

Reactive nitrogen partitioning fuels contribution of Canadian wildfire plumes to U.S. ozone air quality

Meiyun Lin^{1*}, Larry W. Horowitz¹, Lu Hu², Wade Permar²

¹ NOAA Geophysical Fluid Dynamics Laboratory, Princeton, NJ, USA

² Department of Chemistry and Biochemistry, University of Montana, Missoula, MT, USA

*Corresponding author: Meiyun Lin (Meiyun.Lin@noaa.gov)

Submitted to AGU GRL (12 Publication Unit: 6 Figures, ~3200 words), March 18, 2024

Key Points (140 characters including spaces):

- 1) Sequestration of NO_x emissions to PAN in fresh Canadian wildfire plumes allows for their downwind impacts on US O₃ air quality.
- 2) PAN decomposition to NO_x fuels the contribution of O₃ from aged Canadian smoke plumes to cities in Washington, Utah, Colorado and Texas.
- 3) Accounting for this effect in a variable-resolution global chemistry-climate model enhances smoke-influenced O₃ events in US cities.

Abstract (150 words). Accurately quantifying wildfire impacts on ozone air quality is challenging due to complex physical and chemical processes in wildfire smoke. Here we use measurements from the 2018 WE-CAN aircraft campaign to parameterize emissions of reactive nitrogen (NO_y) from wildfires into PAN (37%), NO₃⁻ (27%), and NO (36%) in a global chemistry-climate model with 13 km horizontal resolution over the contiguous US. The NO_y partitioning, compared with emitting all NO_y as NO, reduces model ozone bias in near-fire smoke plumes sampled by the aircraft but significantly enhances ozone downwind when Canadian smoke plumes reach cities in Washington state, Utah, Colorado, and Texas. Using multi-platform observations, we identify the smoke-influenced days with daily maximum 8-h average (MDA8) ozone of 70-85 ppbv in Spokane, Salt Lake City, Denver and Dallas. On these days, mixing of wildfire smoke into urban pollution enhances simulated MDA8 ozone by 10–20 ppbv.

Plain Language Summary (200 words). 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 elucidate these processes. We show that conversion of NO_x emissions from wildfires to more oxidized forms reduces their localized impacts on ozone. When Canadian smoke plumes descend towards US cities, including Spokane, Salt Lake City, Denver and Dallas, higher temperatures cause a restoration of NO_x and thus facilitate production of ozone in transit. On days when the observed daily maximum

8-h average ozone exceeds the health-based limit (70 ppbv), mixing of wildfire smoke into urban pollution can contribute 10–20 ppbv.

1. Introduction

Large wildfires have become increasingly common during recent decades in the Canadian province of British Columbia, the US Pacific Northwest, and California, causing severe air pollution, loss of human life, and property damage [Westerling *et al.*, 2006; 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 (NO_x), nitrous acid (HONO), carbon monoxide (CO), ammonia (NH₃), and an enormous diversity of volatile organic compounds (VOCs) [Hatch *et al.*, 2017; Permar *et al.*, 2021; Liang *et al.*, 2022]. The complex chemical cocktail of wildfire smoke mixed with urban pollution represents a key challenge for understanding fire smoke impacts on secondary air pollutants such as ozone (O₃) [Jaffe *et al.*, 2020].

Wildfire emissions have variable impacts on O₃. In a review of more than 100 studies, Jaffe and Wigder (2012) found that O₃ is usually enhanced downwind from wildfire plumes with moderate smoke levels, and the O₃ production increases with plume age. At high smoke levels, O₃ formation is suppressed, in part due to low-light conditions or to heterogeneous chemistry on smoke particles [e.g., Alvarado *et al.* 2015; Palm *et al.*, 2021]. Observations show that emissions of HONO and NO_x in boreal and temperate smoke plumes are rapidly (within a few hours after emissions) converted into peroxyacyl nitrates (PANs) and particulate nitrate (pNO₃), such that O₃ production in wildfire plumes rapidly becomes NO_x-limited [Alvarado *et al.* 2010; Briggs *et al.*, 2017; Juncosa Calahorrano *et al.*, 2021a; Xu *et al.*, 2021]. The lifetime of NO_x 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 NO_x and can thus facilitate O₃ formation far downwind [Liu *et al.*, 2016; Bourgeois *et al.*, 2021]. Ozone formation is also enhanced when VOC-rich smoke plumes mix into NO_x-rich urban pollution, thereby deteriorating urban air quality [e.g., McClure & Jaffe 2018; Ninneman & Jaffe 2021; Pan & Fanoola, 2022; Langford *et al.*, 2023].

Modeling large fire-to-fire variations in emission factors, smoke physics, plume dynamics and complex chemical evolution is challenging [Paugam *et al.*, 2016; Jaffe *et al.*, 2020; Lindaas *et al.*, 2020; L. Jin *et al.*, 2023; Ye *et al.*, 2021]. Current chemical transport models (CTMs, with horizontal resolution ranging from 4–200 km) typically overestimate O₃ close to the 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]. There are large uncertainties in the partitioning of reactive nitrogen (NO_y), with models typically underestimating organic nitrates and PANs in smoke plumes [Arnold *et al.*, 2015; Cai *et al.*, 2016]. 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; Permar *et al.*, 2021; Warneke *et al.*, 2023].

Here we use airborne measurements from the 2018 Western Wildfire Experiment for Cloud Chemistry, Aerosol Absorption, and Nitrogen (WE-CAN) campaign [Lindaas *et al.*, 2021a; Juncosa Calahorrano *et al.*, 2021ab] to partition BB emissions of NO_y into NO_x , PAN, and NO_3^- ($\text{NO}_3^- = \text{HNO}_3 + p\text{NO}_3$) in a variable-resolution global chemistry-climate model (AM4VR) [Lin *et al.*, 2024]. We show that sequestration of NO_x emissions in PAN from wildfires in the Pacific Northwest enhances their downwind impacts on O_3 in US cities designated as O_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 (see Fig.1 in Lin *et al.*, 2024), AM4VR allows us to investigate interactions between urban pollution and smoke plumes from fires thousands of kilometers away in Canada. We assess the contribution of these interactions to the observed high- O_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_3 days

The buildup of O_3 produced from urban emissions under hot and dry meteorological conditions can complicate the attribution of observed O_3 enhancements to smoke influence [Lin *et al.*, 2017; 2020; Lindaas *et al.*, 2017]. We identify high- O_3 episodes in Colorado and Texas influenced by Canadian wildfire smoke, using these criteria: (1) Satellite observations show enhancements of Aerosol Optical Depth (AOD) across the Great Plains and animation of the GEOS-R images every 10 minutes shows passage of a cold front towards the Southern Great Plains; via NOAA AerosolWatch (<https://star.nesdis.noaa.gov/smcd/spb/aq/AerosolWatch/>); (2) Ground sites in Colorado and Texas record $\text{PM}_{2.5}$ greater than the $35 \mu\text{g}/\text{m}^3$ NAAQS level for 24-h mean; (3) IMPROVE ground sites measure enhancements (+50% above background level) in organic aerosol (OA), a key component of wildfire smoke [Garofalo *et al.*, 2019]; and (4) Ground sites measure surface O_3 above the 70 ppbv NAAQS level for daily maximum 8-h average (MDA8).

[Figure 1 about here]

Applying these criteria to data in 2018, we identify smoke-influenced high- O_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, GOES-East showed heavy smoke from wildfires burning in the Pacific Northwest (**Fig.1a**). On August 20, a cold front passed across the Great Plains, transporting Canadian wildfire smoke towards the US Deep South (**Fig.1b**). By the afternoon of August 20, smoke had reached Amarillo and Dallas, Texas, and lingered in the region on

the next day, as evidenced from AOD enhancements observed by Suomi-NPP (**Fig.1c-d**). Surface PM_{2.5} levels of 30–60 µg/m³ for 24-h mean were observed on August 20–21 at sites across the Front Range Urban Corridor, extending from Cheyenne (Wyoming), Fort Collins, Greeley, Longmont, and Denver, Colorado, to Dallas, Texas, while background PM_{2.5} were <10 µg/m³ at these sites (**Fig.1e-f**). The IMPROVE Rocky Mountain monitor missed the peak smoke on August 20 because measurements are made only every three days. 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 70–85 ppbv were observed at monitors along the smoke transport pathway across Colorado to Texas on August 20–21. During August 22–24, a new cold front transported smoke across the western US, elevating MDA8 O₃, PM_{2.5} and OA in Denver on August 24, but this cold front did not propagate towards the Southern Great Plains. In contrast to the O₃ episodes associated with in-situ production from anthropogenic precursor emissions (e.g. August 1–3), the smoke-influenced high-O₃ episodes exhibit a distinct chemical signature with enhancements in organic-dominated PM_{2.5}.

3. GFDL AM4VR simulations

AM4VR is a new variable-resolution global chemistry-climate model recently developed at NOAA's Geophysical Fluid Dynamics Laboratory (GFDL) 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 (GFED4s, 0.25°x0.25°) [van der Wolf *et al.*, 2017], distributed vertically between the surface and 6 km based on an injection height climatology derived from MISR (Val Martin *et al.*, 2018). AM4VR includes a revised treatment of VOC emissions [Lin *et al.*, 2024], 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 [Horowitz *et al.*, 2020]. Anthropogenic emissions are obtained from the Community Emissions Data System version 2021-04-21 (0.1°x0.1°, O'Rourke *et al.*, 2021).

Four AM4VR model experiments are designed to explore the impacts of oxygenated VOC emissions (OVOC) and NO_y evolution in smoke plumes, in addition to regional anthropogenic emissions (**Table S1**). Fires in our BASE model emit NO_y purely as NO, similar to previous models. Juncosa Calahorrano *et al.* [2021a] showed that, within a few hours after emissions, approximately 37% of the total NO_y species is in the form of PANs and pNO₃ is 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 NO_y emissions from fires into 37% PAN, 27% HNO₃, and 36% NO in a second simulation (hereafter AM4VR), as in Lin *et al.* [2024]. The equilibration between gas-phase HNO₃ and pNO₃ is simulated dynamically depending on temperature, altitude, and NH₃ availability [Fountoukis & Nenes, 2007; Lindass *et al.*, 2021b]. We conduct two additional simulations: one with BB emissions of OVOCs (HCHO, CH₃CHO,

and CH_3COCH_3) increased by a factor of 2 (hereafter OVOCx2), and the other with emissions of NO_y , VOCs, and other gases from fires zeroed out (hereafter noBB). NO_y emissions in the OVOCx2 experiment are treated the same as in BASE.

4. Rapid NO_y evolution slows ozone formation in near-fire smoke plumes

[Figure 2 about here]

We first assess the impacts of NO_y partitioning on O_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). **Fig.2a** shows comparisons of observed and simulated median mixing ratios of PAN between 2.5 and 6 km altitude for each of the WE-CAN flights. The BASE model, with fires emitting NO_y purely as NO, captures only ~50% of the observed PAN abundance. Comparisons of CO, HCHO, CH_3CHO , and CH_3COCH_3 indicate significant under-representation of VOCs in simulated smoke (Text S2 and Fig.S2), consistent with the findings of L. Jin et al. (2023) using the GEOS-Chem model. Doubling OVOC emissions from fires favors PAN formation by producing more acetyl peroxy radical (CH_3CO_3), but it is insufficient to remove the bias, suggesting that CH_3CO_3 has substantial production from oxidation of VOCs not represented by the models (Coggon et al., 2019; Xu et al., 2021; Permar et al., 2023). Even at 13 km resolution, it is challenging for the model to capture rapid photochemical processes that occur in a concentrated smoke plume. Using observations to partition a fraction of NO_y emissions from fires into PAN and NO_3^- thus provides a parameterization to account for additional VOCs and rapid chemistry in smoke. The regression slope of simulated PAN with observations increases from 0.51 in BASE to 0.73 in AM4VR with the NO_y partitioning. The overall root-mean-square-error (RMSE) decreases from 160 to 97 pptv.

Fig.2b shows comparison of median O_3 between 2.5 and 6 km altitude in smoke-influenced air masses, identified with observed CO > 85 ppbv, HCN > 275 pptv, and $\text{CH}_3\text{CN} > 200$ pptv, for each WE-CAN flight. Rapid conversion of NO_x to PAN and NO_3^- reduces excessive O_3 production in near-fire smoke plumes in the model, decreasing the overall RMSE from 11 to 7 ppbv. The effects are as large as 10–23 ppbv in the fresh smoke plumes sampled on July 26 and August 2, 9 and 13. Supporting our findings, Xu et al. (2021) used a box model constrained by observations to show that the partitioning of NO_y species slows O_3 formation in fresh plumes.

[Figure 3 about here]

We analyze several fresh plumes in more detail. On August 13, the aircraft sampled smoke from wildfires burning 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 the background level (**Fig.2c**). On August 2, the aircraft intercepted fresh plumes from fires burning in Southwest Oregon. With the NO_y partitioning, AM4VR captures the observed PAN abundance approaching 3 ppbv on August 13 and 8 ppbv on August 2 within the smoke plumes (**Figs.2c-d**). In contrast, BASE captures less than 30% of observed PAN levels for both plumes. The NO_x loss to NO_3^- and PAN leads to a decrease

of MDA8 O₃ by ~15 ppb in surface air over the burned area around the Idaho/Montana border (**Fig.3a**). The lower O₃ simulated by AM4VR agrees better with WE-CAN observations (**Fig.3d-f**). Doubling OVOC emissions from fires leads to a slight increase in PAN, but this does not systematically reduce model O₃ biases in the fresh plumes. AM4VR also improves upon BASE in representing the observed impacts of aged smoke on MDA8 O₃ exceedances in Salt Lake City on August 13 (**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-c**). PAN was not measured on this flight. Sampled by multiple aircraft transects at ~4 km altitude between 22:30–24:30 UTC, the smoke plume over northern California exhibited O₃ mixing ratios of 85–120 ppbv, compared to ~65 ppbv in the remote Idaho plume (**Fig.3g**). Fires burning in close proximity to NO_x-rich urban areas in California had a greater impact on O₃ formation. Comparisons of CO and O₃ along the flight track show that AM4VR represents the vertical structure of the smoke plume and the observed magnitude of O₃. The BB NO_y 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 NO_x-limited [Xu *et al.*, 2021; X. Jin *et al.*, 2023].

Evaluation with aircraft observations shows that AM4VR captures the large-scale structure of smoke plumes (e.g., July 26, August 2, and 13). 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 thus biased low. However, 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 between 22:00–25:00 UTC, while the model simulated plumes at ~2 km altitude (**Fig.S4**). Despite this bias in altitude, the NO_y partitioning consistently leads to enhanced PAN and reduced O₃ in the simulated fresh plumes.

5. Ozone formation in aged smoke plumes in cities

[Figure 4 about here]

We next examine the influence of smoke plumes on O₃ photochemistry in urban areas, 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 Salt Lake City, the Colorado Front Range Urban Corridor, and the US Deep South (**Fig.4**). Air quality monitors in Washington state recorded hazardous PM_{2.5} pollution of 100–250 µg/m³ for 24-h average on August 19–20. Dense wildfire smoke reduced the intensity of light reaching the surface (**Fig.1**) and increased removal of HO_x radicals on smoke particles, leading to observed suppression of O₃ formation in the region on August 20 (**Fig.5**). AM4VR

accounts for the radiative effects of simulated aerosols on photolysis rates and heterogeneous chemistry on smoke particles [Lin *et al.*, 2024]. But AM4VR with GFED4s emissions captures only 60% of the peak PM_{2.5} levels in Washington state, which partly explains model overestimation of O₃ there on August 20. Enhancements of O₃ in aged wildfire smoke are often greatest when smoke levels are moderate (Buysse *et al.*, 2019; Pan and Faloona, 2022). On August 16 and 22, when PM_{2.5} was 30–60 µg/m³, both observations and model showed elevated MDA8 O₃ above 70 ppbv at monitors in Spokane, Richland-Kennewick, and Portland.

[Figure 5 about here]

Comparisons of surface MDA8 O₃ from the noBB, BASE, and AM4VR experiments demonstrate the critical role of NO_x supply from PAN decomposition and urban pollution on O₃ formation in VOC-rich smoke plumes (**Fig.5**). On August 16 (**Fig.5a**), observed MDA8 O₃ is 80 ppbv at Spokane and 85 ppbv at Richland-Kennewick. Simulated MDA8 O₃ is below 60 ppbv in the noBB experiment, indicating minor influence of O₃ produced from local anthropogenic emissions alone. Accounting for VOC and NO_x emissions from fires, simulated MDA8 O₃ increases to 70–75 ppbv in BASE, still lower than observed. Accounting for enhanced PAN formation in fresh plumes and its subsequent decomposition to NO_x in aged smoke increases MDA8 O₃ by ~5 ppbv in AM4VR, bringing it closer to the observed values. Similarly, the NO_y partitioning led to better agreements of simulated MDA8 O₃ with observations at Richland-Kennewick, Portland, and Mt. Bachelor Observatory on August 22. MDA8 O₃ is 70–80 ppbv from observations, below 55 ppbv in noBB, 55–65 ppbv in BASE, and 70–75 ppbv in AM4VR (**Fig.5b**).

On August 20–21, as smoke descended in the dry air stream of the cold front towards higher temperatures in the US Deep South (**Fig.1 and Fig.4d**), PAN decomposed to release NO_x and thus facilitated O₃ formation (**Fig.5c**). This is clearly demonstrated with the substantial difference between the O₃ simulated in BASE versus AM4VR. The BASE model simulates MDA8 O₃ below 70 ppbv in Denver, Amarillo, and Dallas, inconsistent with observations. With NO_y parameterization, AM4VR simulates well the observed O₃ levels in these areas, increasing MDA8 O₃ by ~8 ppbv relative to BASE and 10–15 ppbv relative to noBB. Most of the sites with observed MDA8 O₃ exceeding 70 ppbv were located downwind of the Denver and Dallas urban areas along the smoke transport pathway, indicating in-situ O₃ production resulting from mixing of smoke VOCs with urban NO_x. During August 21, as smoke further mixed into surface air in Dallas (**Fig.1d**), urban pollution provided a critical NO_x supply to enhance O₃ formation in smoke by ~5 ppbv (**Fig.S5**).

[Fig.6 about here]

During August 23–24, a new cold front transported smoke towards Salt Lake City, Denver, and California's Central Valley (**Fig.4f and Fig.6**). Smoke plumes were intercepted by the WE-CAN aircraft below ~4 km during the ascent from Boise at 2:00PM PDT (21:00 UTC), between 1–3 km off the California coast at 3–6 PM PDT, and below ~4 km during the descent to Boise at 7:30PM (**Figs.6a-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 relatively 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 NO_y parameterization captures better enhancements of O₃ with increased plume age, simulating higher O₃ in aged smoke off the California coast than BASE (**Fig.6b vs 6d**).

As the smoke plumes wafted across the western US and mixed with urban pollution, observations show MDA8 O₃ increased by 10–20 ppbv in Salt Lake City on August 23 and in the Colorado Front Range on August 24 relative to August 22 (**Fig.6e**). AM4VR captures the observed features, simulating increased O₃ in the descending dry air stream of the cold front. With BB emissions of VOCs and NO_y zeroed out, simulated O₃ decreased in Salt Lake City on August 23 and in Colorado on August 24, indicating that the cold front would otherwise transport clean air to these areas in the absence of wildfire smoke (**Fig.6f**). Over Oklahoma and northern Texas, in contrast, noBB showed enhanced MDA8 O₃ on August 23–24, indicating that the ozone pollution was primarily produced from regional anthropogenic emissions. The model 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 smoke (PM_{2.5} = 35–50 µg/m³) on August 24 (**Fig.S6**). Observations show increased sites in California with MDA8 O₃ exceeding 70 ppbv on the smoky day. AM4VR simulates 3–6 ppbv MDA8 O₃ enhancements due to wildfire emissions, implying that the exceedances would not occur if there were no smoke.

6. Conclusions

Due to the large quantity of VOCs emitted by wildfires, O₃ formation in aged smoke is generally NO_x-limited. Through an integrated analysis of observations and global model simulations, we highlight the role of NO_y evolution on O₃ production in aged smoke plumes transported thousands of kilometers downwind. Rapid conversion of NO_x to NO₃⁻ and PAN reduces excessive O₃ production in the model in near-fire smoke plumes sampled by the WE-CAN aircraft campaign. Sequestration of NO_x to PAN from boreal fires fuels downwind O₃ formation. When smoke plumes travel from British Columbia to US cities, including Spokane, Portland, Salt Lake City, Denver, and Dallas, PAN thermally decomposes to release NO_x and thus enhances O₃ production in conjunction with the urban NO_x supply. On days when observed MDA8 O₃ is 70–85 ppbv, mixing of wildfire smoke into urban pollution enhances O₃ production by 10–20 ppbv. 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 O₃ air quality.

Open Research.

Source code of GFDL AM4VR is available at <https://zenodo.org/records/10257866>. WE-CAN data is available at https://data.eol.ucar.edu/master_lists/generated/we-can/. Surface observations of PM_{2.5} and O₃ are available at https://aqsweb.airdata/download_files.html.

Acknowledgements: We thank Songmiao Fan, Emily Fischer, Frank Flocke, Daniel A. Jaffe and Rui Wang for helpful comments. Funding for the WE-CAN data collection was provided by the US National Science Foundation (NSF award numbers: AGS-1650786, AGS-1650275, AGS-1950327, and AGS-1652688) and the US National Oceanic and Atmospheric Administration (NOAA) under award numbers NA17OAR4310010 and NA17OAR4310001. L.H. and W.P. were also supported by NSF grants AGS-2144896 and EPSCoR-2242802.

References:

- Alvarado, M. J., J. A. Logan, J. Mao, et al. 2010. Nitrogen oxides and PAN in plumes from boreal fires during ARCTAS-B and their impact on ozone: an integrated analysis of aircraft and satellite observations. *Atmos. Chem. Phys.* 10 (20):9739-9760. doi: 10.5194/acp-10-9739-2010.
- Alvarado, M. J., C. R. Lonsdale, R. J. Yokelson, et al., 2015. Investigating the links between ozone and organic aerosol chemistry in a biomass burning plume from a prescribed fire in California chaparral. *Atmos. Chem. Phys.* 15 (12):6667-6688. doi: 10.5194/acp-15-6667-2015.
- Arnold, S. R., Emmons, L. K., Monks, S. A., et al: Biomass burning influence on high-latitude tropospheric ozone and reactive nitrogen in summer 2008: a multi-model analysis based on POLMIP simulations, *Atmos. Chem. Phys.*, 15, 6047–6068, <https://doi.org/10.5194/acp-15-6047-2015>, 2015.
- Abatzoglou, J. T. and Williams, A. P.: Impact of anthropogenic climate change on wildfire across western US forests, *P. Natl. Acad. Sci. USA*, 113, 11770–11775, doi:10.1073/pnas.1607171113, 2016.
- Baker, K. R., Woody, M. C., Tonnesen, G. S. et al.: Contribution of regional-scale fire events to ozone and PM_{2.5} air quality estimated by photochemical modeling approaches, *Atmos. Environ.*, 140, 539–554, doi:10.1016/j.atmosenv.2016.06.032, 2016
- Baker, K. R., Woody, M. C., Valin, L. et al.: Photochemical model evaluation of 2013 California wildfire air quality impacts using surface, aircraft, and satellite data, *Sci. Total Environ.*, 637, 1137–1149, <https://doi.org/10.1016/j.scitotenv.2018.05.048>, 2018.
- Bourgeois I. et al., Large contribution of biomass burning emissions to ozone throughout the global remote troposphere. *Proc. Natl. Acad. Sci. U.S.A.* 118, e2109628118 (2021).
- Briggs, N. L., D. A. Jaffe, H. L. Gao, J. R. Hee, P. M. Baylon, Q. Zhang, S. Zhou, S. C. Collier, P. D. Sampson, and R. A. Cary. 2016. Particulate matter, ozone, and nitrogen species in aged wildfire plumes observed at the Mount Bachelor Observatory. *Aerosol Air Qual. Res.* 16 (12), 3075-3087. doi: 10.4209/aaqr.2016.03.0120.
- Brown, P.T., Hanley, H., Mahesh, A. *et al.* Climate warming increases extreme daily wildfire growth risk in California. *Nature* 621, 760–766 (2023). <https://doi.org/10.1038/s41586-023-06444-3>
- Buysse, C. E., A. Kaulfus, U. Nair, and D. A. Jaffe. 2019. Relationships between particulate matter, ozone, and nitrogen oxides during urban smoke events in the western US. *Environ. Sci. Technol.* doi: 10.1021/acs.est.9b05241.
- Cai, C. X., S. Kulkarni, Z. Zhao, A. P. Kaduwela, J. C. Avise et al. (2016). Simulating reactive nitrogen, carbon monoxide, and ozone in California during ARCTAS-CARB 2008 with high wildfire activity. *Atmos. Environ.* 128:28-44. doi: 10.1016/j.atmosenv.2015.12.031.
- Coggon, M. M., C. Y. Lim, A. R. Koss, K. Sekimoto et al. (2019): OH chemistry of non-methane organic gases (NMOGs) emitted from laboratory and ambient biomass burning smoke: evaluating the influence of furans and oxygenated aromatics on ozone and secondary NMOG formation. *Atmos. Chem. Phys.* 19 (23):14875-14899. doi: 10.5194/acp-19-14875-2019.

- 387 Fiore, AM, J.T. Oberman, M.Y. Lin et al. (2014): Estimating North American background ozone in U.S.
 388 surface air with two independent global models: Variability, uncertainties, and
 389 recommendations, *Atmos. Environ.*, 96, 284-300, doi: 10.1016/j.atmosenv.2014.07.045
- 390 Fiore, A.M., E.V. Fischer, G.P. Milly, et al. 2018.: Peroxy acetyl nitrate (PAN) measurements at
 391 northern midlatitude mountain sites in April: a constraint on continental source-receptor
 392 relationships. *Atmos. Chem. Phys.*, 18, no. 20, 15345-15361, doi:10.5194/acp-18-15345-2018.
- 393 Fischer, E. V.; Jacob, D. J.; Yantosca, R. M. et al.: Atmospheric Peroxyacetyl Nitrate (PAN): A Global
 394 Budget and Source Attribution. *Atmospheric Chemistry and Physics* 2014, 14 (5), 2679– 2698,
 395 DOI: 10.5194/acp-14-2679-2014
- 396 Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for
 397 $K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Na^+-SO_4^{2-}-NO_3^- -Cl^- -H_2O$ aerosols, *Atmos. Chem. Phys.*, 7, 4639–4659,
 398 <https://doi.org/10.5194/acp-7-4639-2007>, 2007.
- 399 Garofalo, L. A., Matson A. Pothier, Ezra J. T. Levin, Teresa Campos, Sonia M. Kreidenweis, and
 400 Delphine K. Farmer. Emission and Evolution of Submicron Organic Aerosol in Smoke from
 401 Wildfires in the Western United States, *ACS Earth and Space Chemistry* 2019, 3 (7), 1237-
 402 1247, DOI: 10.1021/acsearthspacechem.9b00125
- 403 Hatch, L. E., R. J. Yokelson, C. E. Stockwell, P. R. Veres, I. J. Simpson, D. R. Blake, J. J. Orlando,
 404 and K. C. Barsanti. 2017. Multi-instrument comparison and compilation of non-methane
 405 organic gas emissions from biomass burning and implications for smoke-derived secondary
 406 organic aerosol precursors. *Atmos. Chem. Phys.* 17 (2):1471-1489. doi: 10.5194/acp-17-1471-
 407 2017.
- 408 Hagmann, R. K. et al. Evidence for widespread changes in the structure, composition, and fire
 409 regimes of western North American forests. *Ecol. Appl.* 31, e02431.
 410 <https://doi.org/10.1002/eap.2431> (2021).
- 411 Horowitz, L.W. et al. (2020): The GFDL Global Atmospheric Chemistry-Climate Model AM4.1: Model
 412 Description and Simulation Characteristics. *Journal of Advances in Modeling Earth Systems*,
 413 12(10), DOI:10.1029/2019MS002032.
- 414 Jacob D. (1999); *Introduction to Atmospheric Chemistry*. Page 212-215. Princeton University Press.
- 415 Jaffe, D. A., and N. L. Wigder. 2012. Ozone production from wildfires: A critical review. *Atmos.*
 416 *Environ.* 51:1-10. doi: 10.1016/j.atmosenv.2011.11.063.
- 417 Jaffe, Daniel A., Susan M. O'Neill, Narasimhan K. Larkin, Amara L. Holder, David L. Peterson,
 418 Jessica E. Halofsky & Ana G. Rappold (2020). Wildfire and prescribed burning impacts on air
 419 quality in the United States, *Journal of the Air & Waste Management Association*, 70:6, 583-
 420 615, DOI: 10.1080/10962247.2020.1749731
- 421 Juncosa Calahorrano, J. F., Lindaas, J., O'Dell, K., Palm, B. B., Peng, Q., Flocke, F., et al. (2021a).
 422 Daytime oxidized reactive nitrogen partitioning in western U.S. wildfire smoke plumes. *Journal*
 423 *of Geophysical Research: Atmospheres*, 126, e2020JD033484.
 424 <https://doi.org/10.1029/2020JD033484>
- 425 Juncosa Calahorrano, J., V. H. Payne, S. S. Kulawik, B. Ford, F. M. Flocke, T. Campos, and E. V.
 426 Fischer (2021b), Evolution of Peroxyacetyl Nitrate (PAN) in wildfire smoke plumes detected by
 427 the Cross-Track Infrared Sounder (CrIS) over the western U.S. during summer 2018,
 428 *Geophysical Research Letters*,
 429 <https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2021GL093405>.
- 430 Jin, L., Permar, W., Selimovic, V. et al: Constraining emissions of volatile organic compounds from
 431 western US wildfires with WE-CAN and FIREX-AQ airborne observations, *Atmos. Chem.*
 432 *Phys.*, 23, 5969–5991, <https://doi.org/10.5194/acp-23-5969-2023>, 2023.

- 433 Jin, X., A. M. Fiore, and R. C. Cohen. Space-Based Observations of Ozone Precursors within
 434 California Wildfire Plumes and the Impacts on Ozone-NO_x-VOC Chemistry Environmental
 435 Science & Technology, 57 (39), 14648-14660, DOI: 10.1021/acs.est.3c04411, 2023
- 436 Langford, A. O., Senff, C. J., Alvarez, R. J. II, Aikin, K. C., Ahmadov, R., Angevine, W. M., et al.
 437 (2023). Were wildfires responsible for the unusually high surface ozone in Colorado during
 438 2021? Journal of Geophysical Research: Atmospheres, 128, e2022JD037700.
 439 <https://doi.org/10.1029/2022JD037700>
- 440 Liang, Y., Stamatis, C., Fortner, E. C., Wernis, R. A. et al: Emissions of organic compounds from
 441 western US wildfires and their near-fire transformations, Atmos. Chem. Phys., 22, 9877–9893,
 442 <https://doi.org/10.5194/acp-22-9877-2022>, 2022.
- 443 Lin, M., T. Holloway, G. R. Carmichael and A. M. Fiore: Quantifying pollution inflow and outflow over
 444 East Asia in spring with regional and global models. Atmos. Chem. Phys., 10, 4221-4239,
 445 2010.
- 446 Lin, M. et al. (2017), US surface ozone trends and extremes over 1980-2014: Quantifying the roles of
 447 rising Asian emissions, domestic controls, wildfires, and climate. Atmos. Chem. Phys., 17 (4),
 448 doi:10.5194/acp-17-2943-2017.
- 449 Lin, M., et al. (2020): Vegetation feedbacks during drought exacerbate ozone air pollution extremes in
 450 Europe. Nature Climate Change, 10(5), DOI:10.1038/s41558-020-0743-y.
- 451 Lin, M., L. W. Horowitz, M. Zhao, L. Harris, P. Ginoux, J. P. Dunne, S. Malyshev, E. Shevliakova, H.
 452 Ahsan, S. Garner, F. Paulot, A. Pouyaei, S. J. Smith, Y. Xie, N. Zadeh, L. Zhou. The GFDL
 453 Variable-Resolution Global Chemistry-Climate Model for Research at the Nexus of US Climate
 454 and Air Quality Extremes. Journal of Advances in Modeling Earth Systems, in press,
 455 <https://doi.org/10.1029/2023MS003984>, 2024. [Full text available here.](#)
- 456 Lindaas, J., D. K. Farmer, I. B. Pollack et al. (2017), The impact of aged wildfire smoke on atmospheric
 457 composition and ozone in the Colorado Front Range in summer 2015, Atmos. Chem. Phys.,
 458 <https://doi.org/10.5194/acp-2017-171>.
- 459 Lindaas, J.; Pollack, I. B.; Garofalo, L. A. et al (2021a): Emissions of Reactive Nitrogen From Western
 460 U.S. Wildfires During Summer 2018. J. Geophys Res. Atmospheres, 2021, 126 (2). DOI:
 461 10.1029/2020JD032657
- 462 Lindaas, J., Pollack, I. B., Calahorrano, J. J., O'Dell, K., Garofalo, L. A., Pothier, M. A., et al. (2021b).
 463 Empirical insights into the fate of ammonia in western U.S. wildfire smoke plumes. Journal of
 464 Geophysical Research: Atmospheres, 126, e2020JD033730.
 465 <https://doi.org/10.1029/2020JD033730>
- 466 Liu, X., et al. (2016), Agricultural fires in the southeastern US during SEAC(4)RS: Emissions of trace
 467 gases and particles and evolution of ozone, reactive nitrogen, and organic aerosol, J.
 468 Geophys. Res.-Atmos., 121(12), 7383-7414, doi:10.1002/2016jd025040
- 469 McClure and Jaffe (2018): Investigation of high ozone events due to wildfire smoke in an urban area,
 470 Atmospheric Environment 194 (2018), 146–157, doi:10.1016/j.atmosenv.2018.09.021
- 471 Ninneman, M.; Jaffe, D. A. The Impact of Wildfire Smoke on Ozone Production in an Urban Area:
 472 Insights from Field Observations and Photochemical Box Modeling. Atmos. Environ. 2021,
 473 267, 118764 DOI: 10.1016/j.atmosenv.2021.118764
- 474 O'Dell, K., R. Hornbrook, W. Permar et al. (2020), Hazardous air pollutants in fresh and aged western
 475 U.S. wildfire smoke and implications for long-term exposure, Environmental Science &
 476 Technology, <https://doi.org/10.1021/acs.est.0c04497>.
- 477 O'Rourke, P. R, Smith, S. J., Mott, A., Ahsan, H., McDuffie, E. E., Crippa, M., Klimont, S., McDonald,
 478 B., Z., Wang, Nicholson, M. B, Feng, L., and Hoesly, R. M. (2021, April 21). CEDS v-2021-04-

- 21 Emission Data 1975-2019 (Version 04-21-2021). <https://data.pnnl.gov/dataset/CEDS-4-21-21>.
- Pan, K. and Faloon, I. C.: The impacts of wildfires on ozone production and boundary layer dynamics in California's Central Valley, *Atmos. Chem. Phys.*, 22, 9681–9702, <https://doi.org/10.5194/acp-22-9681-2022>, 2022.
- Parisien, M.A., Barber, Q.E., Bourbonnais, M.L. et al. Abrupt, climate-induced increase in wildfires in British Columbia since the mid-2000s. *Commun Earth Environ* 4, 309 (2023). <https://doi.org/10.1038/s43247-023-00977-1>
- Paugam, R., M. Wooster, S. Freitas, and M. V. Martin (2016), A review of approaches to estimate wildfire plume injection height within large-scale atmospheric chemical transport models, *Atmos. Chem. Phys.*, 16(2), 907-925, doi:10.5194/acp-16-907-2016
- Palm, B. B., Peng, Q., Hall, S. R., Ullmann, K., Campos, T. L., Weinheimer, A., et al. (2021). Spatially resolved photochemistry impacts emissions estimates in fresh wildfire plumes. *Geophysical Research Letters*, 48, e2021GL095443. <https://doi.org/10.1029/2021GL095443>
- Permar, W., Q. Wang, V. Selimovic, C. Wielgasz, R. J. Yokelson, R. S. Hornbrook, A. J. Hills, E. C. Apel, I.-T. Ku, Y. Zhou, B. C. Sive, A. P. Sullivan, J. L. Collett Jr., T. L. Campos, B. B. Palm, Q. Peng, J. A. Thornton, L. A. Garofalo, D. K. Farmer, S. M. Kreidenweis, E. J. T. Levin, P. J. DeMott, F. Flocke, E. V. Fischer, and L. Hu (2021), Emissions of trace organic gases from western U.S. wildfires based on WE-CAN aircraft measurements, 126, e2020JD033838. <https://doi.org/10.1029/2020JD033838>
- Permar, W., Jin, L., Peng, Q., O'Dell, K., Lill, E., Selimovic, V., Yokelson, R. J., Hornbrook, R. S., Hills, A. J., Apel, E. C., Ku, I.-T., Zhou, Y., Sive, B. C., Sullivan, A. P., Collett, J. L., Palm, B. B., Thornton, J. A., Flocke, F., Fischer, E. V., and Hu, L.: Atmospheric OH reactivity in the western United States determined from comprehensive gas-phase measurements during WE-CAN, *Environ. Sci. Atmos.*, 3, 97–114, <https://doi.org/10.1039/D2EA00063F>, 2023.
- Singh, H. B., C. Cai, A. Kaduwela, A. Weinheimer, and A. Wisthaler (2012), Interactions of fire emissions and urban pollution over California: Ozone formations and air quality simulations, *Atmos Environ.*, 56, 45-51, doi:10.1016/j.atmosenv.2012.03.046.
- Tang, W., Emmons, L. K., Buchholz, R. R., Wiedinmyer, C., Schwantes, R. H., He, C., ... Campos, T. L. (2022). Effects of fire diurnal variation and plume rise on U.S. air quality during FIREX-AQ and WE-CAN based on the Multi-Scale Infrastructure for Chemistry and Aerosols (MUSICA_{v0}). *Journal Of Geophysical Research: Atmospheres*, 127, e2022JD036650. doi:10.1029/2022JD036650
- US EPA 2024. 8-Hour Ozone Nonattainment Areas for the 2015 National Ambient Air Quality Standards (NAAQS). https://www3.epa.gov/airquality/greenbook/map8hr_2015.html
- Val Martin, M., Kahn, R., & Tosca, M. (2018). A global analysis of wildfire smoke injection heights derived from space-based multi-angle imaging. *Remote Sensing*, 10(10), 1609. <https://doi.org/10.3390/rs10101609>
- van der Werf, G. R., Randerson, J. T., Giglio, L. et al. (2017). Global fire emissions estimates during 1997–2016. *Earth System Science Data*, 9(2), 697–720. <https://doi.org/10.5194/essd-9-697-2017>. Latest data for 1997-2023 available at <https://www.geo.vu.nl/~gwerf/GFED/GFED4/>, last assessed October 1, 2022.
- Warneke, C., Schwarz, J. P., Dibb, J., Kalashnikova, O., Frost, G., Al-Saad, J., et al. (2023). Fire influence on regional to global environments and air quality (FIREX-AQ). *Journal of Geophysical Research: Atmospheres*, 128, e2022JD037758. <https://doi.org/10.1029/2022JD037758>

- 525 Westerling, A. L.; Hidalgo, H. G.; Cayan, D. R.; Swetnam, T. W. Warming and Earlier Spring Increase
 526 Western US Forest Wildfire Activity. *Science* 2006, 313 (5789), 940– 943, DOI:
 527 10.1126/science.1128834
- 528 Xie, Y., M. Lin, and L.W. Horowitz (2020): Summer PM_{2.5} Pollution Extremes Caused by Wildfires
 529 Over the Western United States During 2017–2018. *Geophys. Res. Lett.*, 47(16),
 530 DOI:10.1029/2020GL089429.
- 531 Xie, Y., M. Lin, Bertrand Decharme, Christine Delire, Larry W. Horowitz, David M. Lawrence, Fang Li,
 532 Roland Séférian (2021). Tripling of western US particulate pollution from wildfires in a warming
 533 climate. *Proc. Natl Acad. Sci. USA* 119, e2111372119 (2022).
- 534 Xu, L., J.D. Crounse, K.T. Vasquez, et al. Ozone Chemistry in Western U.S. Wildfire Plumes. *Science*
 535 *Advances*, 7(50), <https://doi.org/10.1126/sciadv.abl3648>, 2021.
- 536 Ye, X., Arab, P., Ahmadov, R., et al.: Evaluation and intercomparison of wildfire smoke forecasts from
 537 multiple modeling systems for the 2019 Williams Flats fire, *Atmos. Chem. Phys.*, 21, 14427–
 538 14469, <https://doi.org/10.5194/acp-21-14427-2021>, 2021.
- 539 Zhang, L., Jacob, D. J., Yue, X., Downey, N. V., Wood, D. A., and Blewitt, D.: Sources contributing to
 540 background surface ozone in the US Intermountain West, *Atmos. Chem. Phys.*, 14, 5295–
 541 5309, doi:10.5194/acp-14-5295-2014, 2014
- 542 Zhang, L., Lin, M., Langford, A. O., Horowitz, L. W., Senff, C. J., Klovenski, E., Wang, Y., Alvarez II,
 543 R. J., Petropavlovskikh, I., Cullis, P., Sterling, C. W., Peischl, J., Ryerson, T. B., Brown, S. S.,
 544 Decker, Z. C. J., Kirgis, G., and Conley, S.: Characterizing sources of high surface ozone
 545 events in the southwestern US with intensive field measurements and two global models,
 546 *Atmos. Chem. Phys.*, 20, 10379–10400, <https://doi.org/10.5194/acp-20-10379-2020>, 2020

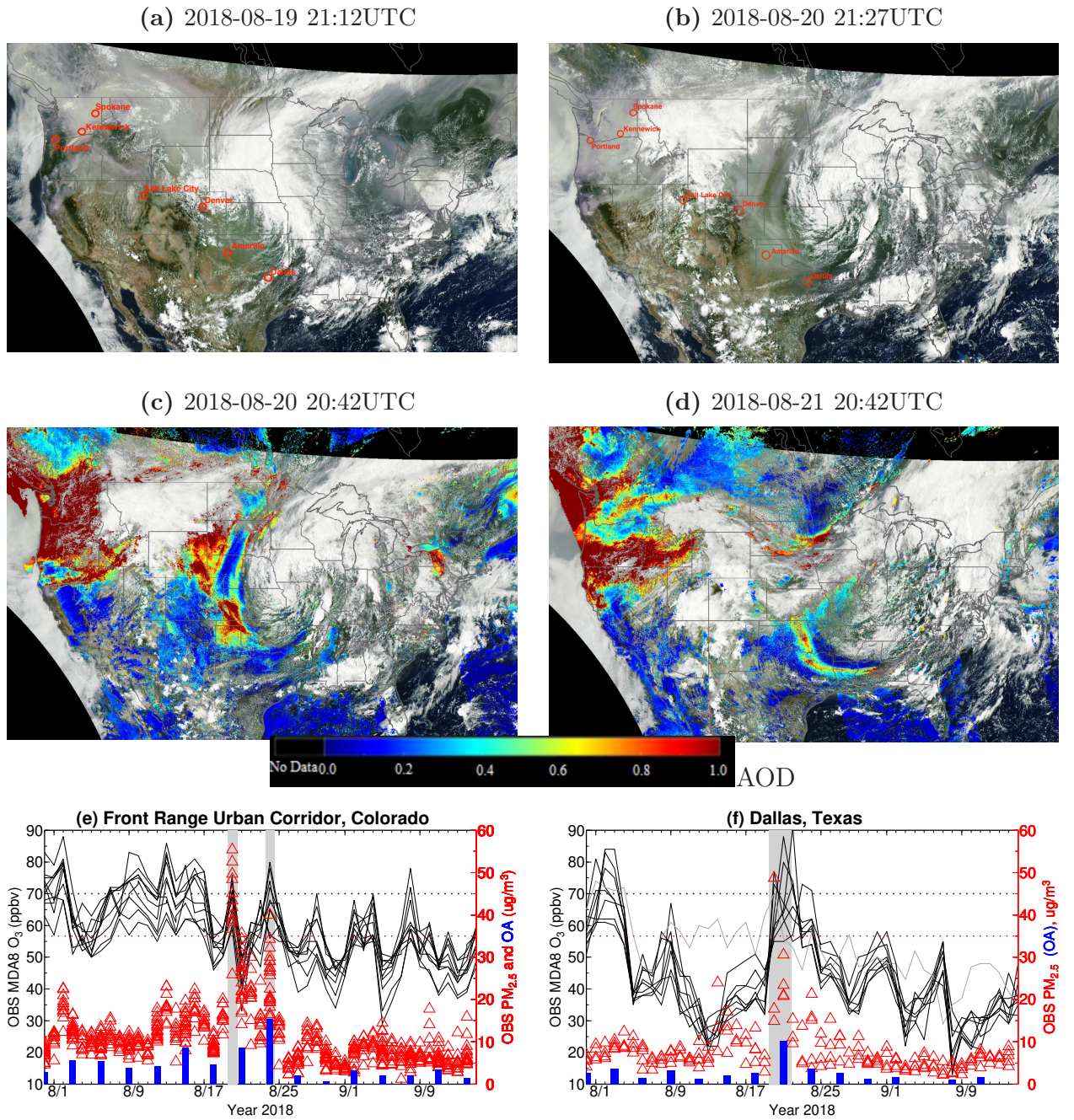


Figure 1. (a-b) GOES images on August 19 and 20, 2018. Cities referenced in the article are labeled. (c-d) Suomi-NPP AOD superimposed on the GOES images on August 20 and 21, 2018. (e-f) Time series of observed daily MDA8 O₃ (black lines) and 24-h PM_{2.5} (red triangles) at AQS sites in the Front Range Urban Corridor, Colorado and Dallas, Texas. Also shown is O₃ at Amarillo, Texas (gray line). Blue bars show organic aerosols measured by IMPROVE at Rocky Mountain, Colorado and Wichita Mountains, Oklahoma.

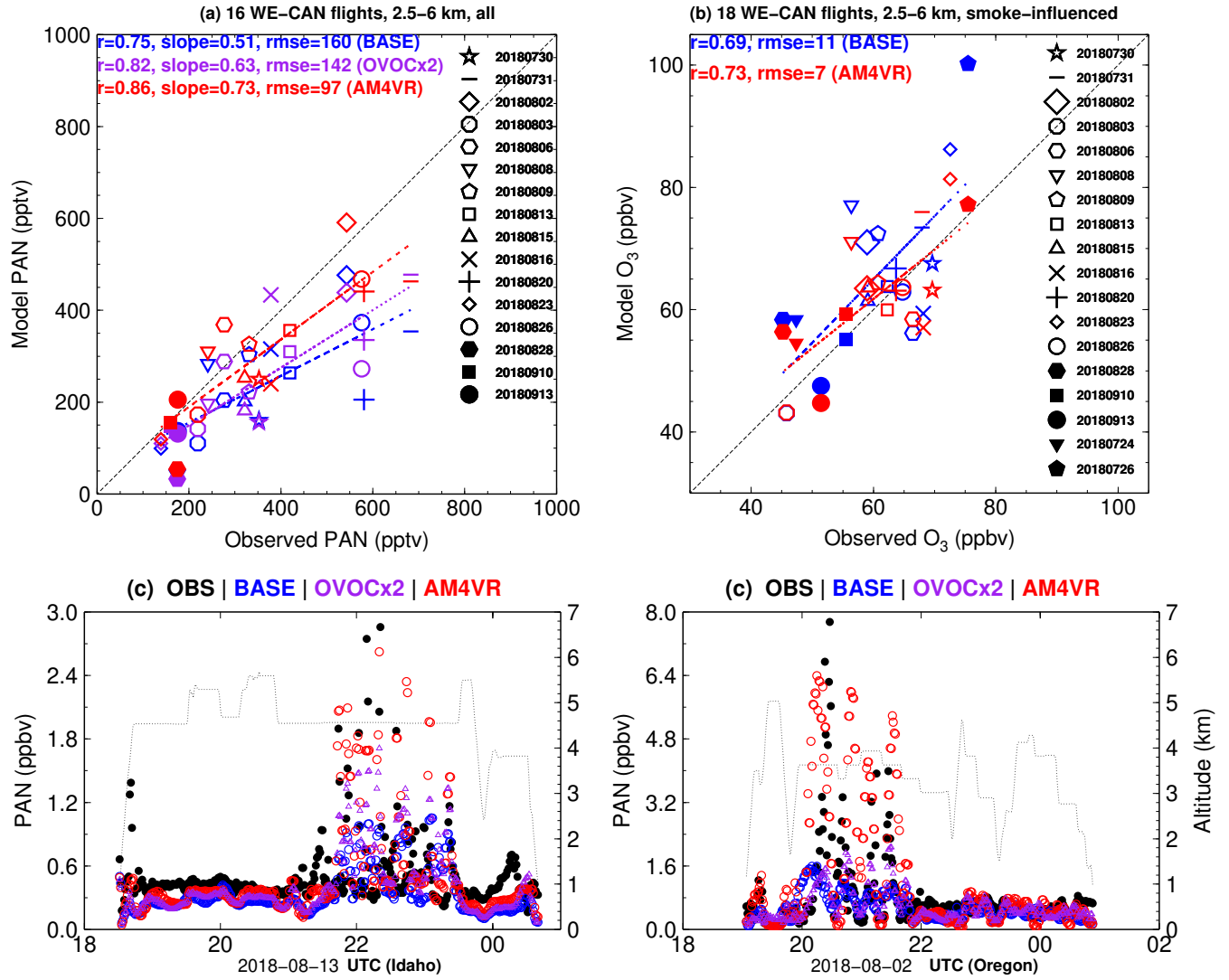


Figure 2. (a) Scatter plots of observed and simulated median mixing ratios of PAN during WE-CAN: each dot represents average of all data between 2.5–6 km altitude for each flight. Results are shown for BASE with BB emitting NO_y as 100% NO (blue), for doubling OVOC BB emissions (purple), and for AM4VR (red) with BB emitting NO (36%), HNO₃ (27%), and PAN (37%); (b) Same as (a) but for median O₃ in smoke-influenced observations (see text) for each WE-CAN flight; (c,d) Comparison of observed and simulated PAN along the WE-CAN flights on August 13 and 2. Dotted lines denote flight altitude using right axis.

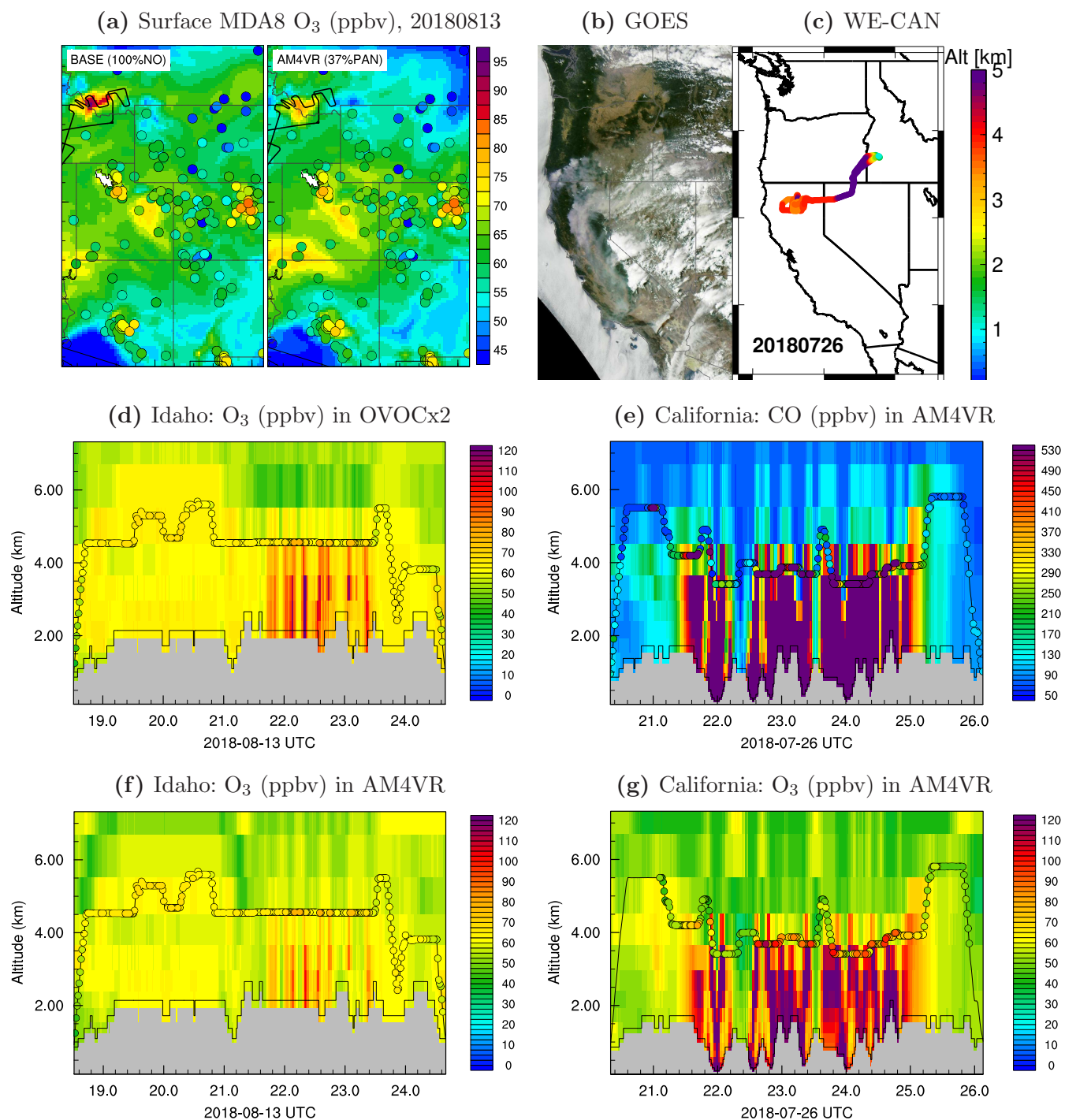


Figure 3. (a) Maps of surface MDA8 O₃ on August 13 from BASE (left) and AM4VR (right) simulations, with color-coded circles representing AQS observations. Thick black lines denote the flight track. (b,c) GOES image and WE-CAN flight on July 26. (d,f) Ozone observed on the August 13 flight superimposed on the time-height curtain plot of O₃ from the OVOCx2 and AM4VR experiments. (e,g) Observed and AM4VR simulated CO and O₃ for the July 26 flight.

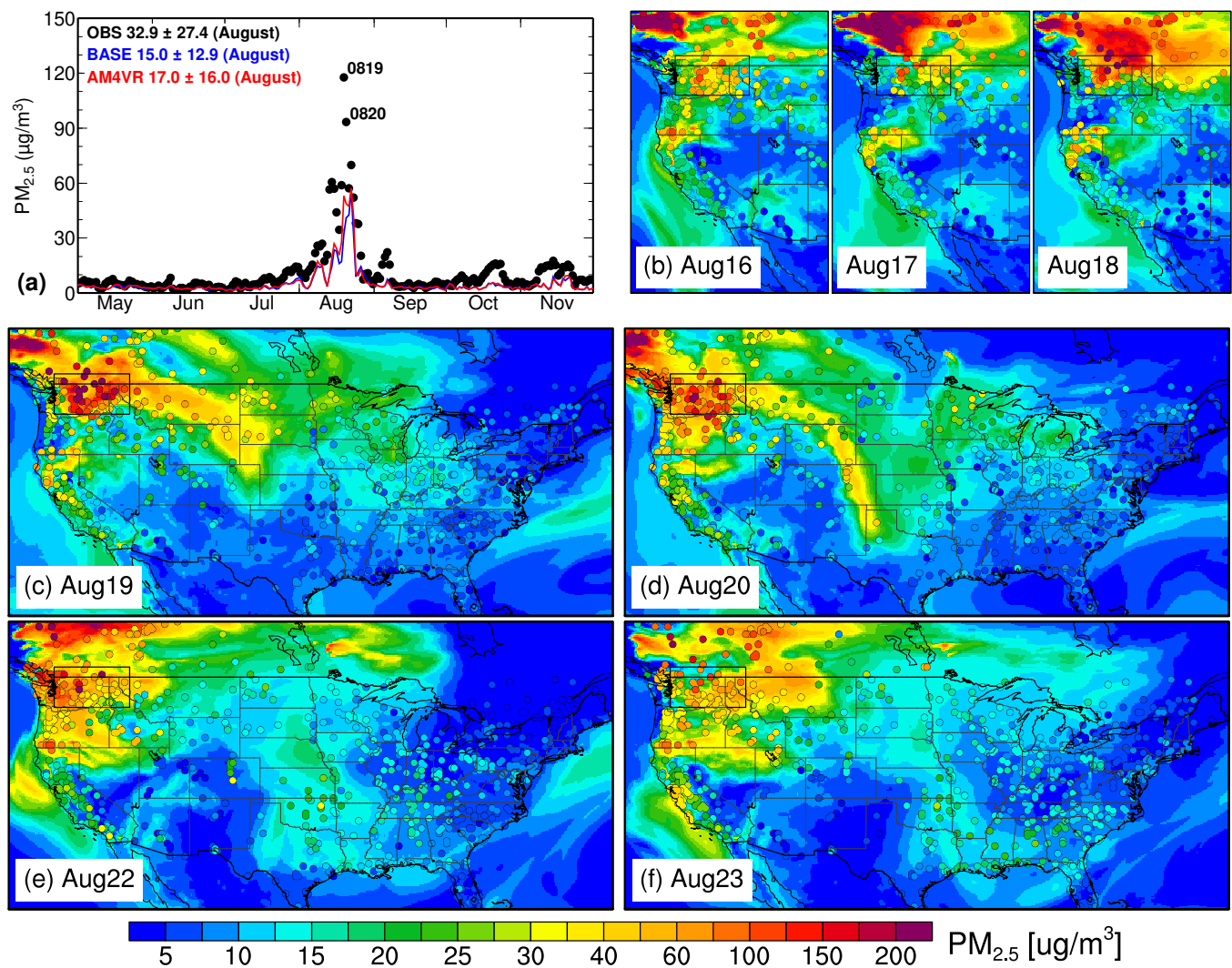


Figure 4. (a) Time series of 24-h mean surface $PM_{2.5}$ averaged over AQS sites in Washington state (box on map). (b-f) Maps of 24-h mean $PM_{2.5}$ from observations (filled circles) and AM4VR simulations (shading) on August 16-18 over the western US, and August 19-23 over the contiguous US.

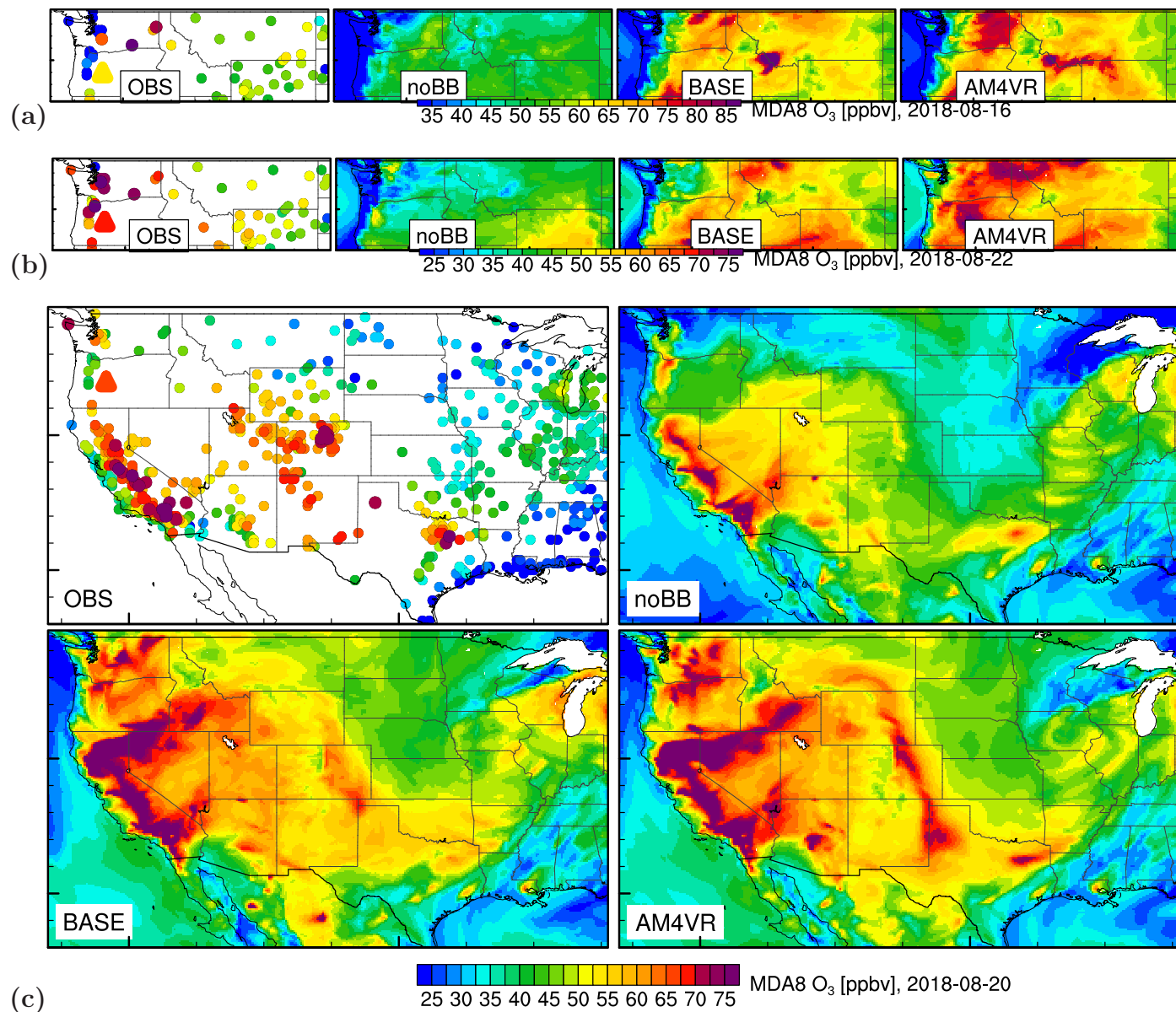
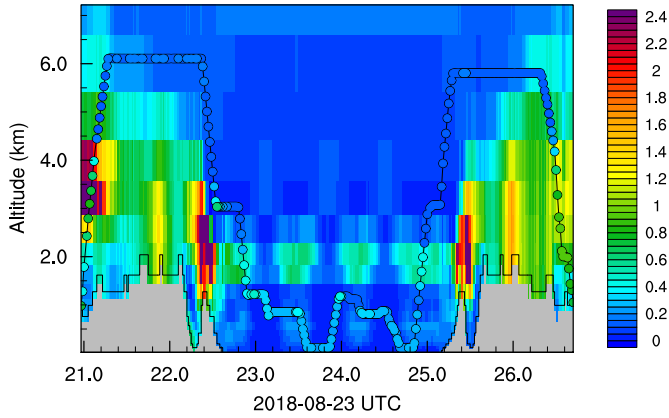
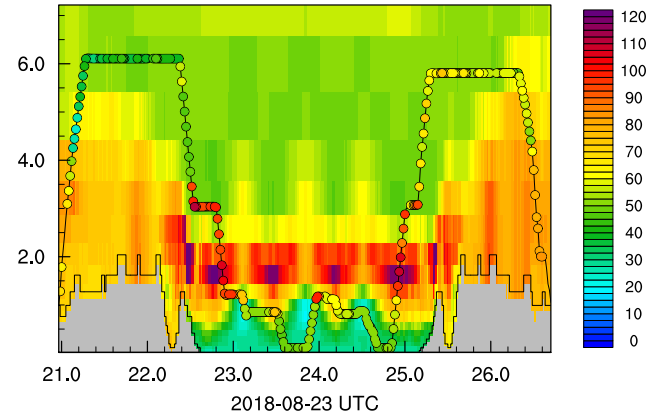


Figure 5. Surface MDA8 O₃ concentrations on August 16, 22 and 20 of 2018 from observations and model simulations with BB emissions of all NO_y and VOCs zero out (noBB), with BB emitting NO_y as 100% NO (BASE), and with AM4VR including the NO_y partitioning.

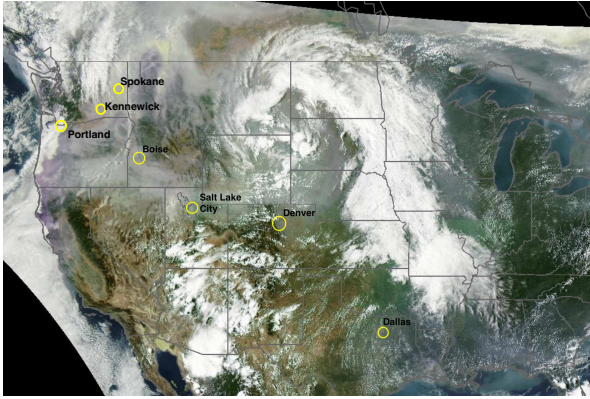
(a) PAN (ppbv) in AM4VR, $r=0.41$, $rmse=0.33$



(b) O₃ (ppbv) in AM4VR, $r=0.28$, $rmse=21$



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



(d) O₃ (ppbv) in BASE, $r=0.08$, $rmse=25$

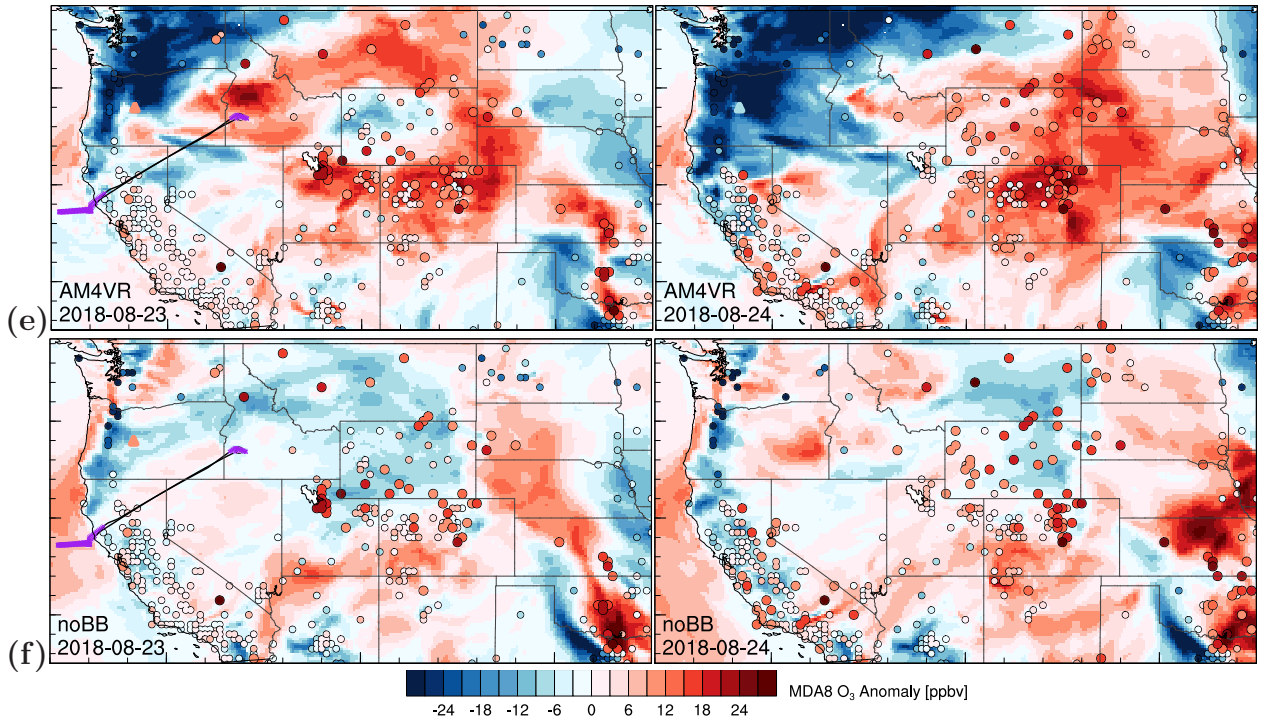
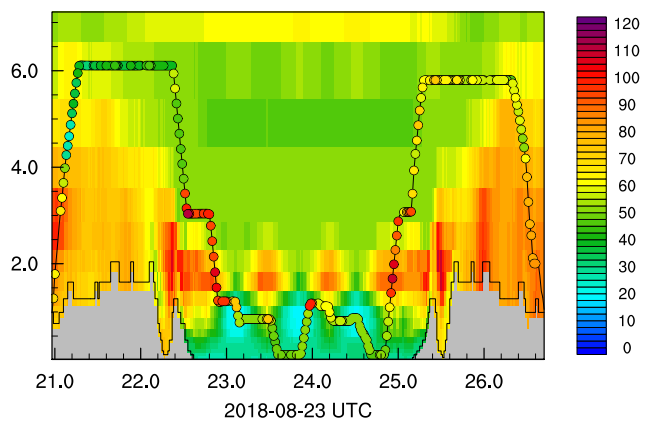


Figure 6. (a,b) Observed (filled circles) and AM4VR simulated PAN and O₃ for the August 23 flight; (c) GOES image; (d) Same as (b) but showing simulated O₃ from BASE. (e) Observed and AM4VR simulated surface MDA8 O₃ anomalies on August 23 and 24 (relative to August 22). (f) Same as (e) but showing noBB model results. The WE-CAN flight track is shown: purple crosses for below 4 km; black dots for above 4 km.