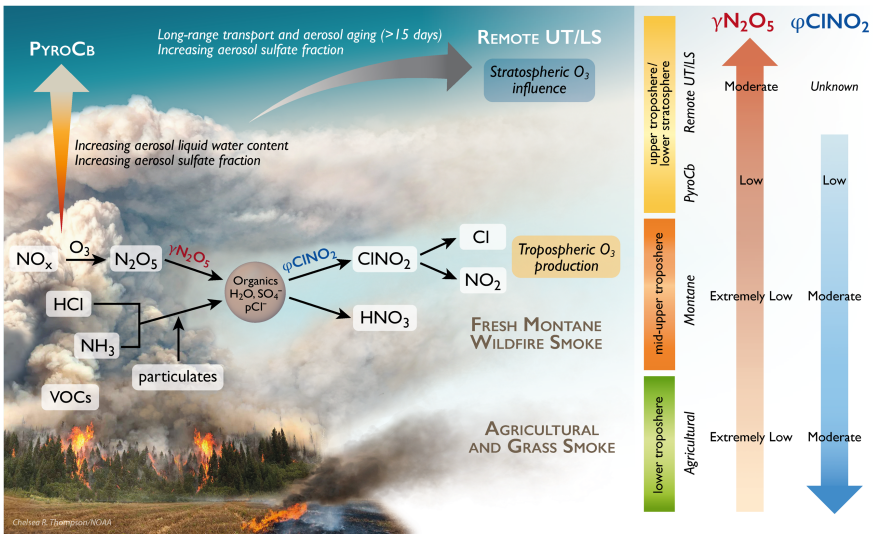

Figure 1. Biomass burning emission to different altitudes and heterogeneous chemistry of N_2O_5 and $ClNO_2$. Arrows on the right-hand side illustrate trends in heterogeneous parameters, $\gamma(N_2O_5)$ and $\phi(ClNO_2)$, determined from aircraft observations in this work**.**

Rates and yields of N_2O_5 heterogeneous chemistry on BB particles are uncertain, especially in the UTLS [*Solomon et al.*, 2022; *Strahan et al.*, 2022; *Yu et al.*, 2021]. Models assume similarity between BB and volcanic particles but are unable to reproduce remote sensing observations of Cl_y and NO_y, suggesting substantial differences in heterogeneous chemistry. There exist limited BB laboratory studies on $\gamma(N_2O_5)$ or $\phi(ClNO_2)$ [*Ahern et al.*, 2018; *Goldberger et al.*, 2019; *Jahl et al.*, 2021] and, to our knowledge, there are no field-derived values. Tropospheric and stratospheric models of BB impacts are poorly constrained for $\gamma(N_2O_5)$ and have not considered $\phi(ClNO_2)$.

We present aircraft observations of N_2O_5, $ClNO_2$ and field-derived values for $\gamma(N_2O_5)$ and $\varphi(ClNO_2)$ in smoke. The analysis utilizes aircraft observations from the 2019 Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ) campaign [*Warneke et al.*, 2023] and the 2017–2018 Atmospheric Tomography mission (ATom) [*Thompson et al.*, 2022]. We derive $\gamma(N_2O_5)$ and $\varphi(ClNO_2)$ for montane and agricultural smoke in the troposphere and a

PyroCB injection of smoke to the upper troposphere from FIREX-AQ. We derive $\gamma(N_2O_5)$ for stratospheric BB-influenced aerosol from ATom. Derived N_2O_5 uptake coefficients are considerably lower than current model parameterizations. Halogen activation through $ClNO_2$ from NO_x and particulate chloride (pCl^-) is prevalent in low altitudes and possible, yet unquantified, at high altitude.

2 Results and Discussion

2.1 $ClNO_2$ and N_2O_5 Observations

Figure 2A shows the flight track of the NASA DC-8 aircraft sampling the Williams Flats fire during FIREX-AQ on 3 Aug 2019 colored and sized by observed $ClNO_2$. Both N_2O_5 and $ClNO_2$ exhibit clear enhancements despite significant photolysis rates of NO_3 (jNO_3) (Figure 2B-C). These enhancements are associated with CO, a smoke tracer, and rapid (>1 ppbv hr^{-1}) NO_3 production, $P(NO_3) = k[NO_2][O_3]$, where k is the bimolecular rate coefficient for reaction of NO_2 with O_3.

Median j_{NO_3} at the center of wildfire and agriculture plume transects (0.14 s^{-1} and 0.19 s^{-1} respectively) were 15–30% lower than values outside of plumes (0.16 and 0.20 s^{-1} respectively). In large wildfire plumes jNO_3 attenuation was a factor of ten or more (Figure 2B and C), but small agricultural plumes exhibited no attenuation (Figure S1). Previous analyses of FIREX-AQ plumes found that NO_3 photolysis and reaction with NO are not major NO_3 loss pathways regardless of time of day [*Decker et al.*, 2021a; *Decker et al.*, 2021b]. Rapid $P(NO_3)$ together with large concentrations of highly reactive VOCs and aerosol surface area control NO_3 and N_2O_5 chemistry. Plumes with measurable daytime N_2O_5 provide measures of NO_3 reactivity and N_2O_5 heterogeneous uptake for these species that are otherwise important only at night in non-fire environments.

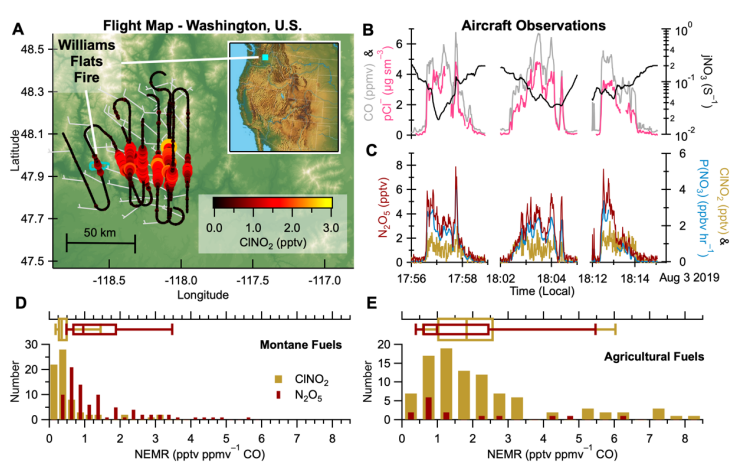

Figure 2. A. NASA DC-8 flight tracks colored and sized by $ClNO_2$ mixing ratio for the Williams Flats fire plume on Aug 3. The inset map shows the approximate location of sampling in Washington State. **B.** Observations of CO (grey), pCl^- (pink), and jNO_3 (black) and **C.** N_2O_5 (red), $ClNO_2$ (yellow) and $P(NO_3)$ (blue) for a subset of crosswind plume transects. **D & E.** Histogram of N_2O_5 and $ClNO_2$ NEMRs from all montane (D) and agricultural (E) fires. Box plots show 10th, 25th, 50th, 75th, and 90th percentiles.

The Normalized Excess Mixing Ratio (NEMR) measures the above background enhancements of a compound *x* relative to the smoke tracer CO (Table S2 and Figure S2-S4). The median N_2O_5 NEMR was 1.0 pptv ppmv^{-1} CO for both agricultural and montane fire groups (Figure 2D and E).The $ClNO_2$ NEMRs, by contrast, differ by a factor of ~6 between montane (0.3 pptv ppmv^{-1}) and agricultural (1.8 pptv ppmv^{-1}) fuels. Agricultural and grass burning emits more Cl^- per kg of fuel burned (emission factor) when compared to temperate and boreal forest burning [*Akagi et al.*, 2011; *Liu et al.*, 2016; *May et al.*, 2014]. Despite considerable variability, the greater median $ClNO_2$ NEMR for agricultural fires is consistent with the observed differences in particulate chloride (pCl^-). DC-8 and Twin Otter observations of the above background pCl^- show that agricultural and grass smoke contains roughly 16× more pCl^- by mass than montane smoke (Text S2 and Figure S5).

2.2 Montane and Agricultural Smoke

To derive $\gamma(N_2O_5)$ from agricultural smoke, we use the calculated NEMR of $ClNO_2$ as a function of the physical plume age shown in Figure 3A. We combine the calculated $ClNO_2$ NEMRs with the relationship between $\gamma(N_2O_5)$ and $\varphi(ClNO_2)$ below to estimate a $\gamma(N_2O_5)$.

$$\gamma(N_2O_5) = 4 \times \frac{k_{N_2O_5}}{c \times SA} \quad (1)$$

$$\phi(ClNO_2) = \frac{k_{ClNO_2}}{k_{N_2O_5}} \quad (2)$$

Here c is the mean molecular speed of N_2O_5 and SA is the aerosol surface area density. Data are arbitrarily separated into low and high NEMR groups. The biexponential fit represents first-order formation (k_{ClNO_2}) and photolytic loss (j_{ClNO_2}) of $ClNO_2$. Constraining the fit to an observed median photolysis rate of j_{ClNO_2} = 3.3 × 10^{-4} s^{-1} (Figure S6A) we find k_{ClNO_2} = 2.0–5.8 × 10^{-4} s^{-1}. Aerosol surface area can vary widely across a plume transect and therefore we chose a range (2–11 × 10^3 μm^2 cm^{-3}) of observed SA representative of most observations in Figure 3A (Figure S6B) and present a sensitivity analysis to this choice in Figure S6C. Finally, we use a median observed temperature of 296 K to find $\gamma(N_2O_5) \times \varphi(ClNO_2)$ = 0.3–4.7 × 10^{-3}.

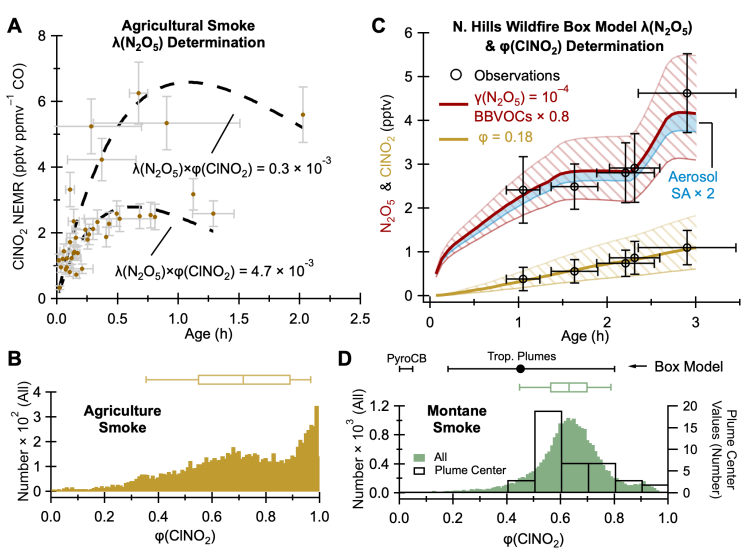

Figure 3. A. Agricultural fire $ClNO_2$ NEMRs vs. plume age. Dashed lines show biexponential fits (see text). **B.** Parametrized $\varphi(ClNO_2)$ of agricultural smoke. **C.** Box model results (lines) compared to observations (markers) of N_2O_5 and $ClNO_2$ from the July 29 North Hills smoke plume with $\gamma(N_2O_5) = 10^{-4}$. The hashed area shows changes to VOCs (N_2O_5) or yield ($ClNO_2$) that encompass observational uncertainty. Transparent blue area shows sensitivity to a factor of 2 increase in aerosol surface area. The apparent discontinuity of N_2O_5 in the model is due to a reduction in the photolysis rate at sunset (2.5 h of age). **D.** Parameterized $\varphi(ClNO_2)$ for montane smoke (filled bars) and transect center observations used in the box model (empty bars). Box model derived $\varphi(ClNO_2)$ is shown as horizontal ranges in black. The black marker indicates the average of the five modeled plumes sampled in the lower troposphere. The range on the model-derived $\varphi(ClNO_2)$ shows the range of the five modeled plumes. Note that within observation uncertainty the full range is 0-1

To estimate $\varphi(ClNO_2)$ we use a laboratory-based parameterization based on observed pCl^- and calculated liquid water content (LWC), hereafter referred to as parameterized $\phi(ClNO_2)$ (section 2.2, S1.4). Figure 3B shows parameterized $\varphi(ClNO_2)$ for all 1 Hz agriculture smoke observations, with median $\varphi(ClNO_2)$ of 0.72. When considering only observations in Figure 2A, used to determine $\gamma(N_2O_5)$, the median is 0.77. Previous field comparisons have shown that parameterized $\varphi(ClNO_2)$ is likely an upper limit [*McDuffie et al.*, 2018b], and therefore the derived $\gamma(N_2O_5)$ is a lower limit range of $0.2–3.6 \times 10^{-3}$.

Montane smoke plumes included several cross-wind transects downwind, which allows for $\gamma(N_2O_5)$ and $\varphi(ClNO_2)$ determination in individual plumes using a constrained 0-D chemical box model [*Decker et al.*, 2021a]. Model input values of $\gamma(N_2O_5)$ were varied between 10^{-4} and 10^{-1} to minimize the difference between the model and observations of N_2O_5. The modeled N_2O_5 is sensitive to NO_3 loss to reactions with VOCs. The model uses VOC emissions from laboratory burn emissions inventories, and these are also varied to improve the agreement between modeled and observed N_2O_5. A comparison of modeled and observed VOCs shows that the majority of the observation-model comparisons remain within the observation uncertainty. Lastly, $\varphi(ClNO_2)$ is varied between 0 and 1. Figures S7-S12 show complete model and observation comparisons.

Figure 3C shows a representative model to observation comparison for N_2O_5 and $ClNO_2$. In all model runs, a $\gamma(N_2O_5)$ of 10^{-4} (one order of magnitude precision, see Figure S7) best reproduces N_2O_5 observations. In these five cases, values of $\gamma(N_2O_5) \geq 10^{-3}$ cannot recreate the N_2O_5 observations without near or complete removal of VOCs, and values of $\gamma(N_2O_5) < 10^{-4}$ require $\varphi(ClNO_2) > 1$ to reproduce $ClNO_2$.

The box model derived $\varphi(ClNO_2)$ ranges from 0.18–0.80 but spans the entire 0-1 range when considering the $ClNO_2$ observational uncertainty (Figure S13). The average model-derived $\varphi(ClNO_2)$ is 0.45 (Figure 3D, black marker). The average of transect-center-parameterized $\varphi(ClNO_2)$ is 0.65, similar to the average of all parameterized $\varphi(ClNO_2)$ of 0.62. Parameterized $\varphi(ClNO_2)$ exceeds the box model, similar to previous field derivations [*McDuffie et al.*, 2018b], although >90% of parameterized $\varphi(ClNO_2)$ lies within the box model derived range (Figure 3D). Lastly, the derived $\varphi(ClNO_2)$ of agricultural smoke is generally greater than montane smoke, consistent with the greater pCl^- in the former.

Values of $\gamma(N_2O_5)$ derived here are smaller than values determined in urban air ($\gamma(N_2O_5)$ 10^{-3} - 10^{-1} [*Brown and Stutz*, 2012; *McDuffie et al.*, 2018a] and comparable to or lower than a limited number of laboratory studies. A chamber study of pyrogenic aerosol for a wire grass fuel

(2.8–6 ± 0.6 × 10^{-3}) and a long leaf pine needle fuel (2.5–3.2 ± 0.4 × 10^{-3}) [*Goldberger et al.*, 2019] are similar to our agricultural fuels result. A flow-tube study of pyrogenic aerosol identified an increase of $\gamma(N_2O_5)$ for high-chloride-containing BB fuels at relative humidity (RH) >80% [*Jahl et al.*, 2021]. This is similar to the average RH (70%) for the agricultural smoke plumes here (Figure S14) and consistent with the observation of greater pCl^- (Figure S5) and larger $\gamma(N_2O_5)$ values (Figure 3) compared to montane smoke.

2.3 PyroCB Processed Smoke

The DC-8 sampled a PyroCB event from the Williams Flats fire on August 8 that reached 6–10 km above sea level, or 5.6 to 1.6 km below the mean tropopause height. We separate our analysis by plume number and transect number as defined by [*Peterson et al.*, 2022].

Observed $P(NO_3)$ and N_2O_5 (Figure 4A) demonstrate the potential for heterogeneous chemistry in the PyroCB injection to the upper atmosphere. Calculated N_2O_5 NEMR increases with calculated physical plume age when separated by plume number (Figure 4B). Enhancement of pCl^- (Figure 4C) demonstrates the potential for $ClNO_2$ production. However, observations of $ClNO_2$ remained at or below the 1Hz I^- CIMS detection limit of 0.05 pptv in Figure 4A and D, limiting the ability to quantify its production. Figure S15 shows that the $ClNO_2$ signal within all PyroCB smoke observations (average ± 1-σ of 0.03 ± 0.10 pptv) is statistically significantly greater ($p<0.001$) than signal outside of the plume (average ± 1-σ of 0.02 ± 0.06 pptv), but the data do not allow quantification of the amount of $ClNO_2$ within the PyroCB.

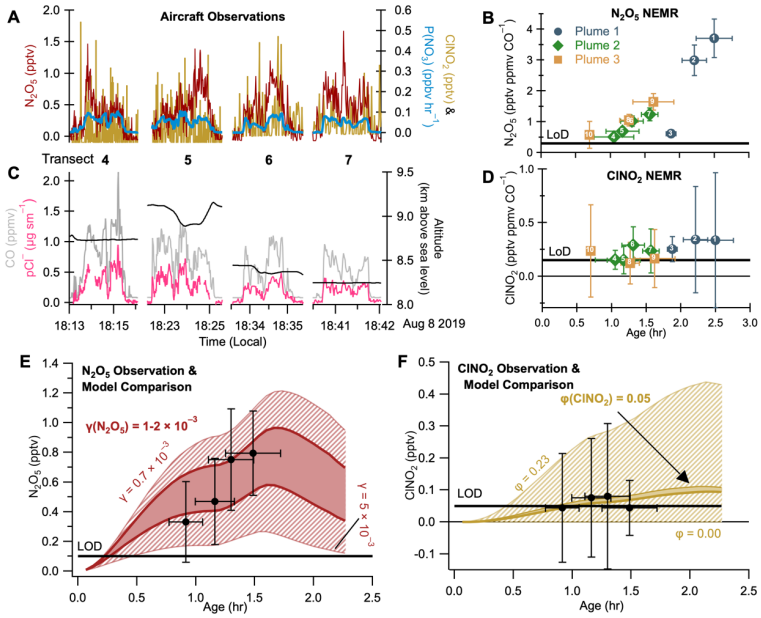

Figure 4. NASA DC-8 observations in a PyroCB. Panels A and B show plume 2 observations only (transects 4–7). **A & C.** Observations of N_2O_5 (red), $ClNO_2$ (yellow) and $P(NO_3)$ (blue), CO (grey), pCl^- (pink), and jNO_3 (black). **B &D.** NEMRs of N_2O_5 and $ClNO_2$. Markers and colors indicate the plume number, and white numbers indicate the transect number. The thick black line indicates the limit of detection (LoD). **E.** Transect center observations of N_2O_5 (black) for plume 2 compared to the model N_2O_5 for a range (7×10^{-4}–5×10^{-3}) of $\gamma(N_2O_5)$. **F.** Transect center observations of $ClNO_2$ (black) for plume 2 compared to the model-derived $ClNO_2$. Solid color is

the result of a $\varphi(ClNO_2) = 0.05$ and a $\gamma(N_2O_5) = 1–2 \times 10^{-3}$ and the hashed area shows a range of possible $\varphi(ClNO_2)$.

Aerosol data are unavailable for plume 3, and plume 1 did not have sufficient semi-Lagrangian crosswind transects required to constrain the model. Therefore, the box model is used to derive $\gamma(N_2O_5)$ and to place an upper limit on $\varphi(ClNO_2)$ for plume 2 only. The model derived $\gamma(N_2O_5) = 0.7–5.0 \times 10^{-3}$ (Figure 4E), which is a factor of 7 – 50 × greater than the $\gamma(N_2O_5)$ values from plumes produced by the same fire but sampled in the lower troposphere.

The model predicts $\varphi(ClNO_2) < 0.05$ to match observations at or below the detection limit (or 0.05 at the LoD), although $\varphi(ClNO_2)$ may be up to 0.23 within the 1-σ determined $ClNO_2$ measurement uncertainty (15% + 0.05 pptv). The average parameterized $\varphi(ClNO_2)$ (0.53) is also lower than tropospheric smoke from the same fire (Figure S16) as a result of increased calculated liquid water fraction (LWF, Figure S17) in the PyroCB. The presence of sufficient pCl^- for average parameterized $\phi(ClNO_2) > 0.5$ suggests that $ClNO_2$ production may occur in PyroCB transported smoke, even if it was observed only at the detection limit in this daytime flight.

2.4 Aged UTLS pyrogenic aerosol

Observations from the ATom campaign provide N_2O_5 observations in the UTLS. We separate our analysis into background and pyrogenic-influenced (defined as >75% of aerosol number concentration containing pyrogenic markers, see SI). The pyrogenic aerosol is estimated to have a physical age of >15 days. A diel model built on the framework of previous model determinations of $\gamma(N_2O_5)$ in the lower troposphere [*McDuffie et al.*, 2018a] is constrained to chemical observations (see SI).

The diel model predicts the median $\gamma(N_2O_5)$ from all background UTLS samples (N=3483) is 2.9×10^{-2} as shown in Figure 5A (grey box and whiskers). The pyrogenic-influenced aerosol has a median $\gamma(N_2O_5)$ of 1.7×10^{-2} (Figure 4A, brown) which is significantly different ($p < 0.001$) than the background aerosol. We also consider a smaller subset of pyrogenic influenced aerosol from ATom previously identified by [*Katich et al.*, 2023] to have originated from PyroCB influence. The resulting $\gamma(N_2O_5)$ of 2.5×10^{-2} is significantly ($p = 0.01$) less than background UTLS aerosol, and greater than our selection of pyrogenic influenced aerosol (Figure S18). Overall, the model predicts that pyrogenic aerosol has a lower rate of N_2O_5 uptake than background UTLS aerosol, yet substantially greater than pyrogenic aerosol in young tropospheric plumes.

The differences in $\gamma(N_2O_5)$ across agricultural, montane, PyroCb, and UTLS data are associated with increased aerosol sulfate fraction. Figure 5B shows a positive trend in $\log(\gamma(N_2O_5))$ as a function of aerosol sulfate fraction distribution. The median sulfate fraction was 1, 5, 9 and 42% in recently-emitted montane, PyroCB, agricultural and aged stratospheric BB aerosol, respectively. Laboratory studies suggest organic coatings inhibit N_2O_5 uptake, which is generally dependent on the organic layer composition and relative humidity [*Gaston et al.*, 2014]. Conversely, increasing sulfate fraction is associated with increasing $\gamma(N_2O_5)$ [*McDuffie et al.*, 2018a]. Sulfate in tropospheric BB plumes arises from oxidation of pyrogenic SO_2 [*Rickly et al.*, 2022], whereas pyrogenic-influenced aerosol in the UTLS takes up sulfate during aging.

Current stratospheric models of BB impacts on stratospheric processes [*Strahan et al.*, 2022; *Yu et al.*, 2021] use a $\gamma(N_2O_5)$ based on aqueous sulfate aerosol. Figure 5C shows $\gamma(N_2O_5)$

values from BB influenced aerosol are a factor of 10–100 lower than pure aqueous sulfate particles [*Burkholder et al.*, 2020]. BB particles are expected to condense organics from low-volatility VOC oxidation products [*Palm et al.*, 2020], forming organic layers that may reduce $\gamma(N_2O_5)$. Evidence of organic markers on stratospheric aerosol was found in some studies of stratospheric BB aerosol [*Bernath et al.*, 2022; *Katich et al.*, 2023], and BB aerosol markers are used here, by definition, to separate BB aerosol from background aerosol.

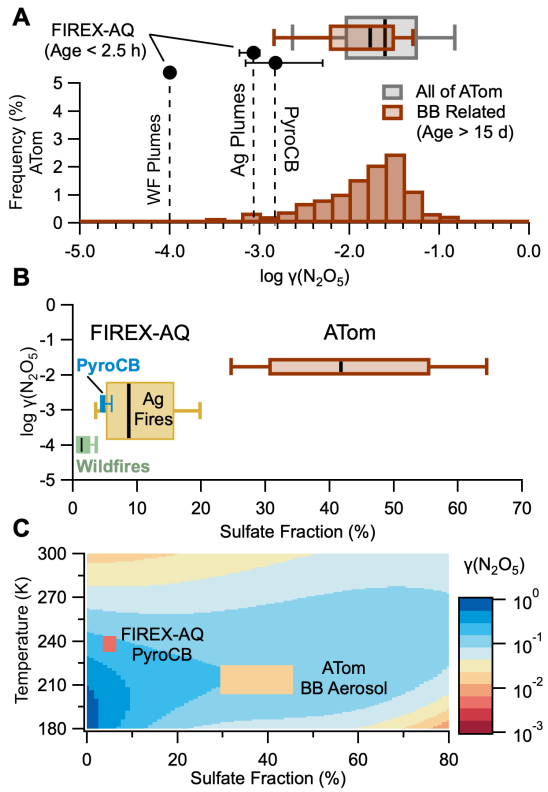

Figure 5. A. Comparison of the model-derived $\gamma(N_2O_5)$ from FIREX-AQ and ATom. Markers show FIREX-AQ results, and the histograms show ATom BB-related $\gamma(N_2O_5)$. The box and whisker plots show the ATom BB-related (brown) and all of the ATom (grey) results from the UTLS. **B**. Log $\gamma(N_2O_5)$ vs aerosol sulfate fraction for FIREX-AQ and ATom. **C**. $\gamma(N_2O_5)$ parametrization from [*Burkholder et al.*, 2020] for aqueous sulfate particles used in stratospheric models compared to results from this work. Marker size represents the interquartile range of temperature and sulfate fraction in this work.

These results indicate $\gamma(N_2O_5)$ values increase for BB particles transported from the troposphere into the UTLS, but never reach values used in stratospheric models. Injection of the chloride-containing aerosol observed in montane smoke or repartitioning of gas phase HCl to particulate organics or reduced nitrogen [*Solomon et al.*, 2023] may result in a non-zero $ClNO_2$ yield, thus introducing chlorine activation pathways currently not considered. Observations presented here cannot quantify $ClNO_2$ production on BB particles transported through a PyroCB but demonstrate potential for this process. Observations of diffuse BB influenced particles in the UTLS from ATom do not have reliable $ClNO_2$ measurements, such that we are unable to assess $ClNO_2$ production on aged, dilute UTLS BB influenced particles. Concentrated BB plumes transported to the stratosphere through PyroCB events, such as the 2020 Australian fires, should

have heterogeneous chemistry similar to that observed here. Recent analysis of high-altitude aircraft data suggests a ubiquitous influence of such events on stratospheric aerosol composition [*Katich et al.*, 2023].

3 Conclusions

Uptake coefficients for N_2O_5 determined from in situ observations are lower on BB aerosol than current model parameterizations. Figure 1 illustrates the observed trends in uptake coefficients from the lower to the upper atmosphere. The $\gamma(N_2O_5)$ on dilute smoke-impacted particles derived in this study is already lower than model parameterizations but likely represents an upper limit for more concentrated smoke such as the 2020 Australian wildfires. We therefore suggest that models of the smoke impact to the UTLS will require revised parameterizations with reduced uptake coefficients.

Second [*Solomon et al.*, 2023] show that chloride uptake by the organic phase of smoke aerosol increases heterogeneous reaction rates of halogen-containing species, thereby activating chlorine radicals that participate in ozone destruction cycles. Our results demonstrate that N_2O_5 uptake on chloride-containing smoke particles produces $ClNO_2$ in the lower atmosphere and has the potential to do so in the upper atmosphere, particularly with increased chloride partitioning to the aerosol phase. We suggest that $ClNO_2$ formation from N_2O_5 uptake on smoke particles injected into the stratosphere during large PyroCB events may be a component of smoke-induced halogen activation cycles that influence stratospheric ozone.

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Data Availability Statement

The aircraft data used in the study are publicly available at https://www-air.larc.nasa.gov/missions/firex-aq/.

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Airborne Observations Constrain Heterogeneous Nitrogen and Halogen Chemistry on Tropospheric and Stratospheric Biomass Burning Aerosol

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Key Points:

- N_2O_5 uptake coefficients are low on young biomass burning smoke and increase with transport through a PyroCB and UTLS aging
- $ClNO_2$ formation is active on biomass burning particles, but decreases with transport to the UTLS
- N_2O_5 uptake coefficients on aged biomass burning particles in the UTLS are significantly lower than those used in model parameterizations

Abstract

Heterogeneous chemical cycles of pyrogenic nitrogen and halides influence tropospheric ozone and affect the stratosphere during extreme pyrocumulonimbus (PyroCB) events. We report field-derived N_2O_5 uptake coefficients, $\gamma(N_2O_5)$, and $ClNO_2$ yields, $\varphi(ClNO_2)$, from two aircraft campaigns observing fresh smoke in the lower and mid troposphere and processed/aged smoke in the upper troposphere and lower stratosphere (UTLS). Derived $\varphi(ClNO_2)$ varied across the full 0–1 range but was typically < 0.5 and smallest in a PyroCB (< 0.05). Derived $\gamma(N_2O_5)$ was low in agricultural smoke ($0.2–3.6 \times 10^{-3}$), extremely low in mid-tropospheric wildfire smoke (0.1×10^{-3}), but larger in PyroCB processed smoke ($0.7–5.0 \times 10^{-3}$). Aged BB aerosol in the UTLS had a higher median $\gamma(N_2O_5)$ of 17×10^{-3} that increased with sulfate and liquid water, but that was nevertheless 1–2 orders of magnitude lower than values for aqueous sulfuric aerosol used in stratospheric models.

Plain Language Summary

The injection of reactive material into Earth's atmosphere from fires affects atmospheric composition at regional and hemispheric scales. Reported stratospheric ozone depletion during extreme events, such as the 2020 Australian wildfires, illustrates one example of fire impacts and the role of heterogeneous (gas-particle) processes. We report field quantification of rates and product yields from airborne observations of smoke. Extremely slow heterogeneous reaction rates on young smoke increase with transport and aging, but upper atmospheric values are still a factor of 10 slower than parameterizations used in stratospheric models. Heterogeneous production of $ClNO_2$, a major lower atmospheric chlorine activation pathway, may be active on biomass burning aerosol in the upper atmosphere.

1 Introduction

Biomass burning (BB) impacts global atmospheric chemical processes and is increasing regionally due to climate-change-induced trends in fire weather [*Jones et al.*, 2022]. Fires emit nitrogen oxides ($NO + NO_2 = NO_x$), volatile organic compounds (VOCs) and aerosol that affect tropospheric oxidants [*Koss et al.*, 2018]. Roughly 10% of global inorganic chloride enters the atmosphere by BB [*Wang et al.*, 2019], and a small fraction may be subsequently activated to inorganic chlorine radicals. The co-emission of NO_x and VOCs enhances tropospheric O_3 globally on a scale comparable to, or greater than, urban pollution [*Bourgeois et al.*, 2021; *Xu et al.*, 2021].

Large wildfires can form pyrocumulonimbus (PyroCB) towers [*Peterson et al.*, 2021; *Peterson et al.*, 2022] that loft pyrogenic emissions to the upper troposphere / lower stratosphere (UTLS). Aerosol injection from the 2019–2020 Australian New Year fires altered the partitioning of total reactive chlorine (Cl_y) and nitrogen (NO_y) species and led to stratospheric O_3 loss through heterogeneous reactions [*Bernath et al.*, 2022; *Solomon et al.*, 2022; *Solomon et al.*, 2023; *Strahan et al.*, 2022]. One of the major heterogeneous reactions is uptake of N_2O_5, which in stratospheric models produces exclusively nitric acid, HNO_3 [*Küll et al.*, 2002; *Zambri et al.*, 2019].

$$N_2O_{5(g)} + H_2O_{(l)} \rightarrow 2HNO_{3(g)} \qquad (R1, \gamma)$$

Here, γ is the reactive uptake coefficient [*Ravishankara*, 1997]. Reaction (1) influences NO_x and O_3 in both the stratosphere and troposphere by altering the partitioning of reactive nitrogen and the availability of NO_x [*Dentener and Crutzen*, 1993; *Solomon*, 1999].

Tropospheric observations have shown substantial yields of nitryl chloride, $ClNO_2$, from chloride-containing aerosol [*McDuffie et al.*, 2018a], represented below as reaction with HCl.

$$N_2O_{5(g)} + HCl_{(aq)} \rightarrow ClNO_{2(g)} + HNO_{3(g)} \qquad (R2, \phi)$$

Photolysis of $ClNO_2$ produces Cl. The yield, ϕ, for R2 is the molar ratio of $ClNO_2$ produced per N_2O_5 reacted. Due in part to the lack of chloride partitioning to highly-acidic stratospheric aerosol, R2 has been considered an unimportant contribution to stratospheric halogen activation [*Solomon*, 1999] despite its prevalence in the troposphere. Figure 1 illustrates biomass burning emissions to and heterogeneous chemistry in different regions of the atmosphere.

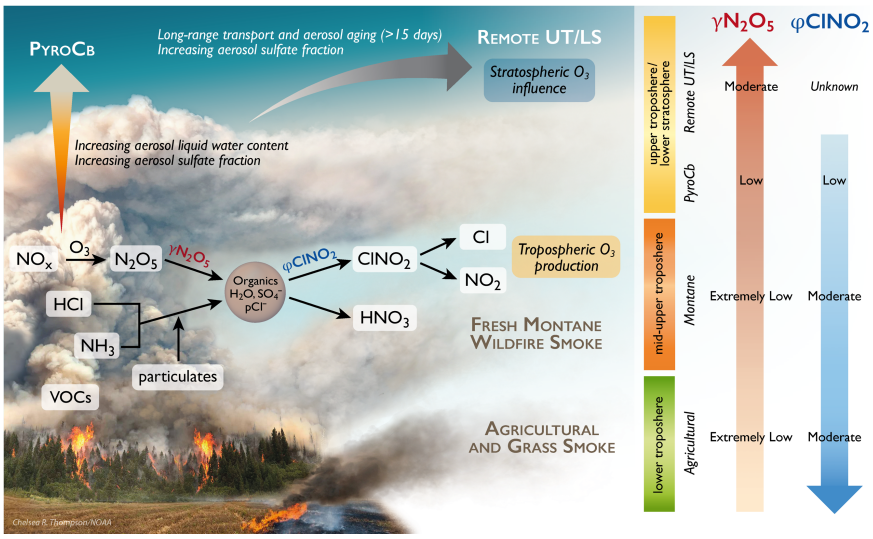

Figure 1. Biomass burning emission to different altitudes and heterogeneous chemistry of N_2O_5 and $ClNO_2$. Arrows on the right-hand side illustrate trends in heterogeneous parameters, $\gamma(N_2O_5)$ and $\phi(ClNO_2)$, determined from aircraft observations in this work**.**

Rates and yields of N_2O_5 heterogeneous chemistry on BB particles are uncertain, especially in the UTLS [*Solomon et al.*, 2022; *Strahan et al.*, 2022; *Yu et al.*, 2021]. Models assume similarity between BB and volcanic particles but are unable to reproduce remote sensing observations of Cl_y and NO_y, suggesting substantial differences in heterogeneous chemistry. There exist limited BB laboratory studies on $\gamma(N_2O_5)$ or $\phi(ClNO_2)$ [*Ahern et al.*, 2018; *Goldberger et al.*, 2019; *Jahl et al.*, 2021] and, to our knowledge, there are no field-derived values. Tropospheric and stratospheric models of BB impacts are poorly constrained for $\gamma(N_2O_5)$ and have not considered $\phi(ClNO_2)$.

We present aircraft observations of N_2O_5, $ClNO_2$ and field-derived values for $\gamma(N_2O_5)$ and $\varphi(ClNO_2)$ in smoke. The analysis utilizes aircraft observations from the 2019 Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ) campaign [*Warneke et al.*, 2023] and the 2017–2018 Atmospheric Tomography mission (ATom) [*Thompson et al.*, 2022]. We derive $\gamma(N_2O_5)$ and $\varphi(ClNO_2)$ for montane and agricultural smoke in the troposphere and a

PyroCB injection of smoke to the upper troposphere from FIREX-AQ. We derive $\gamma(N_2O_5)$ for stratospheric BB-influenced aerosol from ATom. Derived N_2O_5 uptake coefficients are considerably lower than current model parameterizations. Halogen activation through $ClNO_2$ from NO_x and particulate chloride (pCl^-) is prevalent in low altitudes and possible, yet unquantified, at high altitude.

2 Results and Discussion

2.1 $ClNO_2$ and N_2O_5 Observations

Figure 2A shows the flight track of the NASA DC-8 aircraft sampling the Williams Flats fire during FIREX-AQ on 3 Aug 2019 colored and sized by observed $ClNO_2$. Both N_2O_5 and $ClNO_2$ exhibit clear enhancements despite significant photolysis rates of NO_3 (jNO_3) (Figure 2B-C). These enhancements are associated with CO, a smoke tracer, and rapid (>1 ppbv hr^{-1}) NO_3 production, $P(NO_3) = k[NO_2][O_3]$, where k is the bimolecular rate coefficient for reaction of NO_2 with O_3.

Median j_{NO_3} at the center of wildfire and agriculture plume transects (0.14 s^{-1} and 0.19 s^{-1} respectively) were 15–30% lower than values outside of plumes (0.16 and 0.20 s^{-1} respectively). In large wildfire plumes jNO_3 attenuation was a factor of ten or more (Figure 2B and C), but small agricultural plumes exhibited no attenuation (Figure S1). Previous analyses of FIREX-AQ plumes found that NO_3 photolysis and reaction with NO are not major NO_3 loss pathways regardless of time of day [*Decker et al.*, 2021a; *Decker et al.*, 2021b]. Rapid $P(NO_3)$ together with large concentrations of highly reactive VOCs and aerosol surface area control NO_3 and N_2O_5 chemistry. Plumes with measurable daytime N_2O_5 provide measures of NO_3 reactivity and N_2O_5 heterogeneous uptake for these species that are otherwise important only at night in non-fire environments.

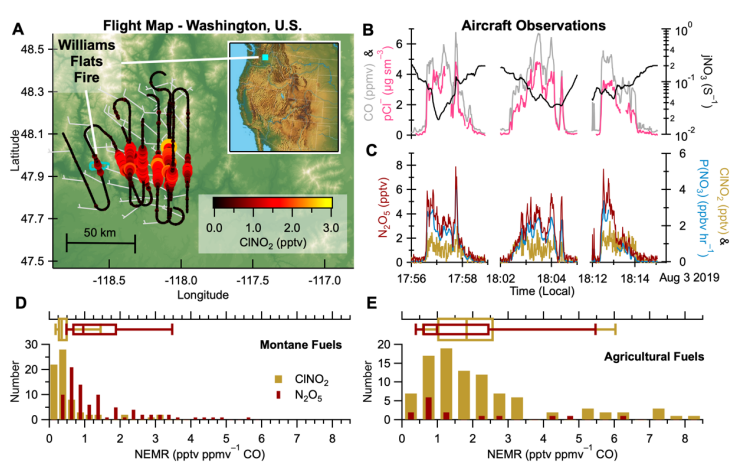

Figure 2. A. NASA DC-8 flight tracks colored and sized by $ClNO_2$ mixing ratio for the Williams Flats fire plume on Aug 3. The inset map shows the approximate location of sampling in Washington State. **B.** Observations of CO (grey), pCl^- (pink), and jNO_3 (black) and **C.** N_2O_5 (red), $ClNO_2$ (yellow) and $P(NO_3)$ (blue) for a subset of crosswind plume transects. **D & E.** Histogram of N_2O_5 and $ClNO_2$ NEMRs from all montane (D) and agricultural (E) fires. Box plots show 10th, 25th, 50th, 75th, and 90th percentiles.

The Normalized Excess Mixing Ratio (NEMR) measures the above background enhancements of a compound *x* relative to the smoke tracer CO (Table S2 and Figure S2-S4). The median N_2O_5 NEMR was 1.0 pptv ppmv^{-1} CO for both agricultural and montane fire groups (Figure 2D and E).The $ClNO_2$ NEMRs, by contrast, differ by a factor of ~6 between montane (0.3 pptv ppmv^{-1}) and agricultural (1.8 pptv ppmv^{-1}) fuels. Agricultural and grass burning emits more Cl^- per kg of fuel burned (emission factor) when compared to temperate and boreal forest burning [*Akagi et al.*, 2011; *Liu et al.*, 2016; *May et al.*, 2014]. Despite considerable variability, the greater median $ClNO_2$ NEMR for agricultural fires is consistent with the observed differences in particulate chloride (pCl^-). DC-8 and Twin Otter observations of the above background pCl^- show that agricultural and grass smoke contains roughly 16× more pCl^- by mass than montane smoke (Text S2 and Figure S5).

2.2 Montane and Agricultural Smoke

To derive $\gamma(N_2O_5)$ from agricultural smoke, we use the calculated NEMR of $ClNO_2$ as a function of the physical plume age shown in Figure 3A. We combine the calculated $ClNO_2$ NEMRs with the relationship between $\gamma(N_2O_5)$ and $\varphi(ClNO_2)$ below to estimate a $\gamma(N_2O_5)$.

$$\gamma(N_2O_5) = 4 \times \frac{k_{N_2O_5}}{c \times SA} \quad (1)$$

$$\phi(ClNO_2) = \frac{k_{ClNO_2}}{k_{N_2O_5}} \quad (2)$$

Here c is the mean molecular speed of N_2O_5 and SA is the aerosol surface area density. Data are arbitrarily separated into low and high NEMR groups. The biexponential fit represents first-order formation (k_{ClNO_2}) and photolytic loss (j_{ClNO_2}) of $ClNO_2$. Constraining the fit to an observed median photolysis rate of j_{ClNO_2} = 3.3 × 10^{-4} s^{-1} (Figure S6A) we find k_{ClNO_2} = 2.0–5.8 × 10^{-4} s^{-1}. Aerosol surface area can vary widely across a plume transect and therefore we chose a range (2–11 × 10^3 μm^2 cm^{-3}) of observed SA representative of most observations in Figure 3A (Figure S6B) and present a sensitivity analysis to this choice in Figure S6C. Finally, we use a median observed temperature of 296 K to find $\gamma(N_2O_5) \times \varphi(ClNO_2)$ = 0.3–4.7 × 10^{-3}.

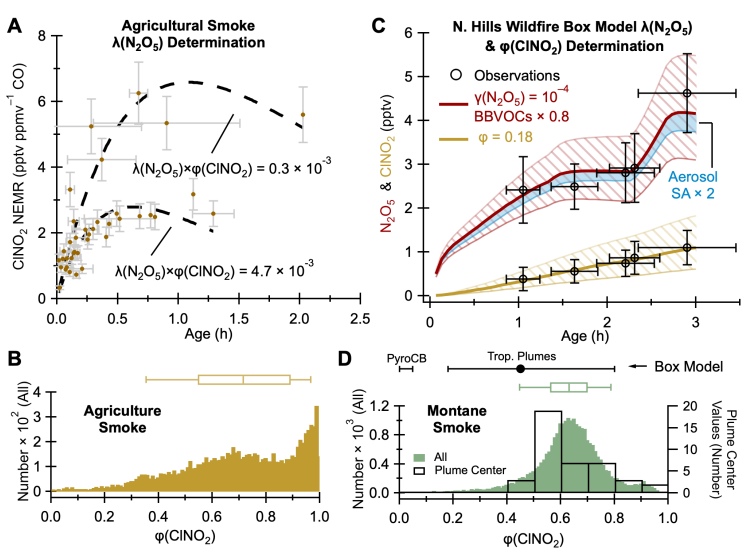

Figure 3. A. Agricultural fire $ClNO_2$ NEMRs vs. plume age. Dashed lines show biexponential fits (see text). **B.** Parametrized $\varphi(ClNO_2)$ of agricultural smoke. **C.** Box model results (lines) compared to observations (markers) of N_2O_5 and $ClNO_2$ from the July 29 North Hills smoke plume with $\gamma(N_2O_5) = 10^{-4}$. The hashed area shows changes to VOCs (N_2O_5) or yield ($ClNO_2$) that encompass observational uncertainty. Transparent blue area shows sensitivity to a factor of 2 increase in aerosol surface area. The apparent discontinuity of N_2O_5 in the model is due to a reduction in the photolysis rate at sunset (2.5 h of age). **D.** Parameterized $\varphi(ClNO_2)$ for montane smoke (filled bars) and transect center observations used in the box model (empty bars). Box model derived $\varphi(ClNO_2)$ is shown as horizontal ranges in black. The black marker indicates the average of the five modeled plumes sampled in the lower troposphere. The range on the model-derived $\varphi(ClNO_2)$ shows the range of the five modeled plumes. Note that within observation uncertainty the full range is 0-1

To estimate $\varphi(ClNO_2)$ we use a laboratory-based parameterization based on observed pCl^- and calculated liquid water content (LWC), hereafter referred to as parameterized $\phi(ClNO_2)$ (section 2.2, S1.4). Figure 3B shows parameterized $\varphi(ClNO_2)$ for all 1 Hz agriculture smoke observations, with median $\varphi(ClNO_2)$ of 0.72. When considering only observations in Figure 2A, used to determine $\gamma(N_2O_5)$, the median is 0.77. Previous field comparisons have shown that parameterized $\varphi(ClNO_2)$ is likely an upper limit [*McDuffie et al.*, 2018b], and therefore the derived $\gamma(N_2O_5)$ is a lower limit range of $0.2–3.6 \times 10^{-3}$.

Montane smoke plumes included several cross-wind transects downwind, which allows for $\gamma(N_2O_5)$ and $\varphi(ClNO_2)$ determination in individual plumes using a constrained 0-D chemical box model [*Decker et al.*, 2021a]. Model input values of $\gamma(N_2O_5)$ were varied between 10^{-4} and 10^{-1} to minimize the difference between the model and observations of N_2O_5. The modeled N_2O_5 is sensitive to NO_3 loss to reactions with VOCs. The model uses VOC emissions from laboratory burn emissions inventories, and these are also varied to improve the agreement between modeled and observed N_2O_5. A comparison of modeled and observed VOCs shows that the majority of the observation-model comparisons remain within the observation uncertainty. Lastly, $\varphi(ClNO_2)$ is varied between 0 and 1. Figures S7-S12 show complete model and observation comparisons.

Figure 3C shows a representative model to observation comparison for N_2O_5 and $ClNO_2$. In all model runs, a $\gamma(N_2O_5)$ of 10^{-4} (one order of magnitude precision, see Figure S7) best reproduces N_2O_5 observations. In these five cases, values of $\gamma(N_2O_5) \geq 10^{-3}$ cannot recreate the N_2O_5 observations without near or complete removal of VOCs, and values of $\gamma(N_2O_5) < 10^{-4}$ require $\varphi(ClNO_2) > 1$ to reproduce $ClNO_2$.

The box model derived $\varphi(ClNO_2)$ ranges from 0.18–0.80 but spans the entire 0-1 range when considering the $ClNO_2$ observational uncertainty (Figure S13). The average model-derived $\varphi(ClNO_2)$ is 0.45 (Figure 3D, black marker). The average of transect-center-parameterized $\varphi(ClNO_2)$ is 0.65, similar to the average of all parameterized $\varphi(ClNO_2)$ of 0.62. Parameterized $\varphi(ClNO_2)$ exceeds the box model, similar to previous field derivations [*McDuffie et al.*, 2018b], although >90% of parameterized $\varphi(ClNO_2)$ lies within the box model derived range (Figure 3D). Lastly, the derived $\varphi(ClNO_2)$ of agricultural smoke is generally greater than montane smoke, consistent with the greater pCl^- in the former.

Values of $\gamma(N_2O_5)$ derived here are smaller than values determined in urban air ($\gamma(N_2O_5)$ 10^{-3} - 10^{-1} [*Brown and Stutz*, 2012; *McDuffie et al.*, 2018a] and comparable to or lower than a limited number of laboratory studies. A chamber study of pyrogenic aerosol for a wire grass fuel

(2.8–6 ± 0.6 × 10^{-3}) and a long leaf pine needle fuel (2.5–3.2 ± 0.4 × 10^{-3}) [*Goldberger et al.*, 2019] are similar to our agricultural fuels result. A flow-tube study of pyrogenic aerosol identified an increase of $\gamma(N_2O_5)$ for high-chloride-containing BB fuels at relative humidity (RH) >80% [*Jahl et al.*, 2021]. This is similar to the average RH (70%) for the agricultural smoke plumes here (Figure S14) and consistent with the observation of greater pCl^- (Figure S5) and larger $\gamma(N_2O_5)$ values (Figure 3) compared to montane smoke.

2.3 PyroCB Processed Smoke

The DC-8 sampled a PyroCB event from the Williams Flats fire on August 8 that reached 6–10 km above sea level, or 5.6 to 1.6 km below the mean tropopause height. We separate our analysis by plume number and transect number as defined by [*Peterson et al.*, 2022].

Observed $P(NO_3)$ and N_2O_5 (Figure 4A) demonstrate the potential for heterogeneous chemistry in the PyroCB injection to the upper atmosphere. Calculated N_2O_5 NEMR increases with calculated physical plume age when separated by plume number (Figure 4B). Enhancement of pCl^- (Figure 4C) demonstrates the potential for $ClNO_2$ production. However, observations of $ClNO_2$ remained at or below the 1Hz I^- CIMS detection limit of 0.05 pptv in Figure 4A and D, limiting the ability to quantify its production. Figure S15 shows that the $ClNO_2$ signal within all PyroCB smoke observations (average ± 1-σ of 0.03 ± 0.10 pptv) is statistically significantly greater ($p<0.001$) than signal outside of the plume (average ± 1-σ of 0.02 ± 0.06 pptv), but the data do not allow quantification of the amount of $ClNO_2$ within the PyroCB.

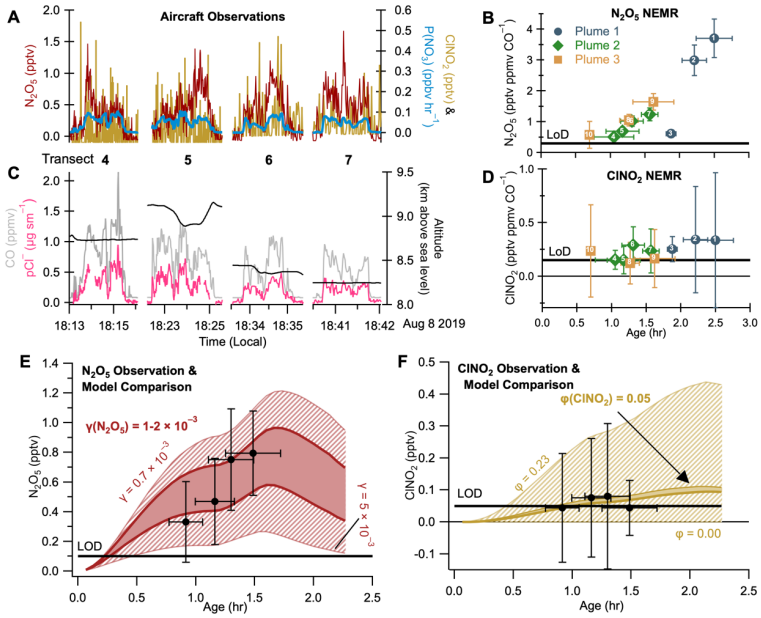

Figure 4. NASA DC-8 observations in a PyroCB. Panels A and B show plume 2 observations only (transects 4–7). **A & C.** Observations of N_2O_5 (red), $ClNO_2$ (yellow) and $P(NO_3)$ (blue), CO (grey), pCl^- (pink), and jNO_3 (black). **B &D.** NEMRs of N_2O_5 and $ClNO_2$. Markers and colors indicate the plume number, and white numbers indicate the transect number. The thick black line indicates the limit of detection (LoD). **E.** Transect center observations of N_2O_5 (black) for plume 2 compared to the model N_2O_5 for a range (7×10^{-4}–5×10^{-3}) of $\gamma(N_2O_5)$. **F.** Transect center observations of $ClNO_2$ (black) for plume 2 compared to the model-derived $ClNO_2$. Solid color is

the result of a $\varphi(ClNO_2) = 0.05$ and a $\gamma(N_2O_5) = 1–2 \times 10^{-3}$ and the hashed area shows a range of possible $\varphi(ClNO_2)$.

Aerosol data are unavailable for plume 3, and plume 1 did not have sufficient semi-Lagrangian crosswind transects required to constrain the model. Therefore, the box model is used to derive $\gamma(N_2O_5)$ and to place an upper limit on $\varphi(ClNO_2)$ for plume 2 only. The model derived $\gamma(N_2O_5) = 0.7–5.0 \times 10^{-3}$ (Figure 4E), which is a factor of 7 – 50 × greater than the $\gamma(N_2O_5)$ values from plumes produced by the same fire but sampled in the lower troposphere.

The model predicts $\varphi(ClNO_2) < 0.05$ to match observations at or below the detection limit (or 0.05 at the LoD), although $\varphi(ClNO_2)$ may be up to 0.23 within the 1-σ determined $ClNO_2$ measurement uncertainty (15% + 0.05 pptv). The average parameterized $\varphi(ClNO_2)$ (0.53) is also lower than tropospheric smoke from the same fire (Figure S16) as a result of increased calculated liquid water fraction (LWF, Figure S17) in the PyroCB. The presence of sufficient pCl^- for average parameterized $\phi(ClNO_2) > 0.5$ suggests that $ClNO_2$ production may occur in PyroCB transported smoke, even if it was observed only at the detection limit in this daytime flight.

2.4 Aged UTLS pyrogenic aerosol

Observations from the ATom campaign provide N_2O_5 observations in the UTLS. We separate our analysis into background and pyrogenic-influenced (defined as >75% of aerosol number concentration containing pyrogenic markers, see SI). The pyrogenic aerosol is estimated to have a physical age of >15 days. A diel model built on the framework of previous model determinations of $\gamma(N_2O_5)$ in the lower troposphere [*McDuffie et al.*, 2018a] is constrained to chemical observations (see SI).

The diel model predicts the median $\gamma(N_2O_5)$ from all background UTLS samples (N=3483) is 2.9×10^{-2} as shown in Figure 5A (grey box and whiskers). The pyrogenic-influenced aerosol has a median $\gamma(N_2O_5)$ of 1.7×10^{-2} (Figure 4A, brown) which is significantly different ($p < 0.001$) than the background aerosol. We also consider a smaller subset of pyrogenic influenced aerosol from ATom previously identified by [*Katich et al.*, 2023] to have originated from PyroCB influence. The resulting $\gamma(N_2O_5)$ of 2.5×10^{-2} is significantly ($p = 0.01$) less than background UTLS aerosol, and greater than our selection of pyrogenic influenced aerosol (Figure S18). Overall, the model predicts that pyrogenic aerosol has a lower rate of N_2O_5 uptake than background UTLS aerosol, yet substantially greater than pyrogenic aerosol in young tropospheric plumes.

The differences in $\gamma(N_2O_5)$ across agricultural, montane, PyroCb, and UTLS data are associated with increased aerosol sulfate fraction. Figure 5B shows a positive trend in $\log(\gamma(N_2O_5))$ as a function of aerosol sulfate fraction distribution. The median sulfate fraction was 1, 5, 9 and 42% in recently-emitted montane, PyroCB, agricultural and aged stratospheric BB aerosol, respectively. Laboratory studies suggest organic coatings inhibit N_2O_5 uptake, which is generally dependent on the organic layer composition and relative humidity [*Gaston et al.*, 2014]. Conversely, increasing sulfate fraction is associated with increasing $\gamma(N_2O_5)$ [*McDuffie et al.*, 2018a]. Sulfate in tropospheric BB plumes arises from oxidation of pyrogenic SO_2 [*Rickly et al.*, 2022], whereas pyrogenic-influenced aerosol in the UTLS takes up sulfate during aging.

Current stratospheric models of BB impacts on stratospheric processes [*Strahan et al.*, 2022; *Yu et al.*, 2021] use a $\gamma(N_2O_5)$ based on aqueous sulfate aerosol. Figure 5C shows $\gamma(N_2O_5)$

values from BB influenced aerosol are a factor of 10–100 lower than pure aqueous sulfate particles [*Burkholder et al.*, 2020]. BB particles are expected to condense organics from low-volatility VOC oxidation products [*Palm et al.*, 2020], forming organic layers that may reduce $\gamma(N_2O_5)$. Evidence of organic markers on stratospheric aerosol was found in some studies of stratospheric BB aerosol [*Bernath et al.*, 2022; *Katich et al.*, 2023], and BB aerosol markers are used here, by definition, to separate BB aerosol from background aerosol.

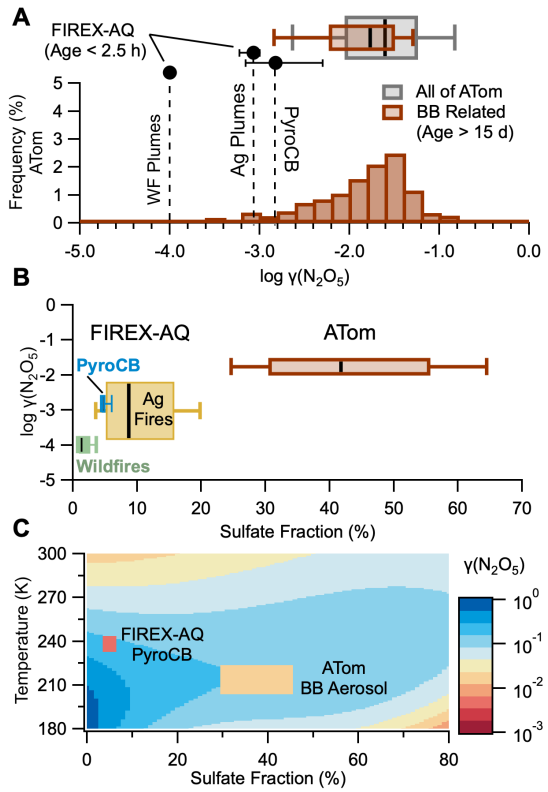

Figure 5. A. Comparison of the model-derived $\gamma(N_2O_5)$ from FIREX-AQ and ATom. Markers show FIREX-AQ results, and the histograms show ATom BB-related $\gamma(N_2O_5)$. The box and whisker plots show the ATom BB-related (brown) and all of the ATom (grey) results from the UTLS. **B**. Log $\gamma(N_2O_5)$ vs aerosol sulfate fraction for FIREX-AQ and ATom. **C**. $\gamma(N_2O_5)$ parametrization from [*Burkholder et al.*, 2020] for aqueous sulfate particles used in stratospheric models compared to results from this work. Marker size represents the interquartile range of temperature and sulfate fraction in this work.

These results indicate $\gamma(N_2O_5)$ values increase for BB particles transported from the troposphere into the UTLS, but never reach values used in stratospheric models. Injection of the chloride-containing aerosol observed in montane smoke or repartitioning of gas phase HCl to particulate organics or reduced nitrogen [*Solomon et al.*, 2023] may result in a non-zero $ClNO_2$ yield, thus introducing chlorine activation pathways currently not considered. Observations presented here cannot quantify $ClNO_2$ production on BB particles transported through a PyroCB but demonstrate potential for this process. Observations of diffuse BB influenced particles in the UTLS from ATom do not have reliable $ClNO_2$ measurements, such that we are unable to assess $ClNO_2$ production on aged, dilute UTLS BB influenced particles. Concentrated BB plumes transported to the stratosphere through PyroCB events, such as the 2020 Australian fires, should

have heterogeneous chemistry similar to that observed here. Recent analysis of high-altitude aircraft data suggests a ubiquitous influence of such events on stratospheric aerosol composition [*Katich et al.*, 2023].

3 Conclusions

Uptake coefficients for N_2O_5 determined from in situ observations are lower on BB aerosol than current model parameterizations. Figure 1 illustrates the observed trends in uptake coefficients from the lower to the upper atmosphere. The $\gamma(N_2O_5)$ on dilute smoke-impacted particles derived in this study is already lower than model parameterizations but likely represents an upper limit for more concentrated smoke such as the 2020 Australian wildfires. We therefore suggest that models of the smoke impact to the UTLS will require revised parameterizations with reduced uptake coefficients.

Second [*Solomon et al.*, 2023] show that chloride uptake by the organic phase of smoke aerosol increases heterogeneous reaction rates of halogen-containing species, thereby activating chlorine radicals that participate in ozone destruction cycles. Our results demonstrate that N_2O_5 uptake on chloride-containing smoke particles produces $ClNO_2$ in the lower atmosphere and has the potential to do so in the upper atmosphere, particularly with increased chloride partitioning to the aerosol phase. We suggest that $ClNO_2$ formation from N_2O_5 uptake on smoke particles injected into the stratosphere during large PyroCB events may be a component of smoke-induced halogen activation cycles that influence stratospheric ozone.

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Data Availability Statement

The aircraft data used in the study are publicly available at https://www-air.larc.nasa.gov/missions/firex-aq/.

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Geophysical Research Letters

Supporting Information for

Airborne Observations Constrain Heterogeneous Nitrogen and Halogen Chemistry on Tropospheric and Stratospheric Biomass Burning Aerosol

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Contents of this file

Introduction

The supporting information includes text describing the FIREX-AQ and ATom observations as well as additional details about analysis methods such as box models and parameterizations. It further includes a series of supporting figures and captions

S1 Observations and Models

FIREX-AQ was a large-scale field research campaign focusing on wildfire smoke plumes in the western U.S. and prescribed agricultural burning smoke plumes in the southeastern U.S. during the summer of 2019. We use observations from the NOAA Chemistry Twin Otter and NASA DC-8 aircraft. The NASA Atmospheric Tomography (ATom) mission was a large-scale research campaign focusing on remote tropospheric, UTLS, and stratospheric air [*Thompson et al.*, 2022]. Data here are from September–October 2017 (ATom-3) and April–May 2018 (ATom-4). Table S1 lists instrumentation used in this analysis. In-situ observations from ATom and FIREX-AQ are available as a merged dataset and found in [*Wofsy et al.*, 2018] and [*Warneke et al.*, 2023], respectively. See further details in the SI.

Two models are used: an iterative 0-D box model constrained to crosswind transects of wildfire plumes sampled during FIREX-AQ and an iterative diel model constrained to observations for each parcel of sampled air above an arbitrary elevation cutoff of 6 km during ATom-3 and ATom-4. Calculated $\varphi(ClNO_2)$ uses a parameterization determined from laboratory experiments [*Bertram et al.*, 2009; *Roberts et al.*, 2009]. See further details below.

S1.1 FIREX-AQ Observations

From the Twin Otter, we use a commercial cavity ringdown spectrometer (Picarro) for measurements of CO. We also use measurements of non-refractory PM_1 chemical composition from an Aerosol Mass Spectrometer (AMS) [*Liggio et al.*, 2016].

From the DC-8, we use measurements of CO from a tunable diode laser spectrometer when available and from an integrated cavity output spectrometer when unavailable. Measurement of NO is by laser-induced fluorescence (LIF). Measurements of NO_y and O_3 are provided by a NOAA chemiluminescence (CL) instrument. We use an average measurement of NO_2 from both the NOAA CL instrument and a NOAA cavity-enhanced spectrometer. Measurements of HONO are taken from the NOAA I^- ToF CIMS. Measurements of VOCs are taken from the NOAA I^- ToF CIMS [*Neuman et al.*, 2016; *Veres et al.*, 2020], NOAA Proton Transfer Reaction (PTR) MS [*Koss et al.*, 2018], and the University of Innsbruck PTR-MS [*Müller et al.*, 2014]. Aerosol surface area measurements are taken from a laser aerosol spectrometer (LAS, 1 Hz) for aerosol sizes between 0.1 μm and 5 μm. Measurements of non-refractory PM_1 are from the CU HR-AMS, 1-5 Hz [*Guo et al.*, 2021]. Spectrally resolved actinic flux was measured with separate upward and downward-facing actinic flux optics.

The sensitivity of the iodide CIMS to $ClNO_2$ was determined using methods similar to those described in [*Lao et al.*, 2020]. A Cl_2 mixture (4.167 ppm Cl_2 in 50% RH zero air) was passed through a $NaNO_2$-coated PFA tube to dynamically produce $ClNO_2$:

$$Cl_2\,(g) + NO_2\,(aq)^- \rightarrow ClNO_2\,(aq) + Cl\,(aq)^- \qquad \text{(RS1)}$$

$ClNO_2$ (aq) $\rightarrow$ $ClNO_2$ (g) (RS2)

The source output was calibrated by a chemiluminescence NO_y instrument that measures NO, NO_2 and $ClNO_2$ as NO_y [*Thaler et al.*, 2011]. The calibrated $ClNO_2$ source was then used for calibration of the iodide CIMS.

An N_2O_5 calibration source was produced online via the reaction of O_3 with NO_2 to form N_2O_5 [*Lee et al.*, 2018]. The output of the calibration source was measured using a cavity ring down instrument for direct detection of N_2O_5 [*Wagner et al.*, 2011]. The iodide CIMS was calibrated by comparing the observed signal at $I{\bullet}N_2O_5^-$ to the CRDS determined N_2O_5 concentration.

$ClNO_2$ is reported with a precision of 0.1 ppt for 1s data and accuracy of 15% + 0.05 ppt and N_2O_5 is reported with a precision of 0.1 ppt for 1s data and accuracy of 15% + 2 ppt. We report the precision as the 1 sigma limit of detection based on signal variability during instrument zeroing in flight. The accuracy of these measurements is quantified as a % based on calibration errors in addition to the error associated with variability instrument background determinations. The latter part of this quantity, 0.05 ppt for $ClNO_2$ and 2 ppt for N_2O_5, is defined as the RMS of consecutive background determinations to quantify the error due to linear interpolation between background points. Instrument backgrounds were performed by overflowing the inlet with humidified nitrogen (N_2) for a period of at least 30 seconds every 10 minutes.

S1.2 ATom Observations

Aerosol sizing and composition data incorporate measurements from the CU HR-AMS [*Guo et al.*, 2021] and bulk aerosol size distributions [*Brock et al.*, 2019]. A Cloud, Aerosol, and Precipitation Spectrometer was used to reject periods of sampling within clouds. Measurements of single particle composition and particle mixing states are from a single-particle laser ionization mass spectrometer (PALMS). The amount of pyrogenic influence is a semi-empirical classification based on the relative peak areas of carbon ($^{12}C^+$) and potassium ($^{39}K^+$) [*Schill et al.*, 2020]. Mixing ratios of NO, NO_2, and O_3 were measured with the NOAA CL and measurements of OH and HO_2 were by LIF. Mixing ratio of N_2O_5 was measured by the NOAA I^- ToF CIMS (LoD = 0.1 pptv, 1-σ, 1Hz, Figure S19) [*Veres et al.*, 2020].

S1.3 Box Models

The iterative 0-D box model of wildfire plumes is described in detail by Decker et al. [*Decker et al.*, 2021] and discussed briefly here. We model six smoke plumes from three fires sampled on six separate days (Williams Flats, North Hills, and Shady – see Table S3). Box modeling was performed using the Framework for 0-D Atmospheric Modeling (F0AM) [*Wolfe et al.*, 2016] and includes chemistry from the Master Chemical Mechanism (MCM, v3.3.1 via http://mcm.york.ac.uk, last access: 23 September 2021) [*Bloss et al.*, 2005], with additional BB mechanisms [*Decker et al.*, 2021]. The model considers only transect-center observations defined as the observations which correspond to the greatest 5% of CO enhancements.

The ATom model builds on the framework of previous model determinations of $\gamma(N_2O_5)$ in the lower troposphere constrained by aircraft measurements [*McDuffie et al.*, 2018a], with changes for the ATom flight scheme and distinct conditions of the UTLS

described here. A run is initiated at the time of local sunset prior to the observation for each 10 s data average and run for a 24-hour diel cycle through to the local sunset after the time of each observation, with diel profiles of photolysis rates and OH concentrations constrained to observations. Mixing ratios of long-lived species, such as H_2O and aerosol surface area, are held constant over the 24 h period. The model iterates the initial NO_x until NO is within 20% of observations while NO_2 remains unconstrained. Next, $k_{N_2O_5}$ is iterated until N_2O_5 is within 20% of observations and $\gamma(N_2O_5)$ is calculated from observed temperature and aerosol surface area. We select only data > 6 km that include the required observations for the model above the instrument LoD (77% of data). Of the points modeled, 48% (17,455 determinations) converge on a $k_{N_2O_5}$ between 1×10^{-8} and 1.

S1.4 Parameterization of $\varphi(ClNO_2)$

Production of $ClNO_2$ is considered to proceed by ionization of N_2O_5 to form $NO_2^+ + NO_3^-$. The formation of either HNO_3 or $ClNO_2$ is based on kinetic competition for the reaction of NO_2^+ with H_2O or Cl^-, respectively [*Bertram et al.*, 2009]. Re-formation of N_2O_5 may also be competitive due to significant concentrations of NO_3^- relative to Cl^- (Figure S20). Therefore, this competitive reaction, derived by [*McDuffie et al.*, 2018b] is also included.

$$\Phi(\mathrm{ClNO2}) = \left(k_a \frac{[H_2O]}{[Cl^-]} + k_b \frac{[NO_3^-]}{[Cl^-]} + 1\right)^{-1} \quad \text{(S1)}$$

Here k_a is taken as 2.1×10^{-3} and k_b as 3.4×10^{-2} from the work of Bertram, 2009 #31}. Both k_a and k_b are ratios of solution phase rate constants and therefore unitless.

We use observations of pCl^-, particulate NO_3^- and calculated LWC to calculate $\varphi(ClNO_2)$. The LWC is estimated as the sum of water associated with individual aerosol species [*Guo et al.*, 2015]. The inorganic part is calculated with ISORROPIA-II thermodynamic model [*Fountoukis and Nenes*, 2007] in the forward mode. The inorganic aerosol composition is measured by an AMS, HNO_3 (from CIMS), NH_3 from PTR-MS, RH, and temperature. The organic part is estimated based on the organic aerosol mass concentration, density, and hygroscopicity (κOA) from AMS, in which the κOA is predicted via the organic aerosol oxygen-to-carbon (O/C) ratio [*Rickards et al.*, 2013].

S1.5 Calculation of NEMRs

The NEMRs are calculated by three different methods depending on the observation. NEMRs of pCl^- are calculated by the linear fit of pCl^- vs. CO while results with an $R^2 < 0.3$ are rejected (11% rejected). NEMRs of N_2O_5 and $ClNO_2$ in Figure 2 are calculated by integrating the analyte and CO for observations > 3-4× the LoD of the analyte based on a transect-by-transect review. Transects with N_2O_5 and $ClNO_2$ below this threshold were rejected (33%). Transect center NEMRs in Figures 3-4 are calculated using transect center observations. The transect center CO value is the average of the top 5 % of CO observations while the transect center analyte value is the analyte observations which align with the top 5 % of CO observations. NEMRs are intended as a metric for the amount of analyte observed relative to the plume size. NEMRs are not equivalent to

emission ratios and are biased by several variables such as plume age, other plume emissions, and fuel type.

Calculation of NEMR values for pCl^-

NEMR values of pCl^- were calculated by linear correlation with CO. All transects for one fire plume were used in the determination of a single NEMR. We use all transects in one determination because we assume pCl^- is an emission with dilution as the main loss process in the young plumes we consider. The slope of the linear fit is taken to be the NEMR. We only consider plumes whose correlation results in an $R^2 > 0.3$. For montane fueled plumes this is 14 out of 16 plumes. For grass fueled plumes this is 83 out of 93.

NEMR values of N_2O_5 and $ClNO_2$ used in Figure 2

NEMR values of N_2O_5 and $ClNO_2$ used for histograms are calculated by integration of individual plume transects as shown by Equation S2.

$$\frac{\int x\, dt - \bar{x} \times \Delta t}{\int CO\, dt - \overline{CO} \times \Delta t} \qquad \text{(S2)}$$

Here x is the analyte within the plume, x_{bg} is the average analyte mixing ratio outside of a plume and Δt is the elapsed time over which the analyte and CO were integrated. The region selection criteria is described further below. The integration method is used, as opposed to a correlation method, because $ClNO_2$ and N_2O_5 are not directly emitted. Chemical production of $ClNO_2$ and N_2O_5 from precursors other than CO do not necessarily result in a linear correlation.

Note that NEMRs are only calculated for plume transects when measurements of the analyte and CO are present throughout the entirety of the transect and the analyte is roughly 3-4× greater than the LoD. As we demonstrate below, observations rejected for the NEMR calculation are associated with the smallest plumes sampled during FIREX-AQ and therefore the CO is near background and analyte near or at the LoD. Calculating an NEMR for measurements near or below the LoD is uninformative due to the division of small numbers which inflates or gives nonsensical NEMR values.

As shown in Table S2, roughly 39 % and 56 % of all N_2O_5 and $ClNO_2$ transects (montane plus agricultural) were used for the NEMR calculation.

NEMRs in montane- and agricultural-fueled fires from FIREX-AQ

In a case study of N_2O_5 NEMRs calculated for agricultural fueled-plumes, which had the greatest number of rejected transects due to near or below LoD observations, we show that the calculated median NEMR is consistent with N_2O_5 observations in all agricultural plumes.

The limited number of available N_2O_5 NEMR calculations for agricultural plumes is due to the smaller plume size, relative to montane smoke plumes, and larger LoD, relative to $ClNO_2$. As shown in Figure S2 below, most of the near or at LoD observations have transect center CO mixing ratios (average of the top 5% of CO within a plume) much less than transects with detectable N_2O_5.

Calculation of NEMR values for transect center observations:

Transect center NEMRs are calculated according to Equation S3 below.

$$\frac{\Delta x}{\Delta CO} \quad \text{(S3)}$$

Here, Δ refers to the difference of transect and background observations. Transect center observations are taken to be an average of values corresponding to the top 5% of CO values within a transect: see [*Decker et al.*, 2021]. The 1-σ uncertainty of the average is added to measurement uncertainties in quadrature (the square root of the sum of squares) to produce the error bars presented throughout the manuscript. Data below the LoD (including negative values) are included in these calculations without modification.

Plume transect boundary determination:

- Smoke region:
- The smoke tracer CO is enhanced above the background (> 2-σ).
- The smoke is defined (had a clear departure from and return to background levels of CO).
- The transect sampled smoke for more than five continuous seconds (five data points) which corresponds to a plume width of roughly 650 m based on average aircraft speed for the NASA DC-8.
- Background region
- A 15 second period beginning roughly 30 seconds before the transect region (or less if there is less than 30 seconds between transect samples.
- Does not overlap with a smoke region.

S2 Chloride emissions from montane and agricultural fires

The formation of $ClNO_2$ requires particulate chloride (pCl^-). It is known from field and laboratory measurements that agricultural and grass burning emits more Cl^- per kg of fuel burned (emission factor) when compared to temperate and boreal forest burning [*Ahern et al.*, 2018; *Liu et al.*, 2016; *May et al.*, 2014]. As we show below, observations from the NASA DC-8 and NOAA Twin Otter aircraft (hereafter DC-8 and Twin Otter) during FIREX-AQ are consistent with these results.

Figure S5A shows a flight track of the DC-8 on 24 July when two fires were sampled in contrasting environments, which offers a case study of contrasting fuels. The Shady fire burned in a mountainous region with timber, tall grass, and logging debris fuels, while the Sheep fire burned sage grass, juniper, and sagebrush in a grassland region (Table S3). As shown in Figure S5B, the Shady and Sheep Fire plumes differ in pCl^- by roughly a factor of 10. A linear fit of pCl^- vs. CO indicates the above background enhancement of pCl^- relative to the smoke tracer CO, also called the normalized excess mixing ratio (NEMR). Observations of pCl^- were frequently linearly correlated with CO (89% of plumes had an $R^2 > 0.3$) and above the reported LoD from the Aerosol Mass Spectrometer (AMS) aboard the Twin otter (0.09 μg sm^{-3}) and the AMS aboard the DC-8 (median/average ± σ LoD of 0.09 / 0.13 ± 0.09 for montane-fueled smoke and 0.19 / 0.19 ± 0.08 for agricultural fueled-smoke). Specifically, we observed 0.6 μg sm^{-3} $ppmv^{-1}$ CO for the montane fire and 6.1 μg sm^{-3} $ppmv^{-1}$ CO for the grass fire. The results from the July 24 case study shown here are consistent with all smoke observations from both the Twin Otter and DC-8 during FIREX-AQ. Median pCl^- NEMR for grass and agricultural

fueled smoke was 9.9 μg sm^{-3} $ppmv^{-1}$ (or 8.0 mg g^{-1}), which is within a factor of two of aircraft-derived NEMR from May et al.'s analysis (5.4 mg g^{-1} for an east coast U.S. grass fire) [*May et al.*, 2014] and within the reported variability of aircraft results by [*Liu et al.*, 2016], but less than the range of laboratory grass burns (11.1 – 25.3 mg g^{-1}). These results show that agricultural and grass fuels have greater potential for $ClNO_2$ formation and activation.

Biomass burning chloride emissions likely occur in the form of HCl in the gas phase or as potassium or other salts [*May et al.*, 2014]. We have not carried out thermodynamic modeling of the subsequent chloride partitioning between the gas and aerosol phases. Measurement of gas phase HCl was unavailable from the aircraft during FIREX-AQ. Emission factors and NEMRs derived in this work are therefore lower limits. We note, however, that the NEMR for reduced nitrogen (NH_3) greatly exceeds that of chloride [*Akagi et al.*, 2011] and that chloride is soluble in organic aerosol [*Solomon et al.*, 2023]. Therefore, we expect a large fraction of the available chloride to be present as pCl^-.

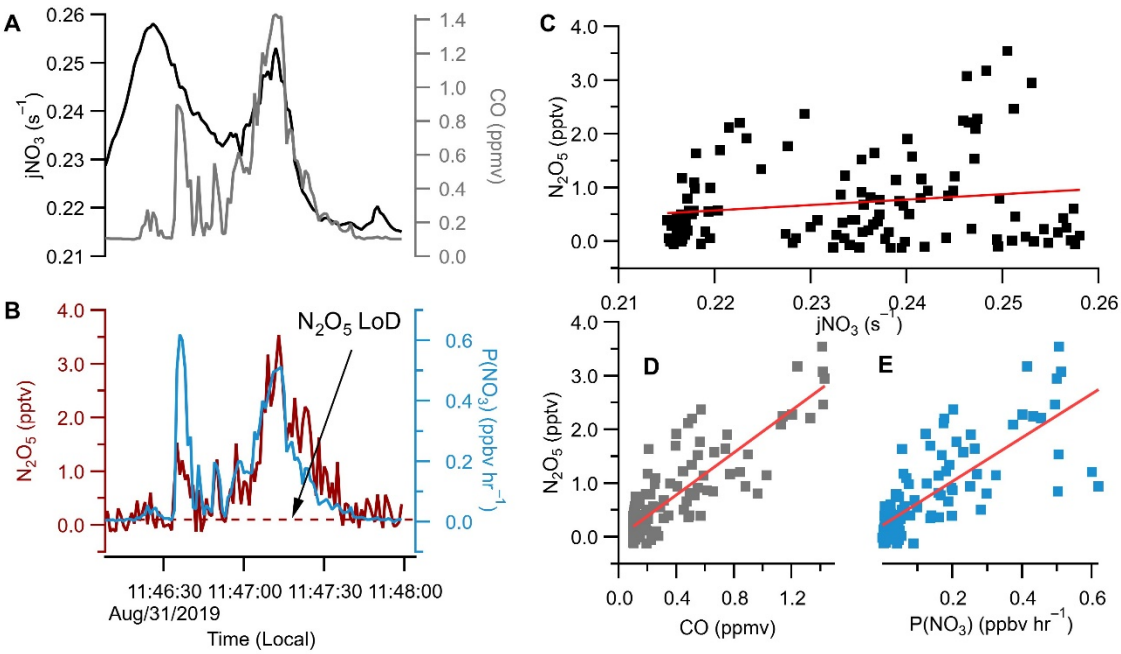

Figure S1. observations taken from a crosswind transect of a small agricultural fire plume at mid-day. (**A**): observations of jNO_3 (left, black) and CO (right, grey). (**B**): observations of N_2O_5 (left, red) and P(NO3) (right, blue). (**C**): correlation plot of N_2O_5 vs. jNO_3 with an $R^2 = 0.03$. (**D**): correlation plot of N_2O_5 vs. CO with an $R^2 = 0.73$. (**E**): correlation plot of N_2O_5 vs. $P(NO_3)$ with an $R^2 = 0.60$.

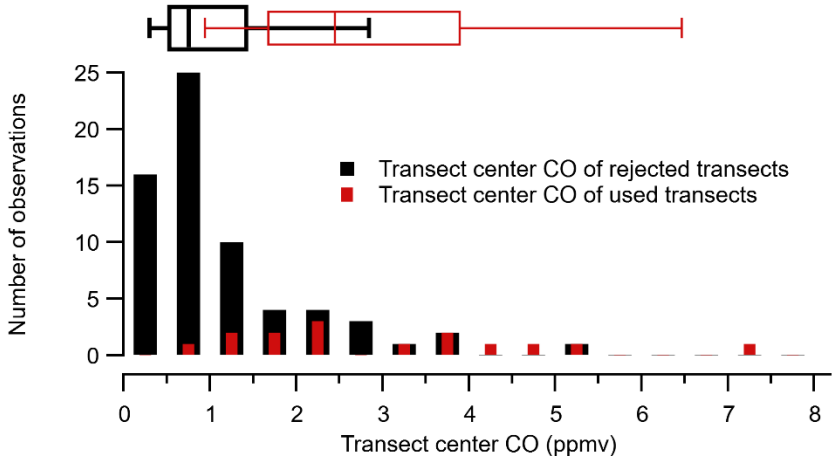

Figure S2. Histogram of transect center CO for transects rejected (black) or used (red) (see Table S2) for NEMR calculations. Box plots show 10th, 25th, 50th, 75th, and 90th percentiles. The median/average ± σ of observations above the LoD is 2.4 / 3.0 ±1.8 and for observations below the LoD it is 0.75 / 1.2 ±1.3. Assuming an NEMR of 1.0 pptv $ppmv^{-1}$ CO (the median result determined in the main text) the expected N_2O_5 mixing ratio shows that the majority of N_2O_5 is expected to be at or below the LoD (Figure S3) and would be rejected by a 3-4× LoD threshold.

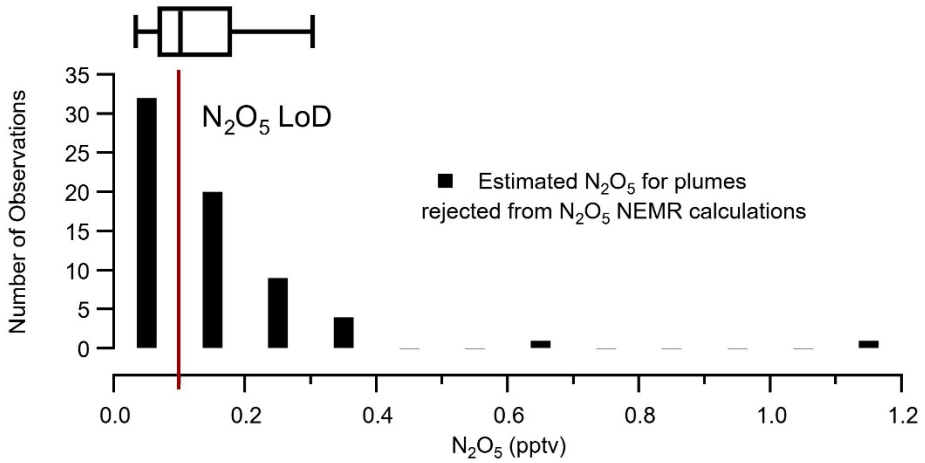

Figure S3. Histogram of estimated N_2O_5 mixing ratio for transects rejected for NEMR calculations. The estimation is based on the observed CO and an NEMR of 1.0 pptv ppmv^{-1} CO as determined in the main text. Box plots show 10th, 25th, 50th, 75th, and 90th percentiles. The median/average ± σ of estimated N_2O_5 mixing ratio is 0.1 / 0.2 ± 0.2

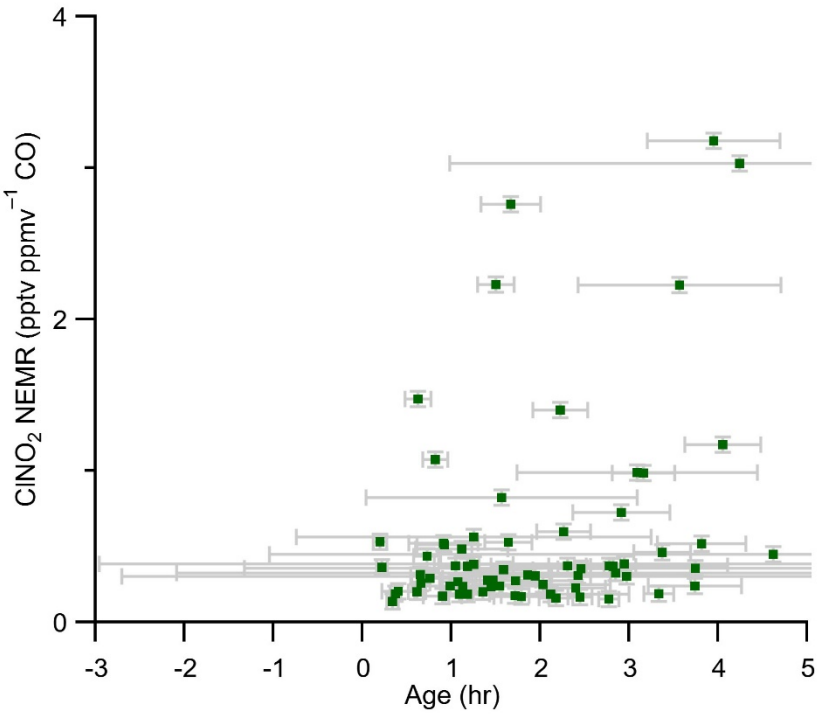

Figure S4. Calculated $ClNO_2$ NEMRs from montane-fueled fires as a function of average plume age.

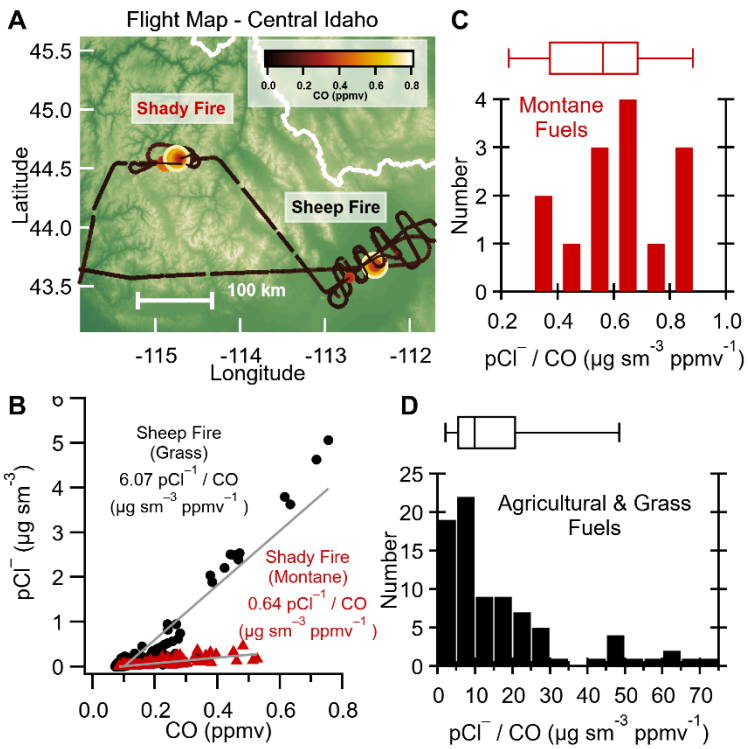

Figure S5. (**A**): flight map (terrain colored by elevation) with the flight path (colored and sized by CO mixing ratio) of the DC-8 sampling the Shady fire plume (red, 17:45–18:15 MDT, including timber, tall grass, and logging debris fuels) and the Sheep fire plume (black, 16:15–16:30 MDT, including sage-grass, juniper, and sagebrush fuels). (**B**) aircraft observations of pCl^- correlated with the CO mixing ratio of the Shady (red, R^2 = 0.62) and Sheep (black, R^2 = 0.87) fire plumes. (**C**) histogram with box and whisker plot of normalized excess mixing ratios of pCl^- for montane fueled smoke observations taken by the DC-8 and the Twin Otter aircraft in FIREX-AQ. (**D**) Similar to panel C but for grass and agricultural fuels. Box plots show 10th, 25th, 50th, 75th, and 90th percentiles. The median NEMR for wildland fuels is 0.6 µg sm^{-3} ppmv^{-1} and the average ± 1-σ is 0.6 ± 0.3 µg sm^{-3} ppmv^{-1}. The median for agricultural fuels is 9.9 µg sm^{-3} ppmv^{-1} and the average ± 1-σ is 16.6 ± 17.1 µg sm^{-3} ppmv^{-1}.

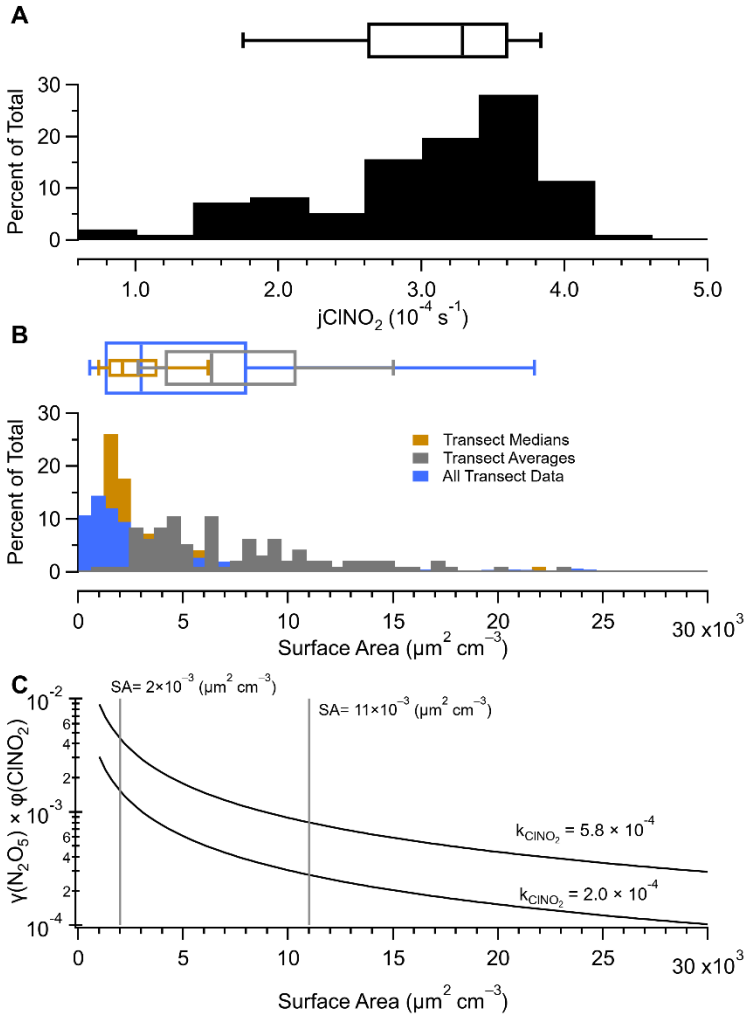

Figure S6. (A) Histogram of observed photolysis rates of $ClNO_2$ ($jClNO_2$) for calculated NEMR in Figure 3A. (B) Histograms of the aerosol surface area in the agricultural-fueled fires sampled by the DC-8 during FIREX-AQ. The transect medians (grey) and averages (brown) represent a median or average of single transects. This is compared to all transect data (blue), which shows all smoke data. Box and whiskers show results for the 10th, 25th, 50th, 75th, and 90th percentiles. In (A) and (B) box and whiskers show results for the 10th, 25th, 50th, 75th, and 90th percentiles. (C) A sensitivity analysis of $\gamma(N_2O_5) \times \varphi(ClNO_2)$ as a function of aerosol surface area. The region between grey vertical lines represents our best estimate range of $\gamma(N_2O_5) \times \varphi(ClNO_2)$ based on a range of aerosol surface area (SA) and the observed $kClNO_2$ in Figure 3A.

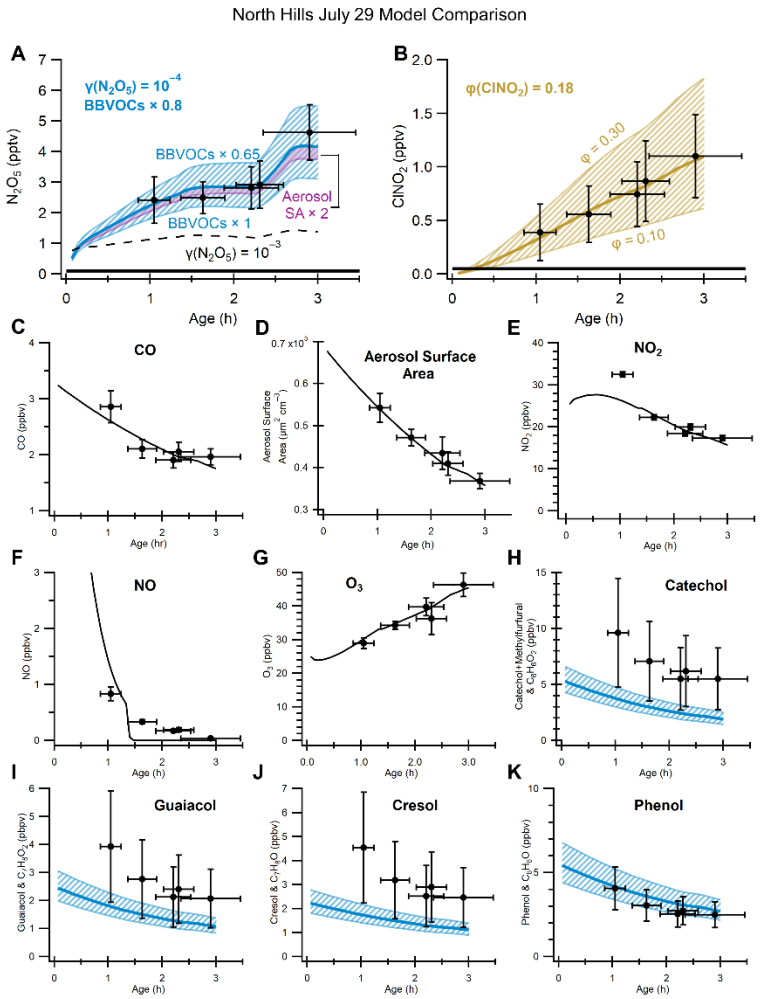

Figure S7. Comparison of box model results to observations for the North Hills Fire on July 29. Observations are shown as black markers while model results are shown as solid lines. Vertical error bars include instrument uncertainty and 1-σ variability (added in quadrature: the square root of the sum of squares) of the average of the transect center observations (observations aligned with the top 5% of CO). The blue shading in H–K corresponds to model results shown in A.

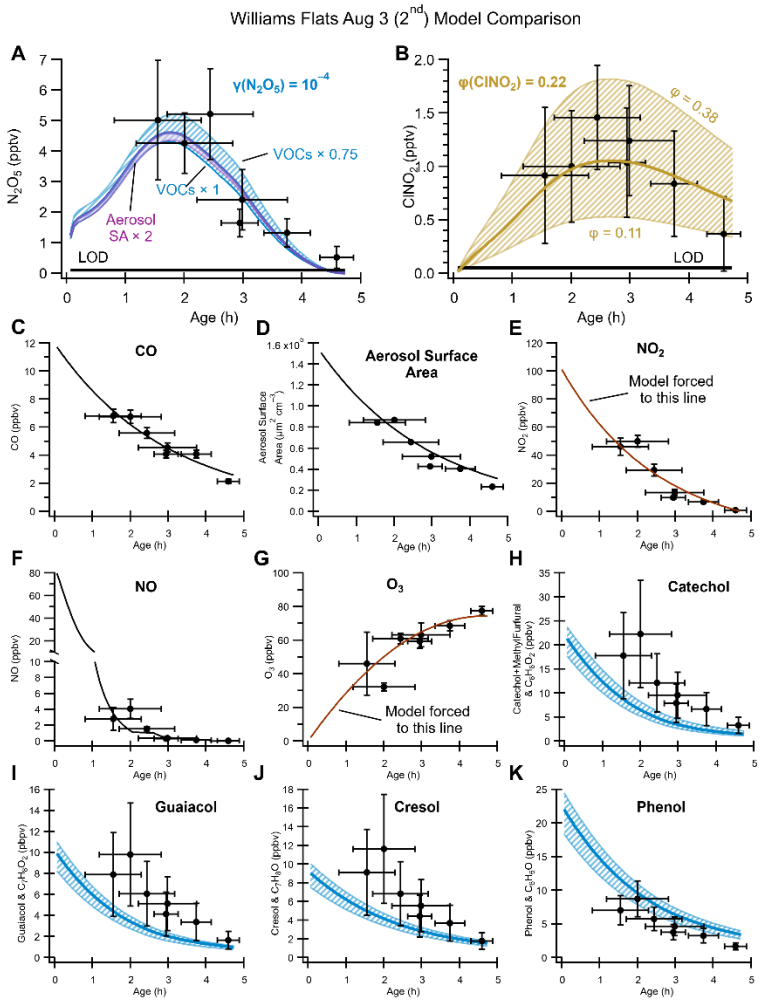

Figure S8. Comparison of box model results to observations for the Williams Flats fire on Aug 3 (2nd sampling). Observations are shown as black markers while model results are shown as solid lines. Vertical error bars include instrument uncertainty and 1-σ variability (added in quadrature: the square root of the sum of squares) of the average of the transect center observations (observations aligned with the top 5% of CO). The blue shading in H–K corresponds to model results shown in A. In this model, red lines indicate when a compound was forced to a guiding line as it was unable to be reproduced by the model for reasons discussed in Decker et al.(2)

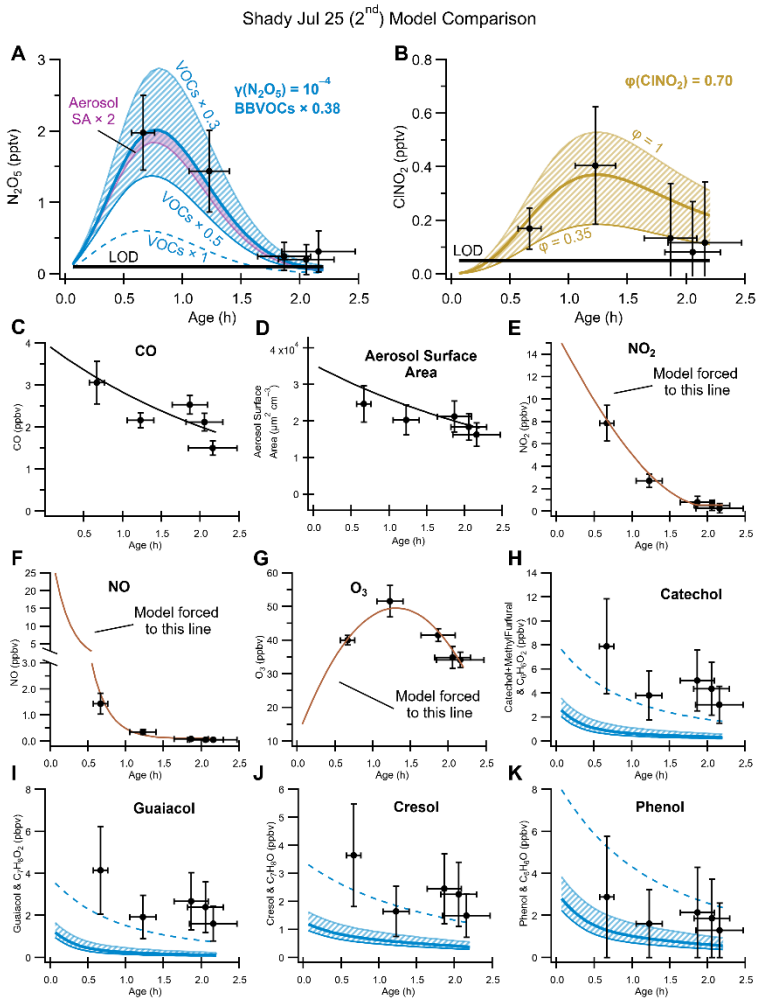

Figure S9. Comparison of box model results to observations for the Shady fire on July 25 (2nd sampling). Observations are shown as black markers while model results are shown as solid lines. Vertical error bars include instrument uncertainty and 1-σ variability (added in quadrature: the square root of the sum of squares) of the average of the transect center observations (observations aligned with the top 5% of CO). The blue shading in H–K corresponds to model results shown in A. In this model, red lines indicate when a compound was forced to a guiding line as it was unable to be reproduced by the model for reasons discussed in Decker et al.(2)

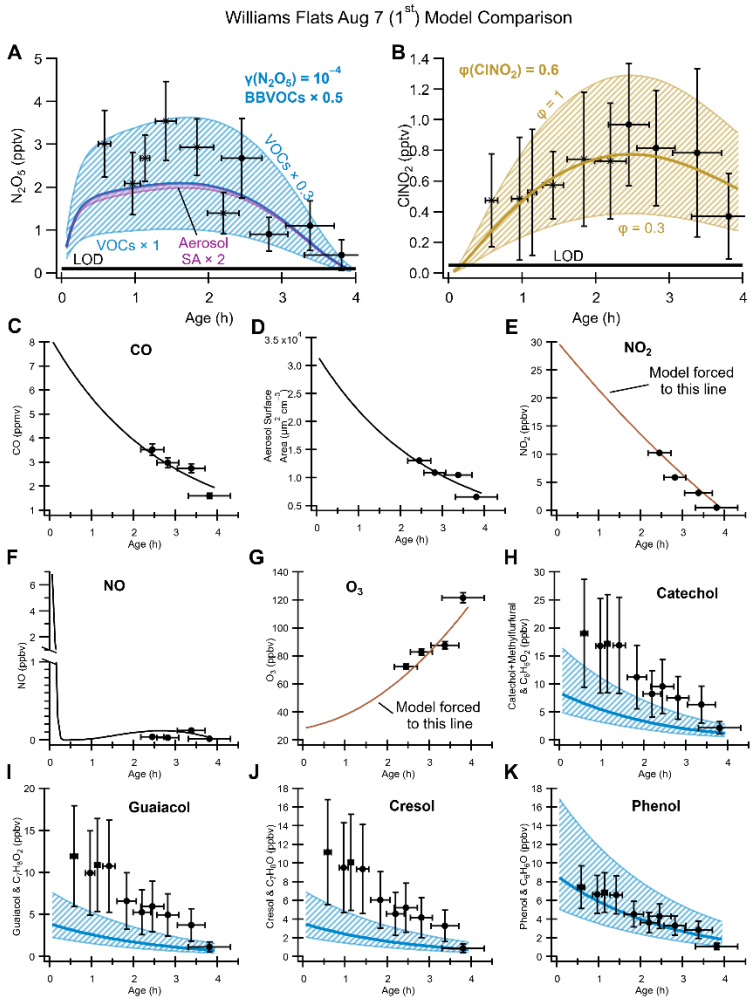

Figure S10. Comparison of box model results to observations for the Williams Flats fire on Aug 7 (1st sampling). Observations are shown as black markers while model results are shown as solid lines. Vertical error bars include instrument uncertainty and 1-σ variability (added in quadrature: the square root of the sum of squares) of the average of the transect center observations (observations aligned with the top 5% of CO). The blue shading in H–K corresponds to model results shown in A. In this model, red lines indicate when a compound was forced to a guiding line as it was unable to be reproduced by the model for reasons discussed in Decker et al.(2)

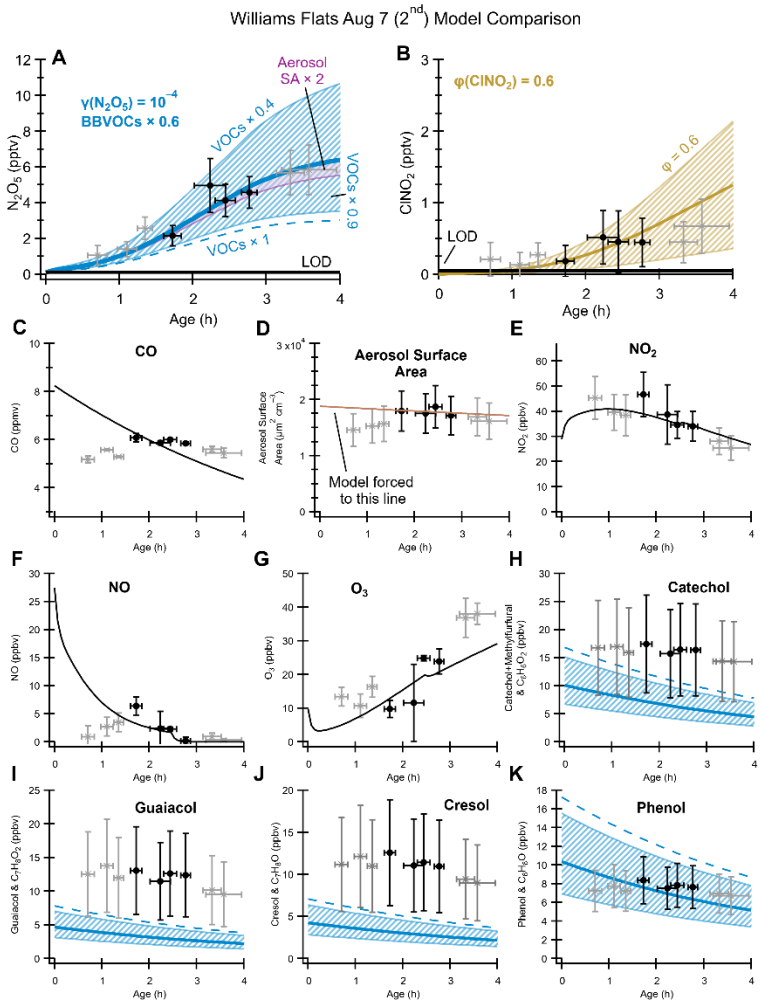

Figure S11. Comparison of box model results to observations for the Williams Flats fire on Aug 7 (2nd sampling). Observations are shown as markers while model results are shown as solid lines. Grey markers indicate observation excluded from the model for reasons discussed in Decker et al.(2) Vertical error bars include instrument uncertainty and 1-σ variability (added in quadrature: the square root of the sum of squares) of the average of the transect center observations (observations aligned with the top 5% of CO). The blue shading in H–K corresponds to model results corresponding shown in A. In this model, red lines indicate when a compound was forced to a guiding line as it was unable to be reproduced by the model for reasons discussed in Decker et al.(2)

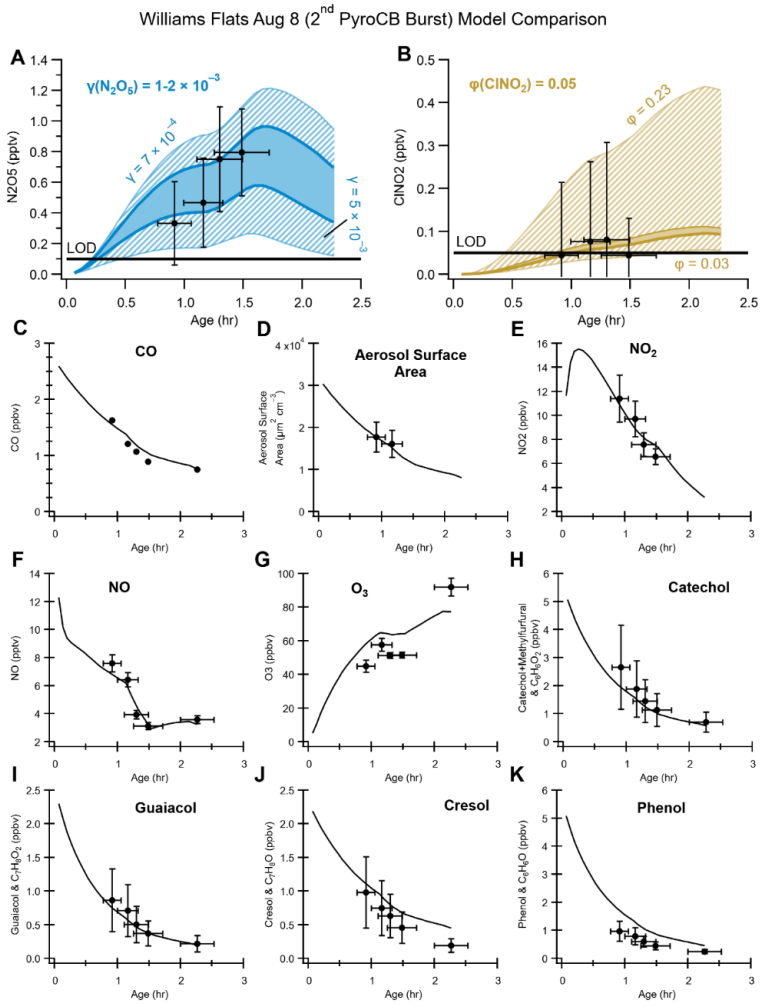

Figure S12. Comparison of box model results to observations for the Williams Flats fire on Aug 8 (2nd PyroCB burst). Error bars include instrument error with 1-σ uncertainty from the average of the transect center in added in quadrature (the square root of the sum of squares) observations as well as plume age uncertainty.

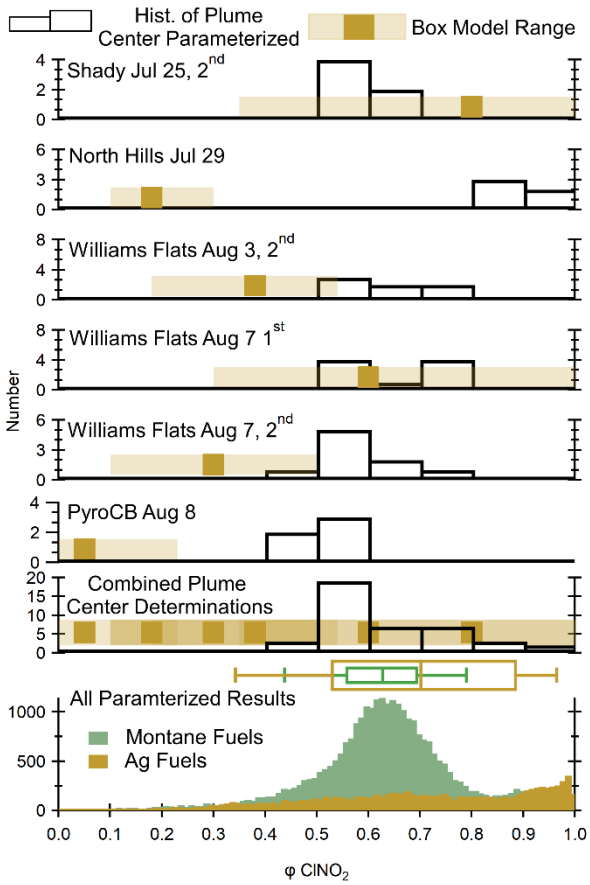

Figure S13. Comparison of the box model derived φ($ClNO_2$) for five montane plumes and the PyroCB event compared with parametrized φ($ClNO_2$). Box model derived values are shown as the gold horizontal bars. Parameterized φ($ClNO_2$) is shown in the histograms (vertical bars) for the transect center observations used in the box model (hollow bars) and for all observations from FIREX-AQ (solid bars). Box and whiskers show results for the 10th, 25th, 50th, 75th, and 90th percentiles.

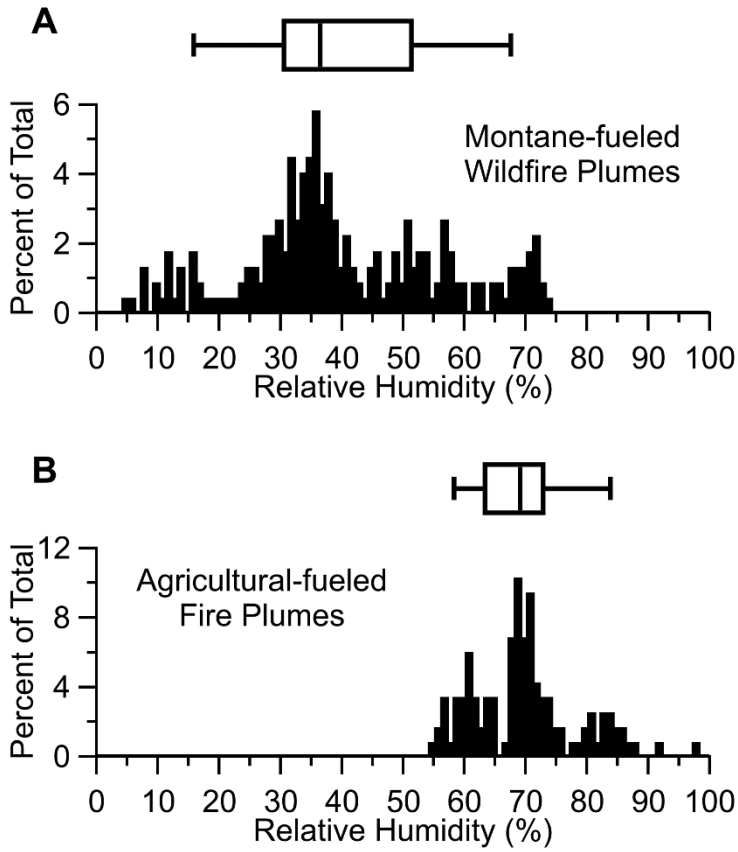

Figure S14. (A) and (B) show histograms of plume transect averaged relative humidity (RH). Each plume transect is averaged and combined as a histogram. For Montane-fueled wildfire plumes the average RH is 40% and the median is 36%. For agricultural-fueled plumes the average is 70% and the median is 69%. Box and whiskers show results for the 10th, 25th, 50th, 75th, and 90th percentiles.

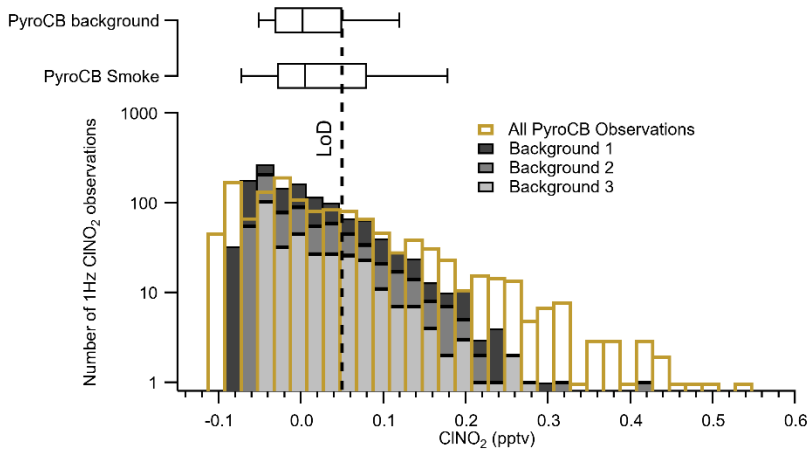

Figure S15. Histogram of $ClNO_2$ observations from the NOAA I^- CIMS on Aug 8 while sampling the PyroCB. The grey fill is stacked and indicates measurements taken from three background regions: one before the first measurement of PyroCB smoke, one after

the last measurement, and one in between two PyroCB transects. The transparent gold bars indicate measurements within the smoke. Box and whiskers show results for the 10th, 25th, 50th, 75th, and 90th percentiles. The median/average ± σ for plume $ClNO_2$ mixing ratios is 0.01 / 0.03 ± 0.10 pptv. The median/average ± σ for background $ClNO_2$ mixing ratios is 0.00 / 0.02 ± 0.06 pptv. The two averages are statistically different ($p < 0.001$).

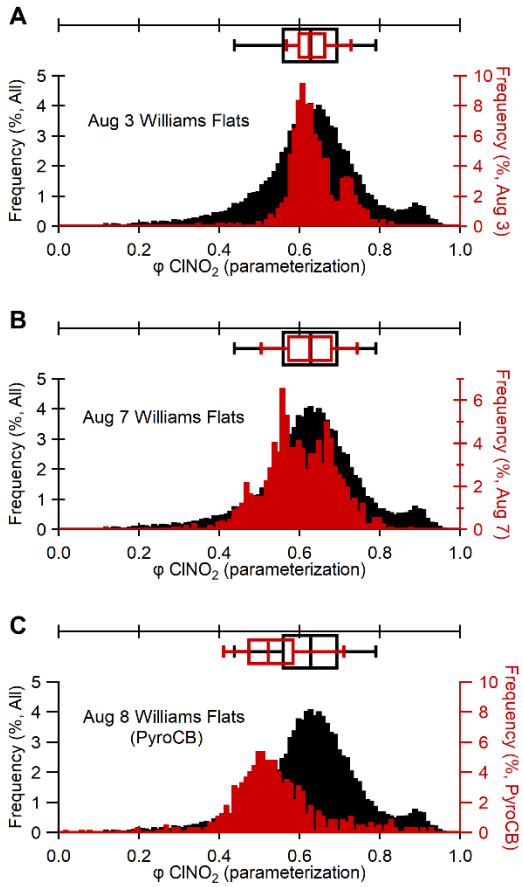

Figure S16. Comparison of parameterized φ($ClNO_2$) values for samplings of the Williams Flats fire smoke on three different days including the PyroCB on Aug 8. Results in black represent all observed wildfire smoke while observations in red show the Williams Flats fire sampled on Aug 3 (**A**) with a median of 0.62, on Aug 7 (**B**) with a median of 0.63, and on Aug 8 (PyroCB event, **C**) with a median of 0.52. Box and whiskers show results for the 10th, 25th, 50th, 75th, and 90th percentiles.

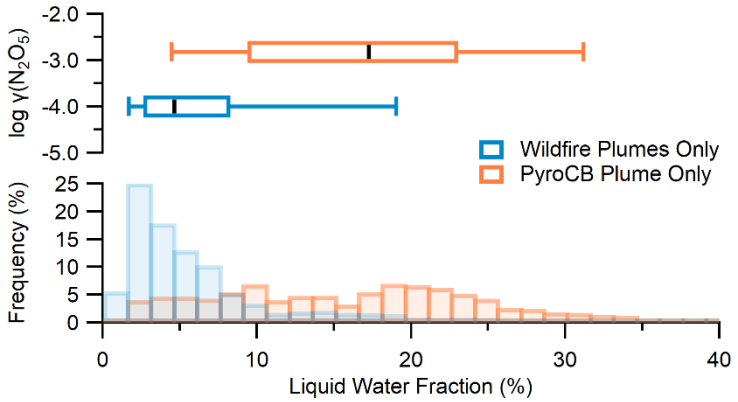

Figure S17. Comparison of liquid water fraction for all modeled wildfires except the PyroCB (blue) and only the PyroCB (orange). Liquid water fraction is defined as the liquid water content mass divided by the sum mass of the organic, ammonium, chloride, nitrate, sulfate, and liquid water). The box and whisker plots show the $\gamma(N_2O_5)$ as a function of liquid water content with 10th, 25th, 50th, 75th, and 90th percentiles shown. The histograms show the frequency of observations as a function of liquid water fraction. The median liquid water fraction for the wildfire plumes was 5%. The median liquid water fraction for the PyroCB was 17%).

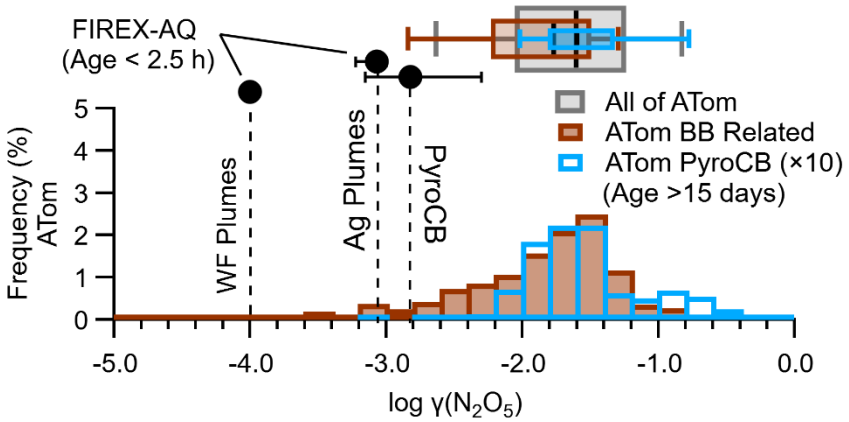

Figure S18. Comparison of the model-derived or fitted $\gamma(N_2O_5)$ values from FIREX-AQ and ATom as shown in Figure 5A, but with the addition of a subset of data identified by Katich et al. (33) in ATom-3 to have PyroCB influence. Markers show FIREX-AQ results, and the histograms show ATom BB-related $\gamma(N_2O_5)$ values. The box and whisker plots show the ATom BB-related (brown) (Methods), ATom-3 aerosol with PyroCB influence (33) (blue), and all of the ATom (grey) results from the UTLS.

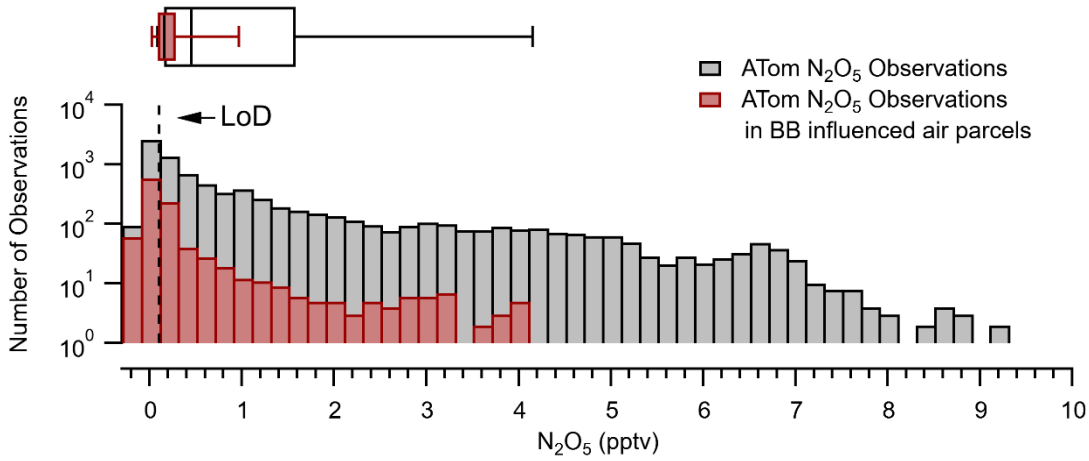

Figure S19. Observations of N_2O_5 (pptv) from the NOAA I^- CIMS aboard the NASA DC-8 during the ATom campaign. Grey bars indicate all observations while red bars indicate observations in BB influenced air. The median/average ± σ for BB influenced N_2O_5 mixing ratios during ATom is 0.16 / 0.38 ± 0.71. The median/average ± σ for all N_2O_5 mixing ratios during ATom is 0.45 / 1.27 ± 1.82.

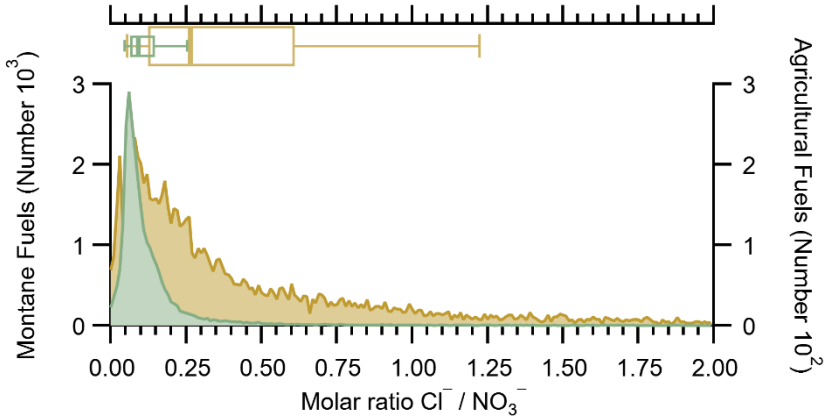

Figure S20. Histograms of the molar ratio of aerosol Cl^- to NO_3^- for montane fueled smoke (green) and agricultural-fueled smoke (brown). The montane-fueled smoke median/average ± σ is 0.1 / 0.1 ± 0.2 and the agricultural fueled smoke median/average ± σ is 0.3 / 0.4 ± 0.4. Box plots show 10th, 25th, 50th, 75th, and 90th percentiles.

Measurements Used	Method	Platform	Campaign	Sample Frequency
CO	Picarro G2401-m, cavity ringdown spectrometer.	Twin Otter	FIREX-AQ	0.5 Hz
Non-refractory PM_1 chemical composition	ECCC aircraft High-resolution Aerosol Mass Spectrometer (HR-AMS)	Twin Otter	FIREX-AQ	1 Hz
CO	Tunable diode laser spectrometer	DC-8	FIREX-AQ	1 Hz
CO	Cavity enhanced spectrometer	DC-8	FIREX-AQ	1 Hz
NO_2, NO_y, and O_3	NOAA chemiluminescence	DC-8	FIREX-AQ ATom	1 Hz
NO_2, HONO	NOAA broadband Airborne Cavity Enhanced Spectrometer (ACES)	DC-8	FIREX-AQ	1 Hz
NO	NOAA laser induced fluorescence	DC-8	FIREX-AQ	1 Hz
$C_6H_6O_2$, C_6H_6O, C_7H_8O, $C_7H_8O_2$.	NOAA Proton Transfer Reaction Time of Flight Mass Spectrometer	DC-8	FIREX-AQ	1 Hz
$C_6H_6O_2$, C_6H_6O, C_7H_8O, $C_7H_8O_2$.	University of Innsbruck Proton Transfer Reaction Time of Flight Mass Spectrometer	DC-8	FIREX-AQ	1 Hz
HONO, N_2O_5, $ClNO_2$	NOAA Iodide Time of Flight Chemical Ionization Mass Spectrometer (I^- ToF CIMS)	DC-8	FIREX-AQ ATom (N_2O_5)	1 Hz
Aerosol Size Distribution and Derived Surface Area	Scanning mobility particle sizer (SMPS) Laser Aerosol Spectrometer (LAS)	DC-8	FIREX-AQ	60 sec 1 Hz
Non-refractory PM_1 chemical composition	CU aircraft High Resolution Aerosol Mass Spectrometer (HR-AMS)	DC-8	FIREX-AQ ATom	1 Hz
Photolysis rates	Charged-coupled device Actinic Flux Spectroradiometer (CAFS)	DC-8	FIREX-AQ ATom	1-5 Hz 1-3 Hz
bulk aerosol size distributions	Combination of techniques for dry diameters 2.7 nm – 4.8 µm	DC-8	ATom	1 Hz
Identification of cloud periods	Cloud, Aerosol, and Precipitation Spectrometer (CAPS)	DC-8	ATom	1 Hz
Identification of pyrogenic-influenced aerosol	Particle Analysis by Laser Mass Spectrometry (PALMS)	DC-8	ATom	1Hz

Table S1. Table of instrumentation used in this work.

	Transects used for the NEMR calculation	Transects rejected for the NEMR calculation
N_2O_5 (Agricultural)	15	68
$ClNO_2$ (Agricultural)	90	29
N_2O_5 (Montane)	95	104
$ClNO_2$ (Montane)	70	98

Table S2. A count of transects used or rejected for the calculation of N_2O_5 or $ClNO_2$. Roughly 37 % and 46 % of plume transects included N_2O_5 and $ClNO_2$, respectively, well in excess of the instrumental detection limits (LoD: N_2O_5=0.1 pptv and $ClNO_2$=0.05 pptv at 1 Hz).

Fire name	State	Latitude	Longitude	Date sampled	Time sampled	Fuel
Shady Fire	Idaho	44.52	-115.02	July 24	17:45–18:15 MDT	Timber, Tall grass, and Logging debris
Sheep Fire	Idaho	43.56	-112.88	July 24	16:15–16:30 MDT	Sage-grass, Juniper, Grass, and Sagebrush
North Hills	Montana	46.75	-111.96	July 29	20:45–21:45 MDT	Managed Xeric, Understory, Sagebrush, Shrubland
Williams Flats	Washington	47.94	-118.62	Aug 03	17:30–19:30 PDT	Short grass, Ponderosa timber
				Aug 07	16:30–17:45 PDT & 18:00–19:30 PDT	
				Aug 08	17:45–19:15 PDT	

Table S3. List of wildfires referenced in the main text. A complete list of fires from FIREX-AQ is found in [*Warneke et al.*, 2023].

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