Reactive nitrogen partitioning enhances the contribution of Canadian wildfire plumes to US ozone air quality

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Key Points:
1) Sequestration of wildfire NOx emissions in Canada as PAN enhances the downwind impacts on US O3 air quality.
2) Pyrogenic VOCs and PAN decomposition increase the contribution of aged Canadian smoke plumes to O3 in US cities.
3) Accounting for these effects in a high-resolution chemistry-climate model improves simulation of smoke-impacted high-O3 events in US cities.

Abstract. Quantifying the variable impacts of wildfire smoke on ozone air quality is challenging. Here we use measurements from the 2018 WE-CAN aircraft campaign to parameterize emissions of reactive nitrogen (NOy) from wildfires into PAN (37%), NO3 (27%), and NO (36%) in a global chemistry-climate model with 13 km spatial resolution over the contiguous US. The NOy partitioning, compared with emitting all NOy as NO, reduces model ozone bias in near-fire smoke plumes sampled by the aircraft and enhances ozone downwind by 5–10 ppbv when Canadian smoke plumes travel to Washington, Utah, Colorado, and Texas. Using multi-platform observations, we identify the smoke-influenced days with daily maximum 8-h average (MDA8) ozone of 70–88 ppbv in Kennewick, Salt Lake City, Denver and Dallas. On these days, wildfire smoke enhanced MDA8 ozone by 5–25 ppbv, through ozone produced remotely during plume transport and locally via interactions of smoke plume with urban emissions.

Plain Language Summary. Wildfires have torn across western North America over the last decade. Smoke from wildland fires in Canada can travel thousands of kilometers to US cities and reacts with urban pollution to create harmful ozone, a criteria pollutant regulated by the US Environmental Protection Agency. Accurately quantifying this impact is needed to inform US air quality policy, but is challenging due to complex physical and chemical processes. In this study, we analyze surface and airborne measurements, alongside a new variable-resolution global chemistry-climate model, to better understand these processes. We show that the near-field conversion of nitrogen oxide (NOx) emissions from wildfires to peroxyacetyl nitrate (PAN) and other more oxidized forms reduces their localized impacts on ozone. PAN is the principal tropospheric reservoir for NOx radicals. When aged smoke plumes descend southward from Canada towards US cities, higher temperatures cause PAN to decompose and thus help production of ozone during smoke transport. On days when the observed
ozone levels exceed the air quality limit (70 ppbv for 8-h average), wildfire smoke can contribute 5–25 ppbv.

1. Introduction

Large wildfires have become increasingly common during recent decades in Canada, the Pacific Northwest, and California, causing severe air pollution, loss of human life, and property damage [Abatzoglou and Williams 2016; Brown et al., 2023]. Five of the most destructive wildfire seasons of the last half-century occurred in the past seven years: 2017, 2018, 2020, 2021, and 2023, raising the possibility that climate change is already driving changes in fire regimes [Hagmann et al., 2021; Xie et al., 2020; 2022; Parisien et al., 2023]. Biomass burning (BB) in wildfires emits particulate matter (PM) along with hundreds of reactive gases, including nitrogen oxides (NOx), nitrous acid (HONO), carbon monoxide (CO), ammonia (NH3), and an enormous diversity of volatile organic compounds (VOCs) [Hatch et al., 2017; Coggon et al., 2019; Permar et al., 2021; Liang et al., 2022]. The complex chemical cocktail of wildfire smoke presents challenges for understanding fire impacts on secondary air pollutants such as ozone (O3) [Jaffe et al., 2020].

Wildfire emissions have variable impacts on O3. O3 is usually enhanced downwind from wildfire plumes with moderate smoke levels, and the O3 production increases with plume age [Jaffe and Wigder, 2012]. At high smoke levels, O3 formation is suppressed, in part due to low-light conditions or heterogeneous chemistry on smoke particles [e.g., Alvarado et al. 2015; Palm et al., 2021]. Observations show that emissions of HONO and NOx in boreal and temperate smoke plumes are rapidly (within minutes to a few hours after emissions) converted into peroxyacyl nitrates (PANs) and particulate nitrate (pNO3), such that O3 production in wildfire plumes rapidly becomes NOx-limited [Alvarado et al. 2010; Juncosa Calahorrano et al., 2021; Xu et al., 2021]. The lifetime of NOx is approximately one day, while the lifetime of PAN in the mid-troposphere is at least a month [Jacob, 1999]. Once ventilated from a source region to the cold free-troposphere where it is more stable, PAN can be efficiently transported on hemispheric scales [Lin et al., 2010; Fischer et al., 2014; Fiore et al., 2018]. When a smoke plume subsides, PAN thermally decomposes to release NOx, thus facilitating O3 formation far downwind [Liu et al., 2016; Bourgeois et al., 2021]. O3 produced during smoke transport appears to be the main driver of O3 increases in NOx-sensitive urban areas [Rickly et al., 2023; Langford et al., 2023]. Injection of VOC-rich smoke plumes into NOx-rich urban areas can enhance O3 production additionally [e.g., McClure & Jaffe 2018; Pan & Fanoola, 2022].

Modeling large fire-to-fire variations in emission factors, smoke physics, plume dynamics and chemical evolution is challenging [Jaffe et al., 2020; L. Jin et al., 2023; Ye et al., 2021]. Current chemical transport models (with horizontal resolution of 4–200 km) typically overestimate O3 close to fires, while having difficulty simulating the long-range influence of aged smoke plumes on downwind O3 [Singh et al., 2012; Fiore et al., 2014; Zhang et al., 2014; Baker et al., 2016, 2018; Zhang et al, 2020; Bourgeois et al., 2021; Tang et al., 2022].
Large uncertainties exist in the partitioning of reactive nitrogen (NO\textsubscript{y}), with models typically underestimating organic nitrates and PANs in smoke [Arnold et al., 2015; Cai et al., 2016]. The 2018 Western Wildfire Experiment for Cloud Chemistry, Aerosol Absorption, and Nitrogen (WE-CAN) and other recent aircraft field campaigns systematically sampled the first few hours of chemical evolution in wildfire plumes, critical for evaluating and improving models [Lindaas et al., 2021a; Juncosa Calahorrano et al., 2021; Permar et al., 2021; Warneke et al., 2023].

Here we use WE-CAN airborne measurements to partition wildfire NO\textsubscript{y} emissions into NO\textsubscript{x}, PAN, and NO\textsubscript{3}\textsuperscript{-} (NO\textsubscript{3}\textsuperscript{-} = HNO\textsubscript{3} + pNO\textsubscript{3}) in a variable-resolution global chemistry-climate model (AM4VR) [Lin et al., 2024]. We show that sequestration of wildfire NO\textsubscript{x} emissions in the Pacific Northwest as PAN enhances their downwind impacts on O\textsubscript{3} in US cities designated as O\textsubscript{3} nonattainment areas, including Salt Lake City, Denver and Dallas [US EPA, 2024]. With regional grid refinements providing 13 km resolution over the contiguous US, AM4VR allows us to investigate interactions between urban pollution and smoke plumes from fires thousands of kilometers away. We assess the contribution of these interactions to the observed high-O\textsubscript{3} episodes by analyzing a suite of model simulations alongside satellite images, aircraft sampling of smoke plumes, and ground-based measurements.

2. Observations and identification of smoke-influenced high-O\textsubscript{3} days

The buildup of O\textsubscript{3} produced from urban emissions under hot and dry meteorological conditions can complicate the attribution of observed O\textsubscript{3} enhancements to smoke influence [Lin et al., 2017; 2020; Lindaas et al., 2017]. We identify high-O\textsubscript{3} episodes in Colorado and Texas influenced by Canadian wildfire smoke, using these criteria: (1) Satellite observations show enhancements of aerosol optical depth across the Great Plains and animation of the GEOS-R images (https://star.nesdis.noaa.gov/smcd/spb/ag/AerosolWatch/) shows passage of a cold front towards the Southern Great Plains; (2) Ground sites in Colorado and Texas record PM\textsubscript{2.5} greater than 35 µg/m\textsuperscript{3} for 24-h mean; (3) IMPROVE ground sites measure enhancements (+50% above background) in organic aerosol (OA), a key component of wildfire smoke [Garofalo et al., 2019]; and (4) Ground sites measure surface O\textsubscript{3} above the 70 ppbv National Ambient Air Quality Standard for daily maximum 8-h average (MDA8).

[Figure 1 about here]

Applying these criteria for 2018, we identify smoke-influenced high-O\textsubscript{3} days in the Colorado Front Range Urban Corridor on August 20 and 24, and in the US Deep South on August 20–21 (Fig.1). On August 19–20, GOES and surface observations showed heavy smoke from wildfires burning in British Columbia and other areas in the Pacific Northwest (Fig.1a-d). A cold front passed across the Great Plains, transporting wildfire smoke towards the US Deep South (Fig.1b). Surface PM\textsubscript{2.5} of 30–60 µg/m\textsuperscript{3} were observed on August 20–21 at sites across the Colorado Front Range Urban Corridor to Amarillo and Dallas, Texas, where background PM\textsubscript{2.5} were <10 µg/m\textsuperscript{3} (Fig.1c-f). The IMPROVE Wichita Mountains monitor located close to the Oklahoma-Texas border, showed increased OA on August 21,
supporting the smoke influence in this region. Surface MDA8 O₃ of 70–88 ppbv was observed at monitors along the smoke transport pathway across Colorado to Texas on August 20–21. During August 23–24, a new cold front transported smoke across the western US, elevating MDA8 O₃, PM₂.₅ and OA in Colorado, but this cold front did not propagate towards Texas. In contrast to the O₃ episodes associated with in-situ production from anthropogenic emissions (e.g. August 1–3), the smoke-impacted periods exhibit a chemical signature with enhancements in organic aerosol.

3. Model simulations

AM4VR is a new variable-resolution global chemistry-climate model developed at NOAA’s Geophysical Fluid Dynamics Laboratory for research at the nexus of US climate and air quality extremes [Lin et al., 2024]. For this study, we conduct nudged AM4VR simulations for 2018 using daily emissions from the Global Fire Emission Database (0.25°x0.25°) [van der Wart et al., 2017], distributed vertically between the surface and 6 km based on an injection height climatology from satellite-based Multi-angle Imaging SpectroRadiometer (MISR) [Val Martin et al., 2018]. AM4VR includes a revised treatment of VOC emissions, accounting for emissions of acetaldehyde (CH₃CHO) and methyl ethyl ketone (MEK, C₄H₈O), both precursors of PAN, from wildfires that are ignored in our previous model AM4.1.

Four AM4VR model experiments are designed to explore the impacts of oxygenated VOC (OVOC) emissions and NOₓ evolution in wildfire smoke (Table S1). Fires in our BASE model emit NOₓ purely as NO, similar to previous models. Juncosa Calahorrano et al. [2021] showed that, within a few hours after emissions, approximately 37% of the total NOₓ species is PANs, with pNO₃ the second largest contributor (27%), based on data averaged over all fresh plume transects during WE-CAN. Since our model does not fully resolve the rapid chemical transformations within concentrated smoke plumes, we thus parameterize NOₓ fire emissions as 37% PAN, 27% HNO₃, and 36% NO in a second simulation (hereafter AM4VR), as in Lin et al. [2024]. Gas-phase HNO₃ and pNO₃ are re-equilibrated each timestep depending on temperature and NH₃ availability [Fountoukis & Nenes, 2007; Lindass et al., 2021b]. We conduct two additional simulations: one with BB emissions of OVOCs (HCHO, CH₃CHO, and CH₂COCH₂) increased by a factor of 2 (hereafter OVOCx2; NOₓ emissions treated as in BASE), and the other with emissions of NOₓ, VOCs, and other gases from fires zeroed out (hereafter noBB).

The average ΔPAN/ΔNOₓ ratio derived from WE-CAN (37%) is within the 30–40% range from other field studies of temperate and boreal fires [Table S2; Alvarado et al. 2010; Liu et al., 2016; Xu et al., 2021]. Thus, our parametrization approach is applicable to other years, although it does not capture fire-to-fire variability (e.g., fires with colder conditions have a higher VOC-to-NOₓ emission ratio, favoring PAN formation). As we have more detailed near-field measurements in the future, geographically varying, biome-dependent NOₓ partitioning can be explored. The approach may be implemented in a similar way as to how
parameterizations have been previously adopted for aircraft and shipping NOx emissions [e.g., Cariolle et al., 2009].

4. Rapid NO\textsubscript{y} evolution slows ozone formation in near-fire smoke plumes

[Figure 2 about here]
We first assess the impacts of NO\textsubscript{y} partitioning on O\textsubscript{3} formation in the near-fire (< 1 day of aging) western US smoke plumes sampled by WE-CAN in summer 2018 (Text S1 and Fig.S1). The BASE model, with fires emitting NO\textsubscript{y} purely as NO, captures up to ~50% of the observed PAN abundance and generally overestimates O\textsubscript{3} in fresh wildfire smoke (Fig.2). Comparisons of CO, HCHO, CH\textsubscript{3}CHO, and CH\textsubscript{3}COCH\textsubscript{3} indicate underestimates of simulated VOCs in smoke, likely resulting from too low primary emissions, missing secondary production pathways, and non-implemented VOCs, thus contributing to the underestimate of PAN (Text S2 and Fig.S2). In addition, numerical dilution of smoke plumes into large model grid boxes presents challenges for our model, even with 13 km resolution, to capture rapid photochemical processes that occur in a concentrated smoke plume within minutes after emissions. Supporting these statements, we find that doubling OVOC emissions from fires favors PAN formation by producing more acetyl peroxy radical (CH\textsubscript{3}CO\textsubscript{3}), but is insufficient to remove the bias. Using the empirical partitioning of NO\textsubscript{y} emissions including PAN and NO\textsubscript{3}\textsuperscript{-} thus accounts for additional VOC emissions and rapid chemistry in smoke.

[Figure 3 about here]
With NO\textsubscript{y} partitioning, the regression slope of simulated PAN with WE-CAN observations increases from 0.51 to 0.73 (Fig.2a). The overall root-mean-square-error (rmse) decreases from 160 to 97 pptv. Rapid conversion of NO\textsubscript{x} to PAN and NO\textsubscript{3} reduces excessive O\textsubscript{3} production simulated in near-fire smoke plumes, decreasing the overall rmse from 11 to 7 ppbv (Fig.2b). O\textsubscript{3} decreases by 10–23 ppbv in the fresh smoke plumes sampled on July 26 and August 2, 9 and 13. On August 13, the aircraft sampled smoke from wildfires in the Salmon Challis National Forest in Idaho (Fig.S1). Intercepted at ~4.5 km altitude between 22:00–23:30 UTC, this smoke plume exhibits factors of 2–5 times enhancements of PAN above its background level (Fig.2c). On August 2, the aircraft intercepted fresh plumes from fires burning in Southwest Oregon. With NO\textsubscript{y} partitioning, AM4VR captures the observed in-plume PAN abundance approaching 3–8 ppbv (Figs.2c-d). In contrast, BASE captures less than 30% of observed PAN levels. The NO\textsubscript{x} loss to NO\textsubscript{3}\textsuperscript{-} and PAN decreases MDA8 O\textsubscript{3} by ~15 ppb in surface air over the burned area around the Idaho/Montana border (Fig.3a). The lower O\textsubscript{3} simulated by AM4VR agrees well with WE-CAN observations (Fig.3c). AM4VR also captures the observed MDA8 O\textsubscript{3} exceedances in Salt Lake City influenced by aged smoke (Fig.3a and Fig.S3).

On July 26, the aircraft sampled smoke from the Carr Fire in the wildland-urban interface of northern California (Fig.3b). PAN was not measured on this flight. The smoke plume over northern California exhibited O\textsubscript{3} mixing ratios of 85–120 ppbv at ~4 km altitude, compared to
~65 ppbv in the remote Idaho plume (Fig.3d). Fires burning in close proximity to NOx-rich urban areas in California had a greater impact on O3 formation. AM4VR represents the vertical structure of the smoke plume and the observed magnitude of O3. The NOy parameterization reduces free tropospheric O3 by ~23 ppbv in smoke-influenced environments (blue versus red pentagons in Fig.2b). This is consistent with box modeling suggesting that O3 formation in VOC-rich smoke plumes is mostly NOx-limited [Xu et al., 2021; X. Jin et al., 2023].

AM4VR captures the large-scale structure of smoke plumes compared with aircraft observations. WE-CAN sampled plumes between 2–5 PM (local time) when fires are active and plumes are injected high in the atmosphere. The injection height derived from MISR with a 10:30 AM overpass is biased low. The simulated vertical distribution of tracers in smoke plumes is not only determined by the MISR injection height climatology but also by strong vertical mixing under hot meteorological conditions. There are cases in which we identified model PAN biases caused by insufficient injection height. On July 30 (stars in Fig.2a-b), for example, the aircraft intercepted fresh smoke plumes at 3–4 km altitude, while the model simulated plumes at ~2 km altitude (Fig.S4). Despite this bias in altitude, the NOy partitioning consistently leads to enhanced PAN and reduced O3 in the simulated fresh plumes.

5. Ozone formation in aged wildfire smoke

[Table 1 and Figure 4 about here]

We next examine the impact of aged wildfire smoke on urban O3 air quality, following long-range transport over thousands of kilometers. We focus on the August 16–24 period when several cold fronts transported smoke from numerous fires burning in the Pacific Northwest to Kennewick, Salt Lake City, Denver, and the US Deep South (Fig.S5). Comparisons of surface MDA8 O3 from observations and model sensitivity experiments demonstrate the role of NOx supply from urban pollution and PAN decomposition on O3 formation in VOC-rich smoke plumes (Table 1).

Over Washington state, enhancements of O3 in wildfire smoke were greatest on August 16 and 22 when smoke levels were moderate (PM2.5 = 30–60 µg/m³, Text S3). Observed MDA8 O3 is 80 ppbv at Spokane and 86 ppbv at Kennewick on August 16 (Fig.4a). Simulated O3 is below 60 ppbv in noBB, indicating minor influence of O3 produced from local anthropogenic emissions alone. Accounting for emissions from fires, simulated O3 increases to 72–74 ppbv in BASE, still lower than observed. When NOy emissions partitioning is included, more PAN is formed in fresh plumes and subsequently decomposes during smoke transport, enhancing downwind O3 formation and increasing simulated MDA8 O3 to 78 ppbv at Spokane and Kennewick. Similarly, NOy parametrization enhances MDA8 O3 by 7–11 ppbv on August 22, leading to better agreement of simulated O3 with observations (Table 1). The enhancement due to NOy parametrization occurs broadly upwind of the urban areas, indicating that O3 was
primarily produced within the smoke and transported into the Tri-Cities airshed (Supporting Movies S1 and S2).

Over the Colorado Front Range and Texas, observations show elevated MDA8 O₃ of 70–88 ppbv in Denver, Amarillo and Dallas during August 20-21 (Fig.4b and Table 1). In these areas, O₃ is enhanced by production during smoke transport plus the in-situ production from mixing of smoke VOCs with urban NOₓ. As smoke descended towards the US Deep South and warmed in the dry air stream of the cold front (Fig.1b), PAN decomposed to release NOₓ and thus facilitated O₃ formation during smoke transport. Supporting this conclusion, AM4VR with NOₓ parameterization simulates well the observed O₃ levels in Denver–Boulder and Dallas on August 20, increasing MDA8 O₃ by 5–12 ppbv relative to BASE and 10–24 ppbv relative to noBB (see also Fig.S6). The NOₓ parameterization accounts for ~30% of the total MDA8 O₃ enhancement due to imported smoke in Denver. Observed O₃ was highest along the foothills west of downtown Denver, suggesting additional O₃ production from reactions of smoke VOCs with urban NOₓ. In Amarillo and Dallas, O₃ produced during smoke transport is the main driver for O₃ increases on August 20, as evidenced from the significant impact of NOₓ parameterization (~50%). During August 21, as smoke further mixed into surface air in Dallas, NOₓ parameterization shows little impact on simulated O₃, implying that urban pollution provided critical NOₓ for O₃ production. Interaction of pyrogenic VOCs with urban NOₓ in Dallas increased MDA8 O₃ by 5–8 ppbv on August 21 (BASE – noBB in Table 1).

[Fig.5 about here]

During August 23–24, a new cold front transported smoke towards Salt Lake City and Denver (Fig.5). Smoke plumes were intercepted by the aircraft below ~4 km during the ascent from Boise, between 1–3 km off the California coast, and below ~4 km during the descent to Boise (Figs.5a-b). The estimated chemical age is 1–3 days for the plumes over Boise and > 3 days for the plume off the California coast [O’Dell et al., 2020; Permar et al., 2023]. These aged smoke plumes exhibit lower PAN and higher O₃ levels compared to the fresh plumes sampled by WE-CAN (Fig.2). The plume off the California coast exhibits O₃ above 100 ppbv and PAN below 0.5 ppbv. AM4VR with NOₓ parameterization better captures enhancements of O₃ with increased plume age, compared with BASE (Fig.5b vs 5d).

As the smoke plumes mixed with urban pollution across the western US, observations show MDA8 O₃ increased by 10–20 ppbv in Salt Lake City on August 23 and in the Denver-Boulder area on August 24 relative to August 22 (Fig.5e). AM4VR captures the observed features, simulating increased O₃ in the descending dry air stream of the cold front. Without BB emissions of VOCs and NOₓ, simulated O₃ decreased in Salt Lake City on August 23 and in Denver on August 24, indicating that the cold front would otherwise transport clean air to these areas (Fig.5f). Over Oklahoma and northern Texas, noBB showed enhanced MDA8 O₃ on August 23–24, indicating that the O₃ pollution was primarily produced from regional anthropogenic emissions. This attribution is consistent with IMPROVE observations showing little OA enhancement at Wichita Mountain on August 24 (Fig.1f). California’s Central Coast
and San Joaquin Valley were also influenced by transported smoke on August 24, with more sites exceeding 70 ppbv MDA8 O$_3$ on the smoky day (Fig. S7).

6. Conclusions

Using observations and a new variable-resolution global model [Lin et al., 2024], we highlight the role of pyrogenic VOCs and NO$_y$ evolution on O$_3$ production in smoke plumes. Rapid conversion of NO$_x$ to NO$_3^-$ and PAN reduces excessive O$_3$ production simulated in near-fire smoke plumes. When aged smoke plumes travel thousands of kilometers southward from Canada towards US cities, PAN thermally decomposes and thus enhances O$_3$ production. We identify the smoke-impacted days in US cities with observed MDA8 O$_3$ of 70–88 ppbv. The enhancement due to wildfire smoke ranges from 5–25 ppbv. For small cities like Kennewick and Boulder, O$_3$ produced during smoke transport is the main driver of O$_3$ increases and the NO$_y$ parameterization can enhance in-plume O$_3$ production by 20–45%. For larger cities like Denver and Dallas, O$_3$ is enhanced by production during smoke transport plus the in-situ production from mixing of smoke VOCs with urban NO$_x$. As large wildfires are projected to increase in western North America due to climate warming [Xie et al., 2022], accurate representation of VOCs and NO$_y$ evolution in smoke is critical to assess the implications for US O$_3$ air quality.

Open Research.

Source code of AM4VR is available at Lin (2023). WE-CAN data is available at https://data.eol.ucar.edu/master_lists/generated/we-can/.

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References:


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https://doi.org/10.1029/2020JD033730


**Supplemental References:**


**Figure Captions:**

**Figure 1.** (a-b) GOES images on August 19 and 20, 2018. Cities referenced in the article are labeled. (c-d) Observed (circles) and simulated (shading) surface PM$_{2.5}$ concentrations. (e-f) Time series of observed daily MDA8 O$_3$ (black lines) and PM$_{2.5}$ (red triangles) at sites in the Front Range Urban Corridor, Colorado and in Dallas (black) and Amarillo (gray), Texas. Blue bars show OA measured by IMPROVE every three days at Rocky Mountain, Colorado and Wichita Mountains, Oklahoma.

**Figure 2.** (a) Scatter plots of observed and simulated median mixing ratios of PAN during WE-CAN: each dot represents average of all data between 2.5-6 km altitude for each flight. Results are shown for BASE with BB emitting NO$_y$ as 100% NO (blue), for doubling fire OVOC emissions (purple), and for AM4VR (red) with BB emitting NO (36%), HNO$_3$ (27%), and PAN (37%); (b) Same as (a) but for median O$_3$ in smoke-influenced environments (observed CO > 85 ppbv, HCN > 275 pptv, and CH$_3$CN > 200 pptv); (c,d) Comparison of observed and simulated PAN for the August 13 and 2 flights (dotted lines denote flight altitude).

**Figure 3.** (a) Maps of surface MDA8 O$_3$ on August 13 from BASE (left) and AM4VR (right) simulations, with color-coded circles representing observations and black lines showing flight track. (b) GOES image and WE-CAN flight on July 26. (c,d) Observed (circles) and AM4VR simulated O$_3$ for the August 13 and July 26 flights.

**Figure 4.** Maps of surface MDA8 O$_3$ on August 16 and 20 from observations (OBS) and model simulations with BB emitting NO$_y$ as 100% NO (BASE), and with the NO$_y$ partitioning (AM4VR). Also shown is the difference between AM4VR and BASE for August 16 and simulated O$_3$ with BB emissions of all NO$_y$ and VOCs zero out (noBB) for August 20.
Figure 5. (a,b) Observed (circles) and AM4VR simulated PAN and O$_3$ for the August 23 flight; (c) GOES image; (d) O$_3$ from BASE; (e) observed and simulated surface MDA8 O$_3$ anomalies on August 23 and 24 (relative to August 22); (f) same as (e) but showing noBB results. The WE-CAN flight track is shown (purple for $\leq$ 4 km).
Table 1. Observed and simulated MDA8 O₃ (ppbv) at western US cities influenced by aged wildfire smoke in August 2018

<table>
<thead>
<tr>
<th>Date</th>
<th>Location</th>
<th>OBS</th>
<th>noBB</th>
<th>BASE</th>
<th>AM4VR</th>
<th>AM4VR - noBB (total smoke impact)</th>
<th>AM4VR - BASE (Impact of NO₃ parameterization)</th>
</tr>
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<tbody>
<tr>
<td>Aug. 16</td>
<td>Spokane</td>
<td>80</td>
<td>59</td>
<td>74</td>
<td>78</td>
<td>19</td>
<td>4 (21%)</td>
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<tr>
<td></td>
<td>Kennewick</td>
<td>86</td>
<td>54</td>
<td>72</td>
<td>78</td>
<td>24</td>
<td>6 (25%)</td>
</tr>
<tr>
<td>Aug. 20</td>
<td>Denver / Boulder (5 sites)</td>
<td>69–74</td>
<td>50–60</td>
<td>61–66</td>
<td>68–74</td>
<td>15–24</td>
<td>5–8 (30%)</td>
</tr>
<tr>
<td></td>
<td>Amarillo</td>
<td>71</td>
<td>41</td>
<td>56</td>
<td>65</td>
<td>24</td>
<td>9 (37%)</td>
</tr>
<tr>
<td></td>
<td>Dallas (3 sites)</td>
<td>73–78</td>
<td>60–66</td>
<td>68–73</td>
<td>10–18</td>
<td>5–12 (50%)</td>
<td></td>
</tr>
<tr>
<td>Aug. 21ᵇ</td>
<td>Dallas (4 sites)</td>
<td>75–88</td>
<td>65-70</td>
<td>70–78</td>
<td>70–75</td>
<td>5–8</td>
<td>N.A.</td>
</tr>
<tr>
<td>Aug. 22</td>
<td>Spokane</td>
<td>68</td>
<td>46</td>
<td>60</td>
<td>67</td>
<td>21</td>
<td>7 (33%)</td>
</tr>
<tr>
<td></td>
<td>Kennewick</td>
<td>73</td>
<td>46</td>
<td>60</td>
<td>71</td>
<td>25</td>
<td>11 (44%)</td>
</tr>
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<td>Portland</td>
<td>75</td>
<td>50</td>
<td>62</td>
<td>70</td>
<td>20</td>
<td>8 (40%)</td>
</tr>
<tr>
<td>Aug. 23</td>
<td>Salt Lake City (4 sites)</td>
<td>67–77</td>
<td>50-55</td>
<td>65-75</td>
<td>65-78</td>
<td>15–20</td>
<td>4 (&lt; 20%)</td>
</tr>
</tbody>
</table>

ᵃ Model does not resolve site-to-site O₃ variations in cities. The range of simulated values in the area is reported.
ᵇ N.A. indicates cases where NO₃ emission partitioning has little impact on simulated urban O₃.
(e) Front Range Urban Corridor, Colorado

(f) Dallas and Amarillo, Texas
(a) 16 WE-CAN flights, 2.5–6 km, all

- r=0.75, slope=0.51, rmse=160 (BASE)
- r=0.82, slope=0.63, rmse=142 (OVOCx2)
- r=0.86, slope=0.73, rmse=97 (AM4VR)

(b) 18 WE-CAN flights, 2.5–6 km, smoke–influenced

- r=0.69, rmse=11 (BASE)
- r=0.73, rmse=7 (AM4VR)

(c) OBS | BASE | OVOCx2 | AM4VR

(d) OBS | BASE | OVOCx2 | AM4VR
Figure 3.
(a) Surface MDA8 O₃ (ppbv), 2018-08-13

(b) GOES 2018-07-26

(c) Idaho: O₃ (ppbv) in AM4VR

(d) California: O₃ (ppbv) in AM4VR
Figure 4.
Figure 5.
(a) PAN (ppbv) in AM4VR, $r=0.41$, rmse=0.33

(b) $O_3$ (ppbv) in AM4VR, $r=0.28$, rmse=21

(c) GOES Image at 21:42UTC on 2018-08-23

(d) $O_3$ (ppbv) in BASE, $r=0.08$, rmse=25

(e)

(f)