

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

3
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13 **Key Points (140 characters including spaces):**

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

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

33
34 **Plain Language Summary (200 words).** Wildfires have torn across western North America
35 over the last decade. Smoke from wildland fires in Canada can travel thousands of kilometers
36 to US cities and reacts with urban pollution to create harmful ozone, a criteria pollutant
37 regulated by the US Environmental Protection Agency. Accurately quantifying this impact is
38 needed to inform US air quality policy, but is challenging due to complex physical and chemical
39 processes. In this study, we analyze surface and airborne measurements, alongside a new
40 variable-resolution global chemistry-climate model, to elucidate these processes. We show
41 that conversion of NO_x emissions from wildfires to more oxidized forms reduces their localized
42 impacts on ozone. When Canadian smoke plumes descend towards US cities, including
43 Spokane, Salt Lake City, Denver and Dallas, higher temperatures cause a restoration of NO_x
44 and thus facilitate production of ozone in transit. On days when the observed daily maximum

45 8-h average ozone exceeds the health-based limit (70 ppbv), mixing of wildfire smoke into
46 urban pollution can contribute 10–20 ppbv.

47

48 **1. Introduction**

49 Large wildfires have become increasingly common during recent decades in the Canadian
50 province of British Columbia, the US Pacific Northwest, and California, causing severe air
51 pollution, loss of human life, and property damage [Westerling *et al.*, 2006; Abatzoglou and
52 Williams 2016; Brown *et al.*, 2023]. Five of the most destructive wildfire seasons of the last half-
53 century occurred in the past seven years: 2017, 2018, 2020, 2021, and 2023, raising the
54 possibility that climate change is already driving changes in fire regimes [Hagmann *et al.*, 2021;
55 Xie *et al.*, 2020; 2022; Parisien *et al.*, 2023]. Biomass burning (BB) in wildfires emits particulate
56 matter (PM) along with hundreds of reactive gases, including nitrogen oxides (NO_x), nitrous
57 acid (HONO), carbon monoxide (CO), ammonia (NH₃), and an enormous diversity of volatile
58 organic compounds (VOCs) [Hatch *et al.*, 2017; Permar *et al.*, 2021; Liang *et al.*, 2022]. The
59 complex chemical cocktail of wildfire smoke mixed with urban pollution represents a key
60 challenge for understanding fire smoke impacts on secondary air pollutants such as ozone (O₃)
61 [Jaffe *et al.*, 2020].

62

63 Wildfire emissions have variable impacts on O₃. In a review of more than 100 studies, Jaffe
64 and Wigder (2012) found that O₃ is usually enhanced downwind from wildfire plumes with
65 moderate smoke levels, and the O₃ production increases with plume age. At high smoke levels,
66 O₃ formation is suppressed, in part due to low-light conditions or to heterogeneous chemistry
67 on smoke particles [e.g., Alvarado *et al.* 2015; Palm *et al.*, 2021]. Observations show that
68 emissions of HONO and NO_x in boreal and temperate smoke plumes are rapidly (within a few
69 hours after emissions) converted into peroxyacyl nitrates (PANs) and particulate nitrate (pNO₃),
70 such that O₃ production in wildfire plumes rapidly becomes NO_x-limited [Alvarado *et al.* 2010;
71 Briggs *et al.*, 2017; Juncosa Calahorrano *et al.*, 2021a; Xu *et al.*, 2021]. The lifetime of NO_x is
72 approximately one day, while the lifetime of PAN in the mid-troposphere is at least a month
73 [Jacob, 1999]. Once ventilated from a source region to the cold free-troposphere where it is
74 more stable, PAN can be efficiently transported on hemispheric scales [Lin *et al.*, 2010; Fischer
75 *et al.*, 2014; Fiore *et al.*, 2018]. When a smoke plume subsides, PAN thermally decomposes to
76 release NO_x and can thus facilitate O₃ formation far downwind [Liu *et al.*, 2016; Bourgeois
77 *et al.*, 2021]. Ozone formation is also enhanced when VOC-rich smoke plumes mix into NO_x-rich
78 urban pollution, thereby deteriorating urban air quality [e.g., McClure & Jaffe 2018; Ninneman
79 & Jaffe 2021; Pan & Fanoola, 2022; Langford *et al.*, 2023].

80

81 Modeling large fire-to-fire variations in emission factors, smoke physics, plume dynamics and
82 complex chemical evolution is challenging [Paugam *et al.*, 2016; Jaffe *et al.*, 2020; Lindaas
83 *et al.*, 2020; L. Jin *et al.*, 2023; Ye *et al.*, 2021]. Current chemical transport models (CTMs, with
84 horizontal resolution ranging from 4–200 km) typically overestimate O₃ close to the fires while
85 having difficulty simulating the long-range influence of aged smoke plumes on downwind O₃
86 [Singh *et al.*, 2012; Fiore *et al.*, 2014; Zhang *et al.*, 2014; Baker *et al.*, 2016, 2018; Zhang *et*

87 *al.*, 2020; Bourgeois *et al.*, 2021; Tang *et al.*, 2022]. There are large uncertainties in the
88 partitioning of reactive nitrogen (NO_y), with models typically underestimating organic nitrates
89 and PANs in smoke plumes [Arnold *et al.*, 2015; Cai *et al.*, 2016]. Recent aircraft field
90 campaigns systematically sampled the first few hours of chemical evolution in wildfire
91 plumes, critical for evaluating and improving models [Lindaas *et al.*, 2021a; Permar *et al.*,
92 2021; Warneke *et al.*, 2023].

93

94 Here we use airborne measurements from the 2018 Western Wildfire Experiment for Cloud
95 Chemistry, Aerosol Absorption, and Nitrogen (WE-CAN) campaign [Lindaas *et al.*, 2021a;
96 *Juncosa Calahorrano et al.*, 2021ab] to partition BB emissions of NO_y into NO_x , PAN, and NO_3^-
97 ($\text{NO}_3^- = \text{HNO}_3 + p\text{NO}_3$) in a variable-resolution global chemistry-climate model (AM4VR) [Lin
98 *et al.*, 2024]. We show that sequestration of NO_x emissions in PAN from wildfires in the Pacific
99 Northwest enhances their downwind impacts on O_3 in US cities designated as O_3
100 nonattainment areas, including Salt Lake City, Denver and Dallas [US EPA, 2024]. With
101 regional grid refinements providing 13 km resolution over the contiguous US (see Fig.1 in Lin
102 *et al.*, 2024), AM4VR allows us to investigate interactions between urban pollution and smoke
103 plumes from fires thousands of kilometers away in Canada. We assess the contribution of
104 these interactions to the observed high- O_3 episodes by analyzing a suite of model simulations
105 alongside satellite images, aircraft sampling of smoke plumes, and ground-based
106 measurements.

107

108 **2. Observations and identification of smoke-influenced high- O_3 days**

109 The buildup of O_3 produced from urban emissions under hot and dry meteorological conditions
110 can complicate the attribution of observed O_3 enhancements to smoke influence [Lin *et al.*,
111 2017; 2020; Lindaas *et al.*, 2017]. We identify high- O_3 episodes in Colorado and Texas
112 influenced by Canadian wildfire smoke, using these criteria: (1) Satellite observations show
113 enhancements of Aerosol Optical Depth (AOD) across the Great Plains and animation of the
114 GEOS-R images every 10 minutes shows passage of a cold front towards the Southern Great
115 Plains; via NOAA AerosolWatch (<https://star.nesdis.noaa.gov/smcd/spb/aq/AerosolWatch/>); (2)
116 Ground sites in Colorado and Texas record $\text{PM}_{2.5}$ greater than the $35 \mu\text{g}/\text{m}^3$ NAAQS level for
117 24-h mean; (3) IMPROVE ground sites measure enhancements (+50% above background
118 level) in organic aerosol (OA), a key component of wildfire smoke [Garofalo *et al.*, 2019]; and
119 (4) Ground sites measure surface O_3 above the 70 ppbv NAAQS level for daily maximum 8-h
120 average (MDA8).

121

122 **[Figure 1 about here]**

123 Applying these criteria to data in 2018, we identify smoke-influenced high- O_3 days in the
124 Colorado Front Range Urban Corridor on August 20 and 24, and in the US Deep South on
125 August 20–21 (**Fig.1**). On August 19, GOES-East showed heavy smoke from wildfires burning
126 in the Pacific Northwest (**Fig.1a**). On August 20, a cold front passed across the Great Plains,
127 transporting Canadian wildfire smoke towards the US Deep South (**Fig.1b**). By the afternoon
128 of August 20, smoke had reached Amarillo and Dallas, Texas, and lingered in the region on

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

144

145 **3. GFDL AM4VR simulations**

146

147 AM4VR is a new variable-resolution global chemistry-climate model recently developed at
148 NOAA's Geophysical Fluid Dynamics Laboratory (GFDL) for research at the nexus of US
149 climate and air quality extremes [Lin et al., 2024]. For this study, we conduct nudged AM4VR
150 simulations for 2018 using daily emissions from the Global Fire Emission Database (GFED4s,
151 0.25°x0.25°) [van der Wolf et al., 2017], distributed vertically between the surface and 6 km
152 based on an injection height climatology derived from MISR (Val Martin et al., 2018). AM4VR
153 includes a revised treatment of VOC emissions [Lin et al., 2024], accounting for emissions of
154 acetaldehyde (CH₃CHO) and methyl ethyl ketone (MEK, C₄H₈O), both precursors of PAN, from
155 wildfires that are ignored in our previous model AM4.1 [Horowitz et al., 2020]. Anthropogenic
156 emissions are obtained from the Community Emissions Data System version 2021-04-21
157 (0.1°x0.1°, O'Rourke et al., 2021).

158

159 Four AM4VR model experiments are designed to explore the impacts of oxygenated VOC
160 emissions (OVOC) and NO_y evolution in smoke plumes, in addition to regional anthropogenic
161 emissions (**Table S1**). Fires in our BASE model emit NO_y purely as NO, similar to previous
162 models. *Juncosa Calahorrano et al.* [2021a] showed that, within a few hours after emissions,
163 approximately 37% of the total NO_y species is in the form of PANs and *p*NO₃ is the second
164 largest contributor (27%), based on data averaged over all fresh plume transects during WE-
165 CAN. Since our model does not fully resolve the rapid chemical transformations within
166 concentrated smoke plumes, we thus parameterize NO_y emissions from fires into 37% PAN,
167 27% HNO₃, and 36% NO in a second simulation (hereafter AM4VR), as in Lin et al. [2024]. The
168 equilibration between gas-phase HNO₃ and *p*NO₃ is simulated dynamically depending on
169 temperature, altitude, and NH₃ availability [Fountoukis & Nenes, 2007; Lindass et al., 2021b].
170 We conduct two additional simulations: one with BB emissions of OVOCs (HCHO, CH₃CHO,

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

174

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

176

177 **[Figure 2 about here]**

178 We first assess the impacts of NO_y partitioning on O_3 formation in the near-fire (< 1 day of
179 aging) western US smoke plumes sampled by WE-CAN in summer 2018 (Text S1 and Fig.S1).

180 **Fig.2a** shows comparisons of observed and simulated median mixing ratios of PAN between
181 2.5 and 6 km altitude for each of the WE-CAN flights. The BASE model, with fires emitting NO_y
182 purely as NO, captures only ~50% of the observed PAN abundance. Comparisons of CO,
183 HCHO, CH_3CHO , and CH_3COCH_3 indicate significant under-representation of VOCs in
184 simulated smoke (Text S2 and Fig.S2), consistent with the findings of L. Jin et al. (2023) using
185 the GEOS-Chem model. Doubling OVOC emissions from fires favors PAN formation by
186 producing more acetyl peroxy radical (CH_3CO_3), but it is insufficient to remove the bias,
187 suggesting that CH_3CO_3 has substantial production from oxidation of VOCs not represented
188 by the models (Coggon et al., 2019; Xu et al., 2021; Permar et al., 2023). Even at 13 km
189 resolution, it is challenging for the model to capture rapid photochemical processes that occur
190 in a concentrated smoke plume. Using observations to partition a fraction of NO_y emissions
191 from fires into PAN and NO_3^- thus provides a parameterization to account for additional VOCs
192 and rapid chemistry in smoke. The regression slope of simulated PAN with observations
193 increases from 0.51 in BASE to 0.73 in AM4VR with the NO_y partitioning. The overall root-
194 mean-square-error (RMSE) decreases from 160 to 97 pptv.

195

196 **Fig.2b** shows comparison of median O_3 between 2.5 and 6 km altitude in smoke-influenced air
197 masses, identified with observed CO > 85 ppbv, HCN > 275 pptv, and CH_3CN > 200 pptv, for
198 each WE-CAN flight. Rapid conversion of NO_x to PAN and NO_3^- reduces excessive O_3
199 production in near-fire smoke plumes in the model, decreasing the overall RMSE from 11 to 7
200 ppbv. The effects are as large as 10–23 ppbv in the fresh smoke plumes sampled on July 26
201 and August 2, 9 and 13. Supporting our findings, Xu et al. (2021) used a box model constrained
202 by observations to show that the partitioning of NO_y species slows O_3 formation in fresh plumes.

203

204 **[Figure 3 about here]**

205 We analyze several fresh plumes in more detail. On August 13, the aircraft sampled smoke
206 from wildfires burning in the Salmon Challis National Forest in Idaho (**Fig.S1**). Intercepted at
207 ~4.5 km altitude between 22:00–23:30 UTC, this smoke plume exhibits factors of 2–5 times
208 enhancements of PAN above the background level (**Fig.2c**). On August 2, the aircraft
209 intercepted fresh plumes from fires burning in Southwest Oregon. With the NO_y partitioning,
210 AM4VR captures the observed PAN abundance approaching 3 ppbv on August 13 and 8 ppbv
211 on August 2 within the smoke plumes (**Figs.2c-d**). In contrast, BASE captures less than 30%
212 of observed PAN levels for both plumes. The NO_x loss to NO_3^- and PAN leads to a decrease

213 of MDA8 O₃ by ~15 ppb in surface air over the burned area around the Idaho/Montana border
214 (**Fig.3a**). The lower O₃ simulated by AM4VR agrees better with WE-CAN observations (**Fig.3d-**
215 **f**). Doubling OVOC emissions from fires leads to a slight increase in PAN, but this does not
216 systematically reduce model O₃ biases in the fresh plumes. AM4VR also improves upon BASE
217 in representing the observed impacts of aged smoke on MDA8 O₃ exceedances in Salt Lake
218 City on August 13 (**Fig.3a and Fig.S3**).

219
220 On July 26, the aircraft sampled smoke from the Carr Fire in the wildland-urban interface of
221 northern California (**Fig.3b-c**). PAN was not measured on this flight. Sampled by multiple
222 aircraft transects at ~4 km altitude between 22:30–24:30 UTC, the smoke plume over northern
223 California exhibited O₃ mixing ratios of 85–120 ppbv, compared to ~65 ppbv in the remote
224 Idaho plume (**Fig.3g**). Fires burning in close proximity to NO_x-rich urban areas in California had
225 a greater impact on O₃ formation. Comparisons of CO and O₃ along the flight track show that
226 AM4VR represents the vertical structure of the smoke plume and the observed magnitude of
227 O₃. The BB NO_y parameterization reduces free tropospheric O₃ by ~23 ppbv in smoke-
228 influenced environments (blue versus red pentagons in **Fig.2b**). This is consistent with box
229 modeling suggesting that O₃ formation in VOC-rich smoke plumes is mostly NO_x-limited [*Xu et*
230 *al.*, 2021; *X. Jin et al.*, 2023].

231
232 Evaluation with aircraft observations shows that AM4VR captures the large-scale structure of
233 smoke plumes (e.g., July 26, August 2, and 13). WE-CAN sampled plumes between 2–5 PM
234 (local time) when fires are active and plumes are injected high in the atmosphere. The injection
235 height derived from MISR with a 10:30 AM overpass is thus biased low. However, the simulated
236 vertical distribution of tracers in smoke plumes is not only determined by the MISR injection
237 height climatology but also by strong vertical mixing under hot meteorological conditions. There
238 are cases in which we identified model PAN biases caused by insufficient injection height. On
239 July 30 (stars in Fig.2a-b), for example, the aircraft intercepted fresh smoke plumes at 3–4 km
240 altitude between 22:00–25:00 UTC, while the model simulated plumes at ~2 km altitude
241 (**Fig.S4**). Despite this bias in altitude, the NO_y partitioning consistently leads to enhanced PAN
242 and reduced O₃ in the simulated fresh plumes.

243

244 **5. Ozone formation in aged smoke plumes in cities**

245

246 **[Figure 4 about here]**

247 We next examine the influence of smoke plumes on O₃ photochemistry in urban areas,
248 following long-range transport over thousands of kilometers. We focus on the August 16–24
249 period when several cold fronts transported smoke from numerous fires burning in the Pacific
250 Northwest to Salt Lake City, the Colorado Front Range Urban Corridor, and the US Deep South
251 (**Fig.4**). Air quality monitors in Washington state recorded hazardous PM_{2.5} pollution of 100–
252 250 µg/m³ for 24-h average on August 19–20. Dense wildfire smoke reduced the intensity of
253 light reaching the surface (**Fig.1**) and increased removal of HO_x radicals on smoke particles,
254 leading to observed suppression of O₃ formation in the region on August 20 (**Fig.5**). AM4VR

255 accounts for the radiative effects of simulated aerosols on photolysis rates and heterogeneous
256 chemistry on smoke particles [Lin *et al.*, 2024]. But AM4VR with GFED4s emissions captures
257 only 60% of the peak PM_{2.5} levels in Washington state, which partly explains model
258 overestimation of O₃ there on August 20. Enhancements of O₃ in aged wildfire smoke are often
259 greatest when smoke levels are moderate (Buysse *et al.*, 2019; Pan and Faloon, 2022). On
260 August 16 and 22, when PM_{2.5} was 30–60 µg/m³, both observations and model showed
261 elevated MDA8 O₃ above 70 ppbv at monitors in Spokane, Richland-Kennewick, and Portland.
262

263 **[Figure 5 about here]**

264 Comparisons of surface MDA8 O₃ from the noBB, BASE, and AM4VR experiments
265 demonstrate the critical role of NO_x supply from PAN decomposition and urban pollution on O₃
266 formation in VOC-rich smoke plumes (Fig.5). On August 16 (Fig.5a), observed MDA8 O₃ is 80
267 ppbv at Spokane and 85 ppbv at Richland-Kennewick. Simulated MDA8 O₃ is below 60 ppbv
268 in the noBB experiment, indicating minor influence of O₃ produced from local anthropogenic
269 emissions alone. Accounting for VOC and NO_x emissions from fires, simulated MDA8 O₃
270 increases to 70–75 ppbv in BASE, still lower than observed. Accounting for enhanced PAN
271 formation in fresh plumes and its subsequent decomposition to NO_x in aged smoke increases
272 MDA8 O₃ by ~5 ppbv in AM4VR, bringing it closer to the observed values. Similarly, the NO_y
273 partitioning led to better agreements of simulated MDA8 O₃ with observations at Richland-
274 Kennewick, Portland, and Mt. Bachelor Observatory on August 22. MDA8 O₃ is 70–80 ppbv
275 from observations, below 55 ppbv in noBB, 55–65 ppbv in BASE, and 70–75 ppbv in AM4VR
276 (Fig.5b).
277

278 On August 20–21, as smoke descended in the dry air stream of the cold front towards higher
279 temperatures in the US Deep South (Fig.1 and Fig.4d), PAN decomposed to release NO_x and
280 thus facilitated O₃ formation (Fig.5c). This is clearly demonstrated with the substantial
281 difference between the O₃ simulated in BASE versus AM4VR. The BASE model simulates
282 MDA8 O₃ below 70 ppbv in Denver, Amarillo, and Dallas, inconsistent with observations. With
283 NO_y parameterization, AM4VR simulates well the observed O₃ levels in these areas, increasing
284 MDA8 O₃ by ~8 ppbv relative to BASE and 10–15 ppbv relative to noBB. Most of the sites with
285 observed MDA8 O₃ exceeding 70 ppbv were located downwind of the Denver and Dallas urban
286 areas along the smoke transport pathway, indicating in-situ O₃ production resulting from mixing
287 of smoke VOCs with urban NO_x. During August 21, as smoke further mixed into surface air in
288 Dallas (Fig.1d), urban pollution provided a critical NO_x supply to enhance O₃ formation in
289 smoke by ~5 ppbv (Fig.S5).
290

291 **[Fig.6 about here]**

292 During August 23–24, a new cold front transported smoke towards Salt Lake City, Denver, and
293 California's Central Valley (Fig.4f and Fig.6). Smoke plumes were intercepted by the WE-CAN
294 aircraft below ~4 km during the ascent from Boise at 2:00PM PDT (21:00 UTC), between 1–3
295 km off the California coast at 3–6 PM PDT, and below ~4 km during the descent to Boise at
296 7:30PM (Figs.6a-b). The estimated chemical age is 1–3 days for the plumes over Boise and >

297 3 days for the plume off the California coast [O'Dell et al., 2020; Permar et al., 2023]. These
298 aged smoke plumes exhibit relatively lower PAN and higher O₃ levels compared to the fresh
299 plumes sampled by WE-CAN (**Fig.2**). The plume off the California coast exhibits O₃ above 100
300 ppbv and PAN below 0.5 ppbv. AM4VR with NO_y parameterization captures better
301 enhancements of O₃ with increased plume age, simulating higher O₃ in aged smoke off the
302 California coast than BASE (**Fig.6b vs 6d**).

303

304 As the smoke plumes wafted across the western US and mixed with urban pollution,
305 observations show MDA8 O₃ increased by 10–20 ppbv in Salt Lake City on August 23 and in
306 the Colorado Front Range on August 24 relative to August 22 (**Fig.6e**). AM4VR captures the
307 observed features, simulating increased O₃ in the descending dry air stream of the cold front.
308 With BB emissions of VOCs and NO_y zeroed out, simulated O₃ decreased in Salt Lake City on
309 August 23 and in Colorado on August 24, indicating that the cold front would otherwise
310 transport clean air to these areas in the absence of wildfire smoke (**Fig.6f**). Over Oklahoma
311 and northern Texas, in contrast, noBB showed enhanced MDA8 O₃ on August 23–24, indicating
312 that the ozone pollution was primarily produced from regional anthropogenic emissions. The
313 model attribution is consistent with IMPROVE observations showing little OA enhancement at
314 Wichita Mountain on August 24 (**Fig.1f**). California's Central Coast and San Joaquin Valley
315 were also influenced by smoke (PM_{2.5} = 35–50 µg/m³) on August 24 (**Fig.S6**). Observations
316 show increased sites in California with MDA8 O₃ exceeding 70 ppbv on the smoky day. AM4VR
317 simulates 3–6 ppbv MDA8 O₃ enhancements due to wildfire emissions, implying that the
318 exceedances would not occur if there were no smoke.

319

320 **6. Conclusions**

321

322 Due to the large quantity of VOCs emitted by wildfires, O₃ formation in aged smoke is generally
323 NO_x-limited. Through an integrated analysis of observations and global model simulations, we
324 highlight the role of NO_y evolution on O₃ production in aged smoke plumes transported
325 thousands of kilometers downwind. Rapid conversion of NO_x to NO₃⁻ and PAN reduces
326 excessive O₃ production in the model in near-fire smoke plumes sampled by the WE-CAN
327 aircraft campaign. Sequestration of NO_x to PAN from boreal fires fuels downwind O₃ formation.
328 When smoke plumes travel from British Columbia to US cities, including Spokane, Portland,
329 Salt Lake City, Denver, and Dallas, PAN thermally decomposes to release NO_x and thus
330 enhances O₃ production in conjunction with the urban NO_x supply. On days when observed
331 MDA8 O₃ is 70–85 ppbv, mixing of wildfire smoke into urban pollution enhances O₃ production
332 by 10–20 ppbv. As large wildfires are projected to increase in western North America due to
333 climate warming [Xie et al., 2022], accurate representation of VOCs and NO_y evolution in
334 smoke is critical to assess the implications for US O₃ air quality.

335

336 **Open Research.**

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

340

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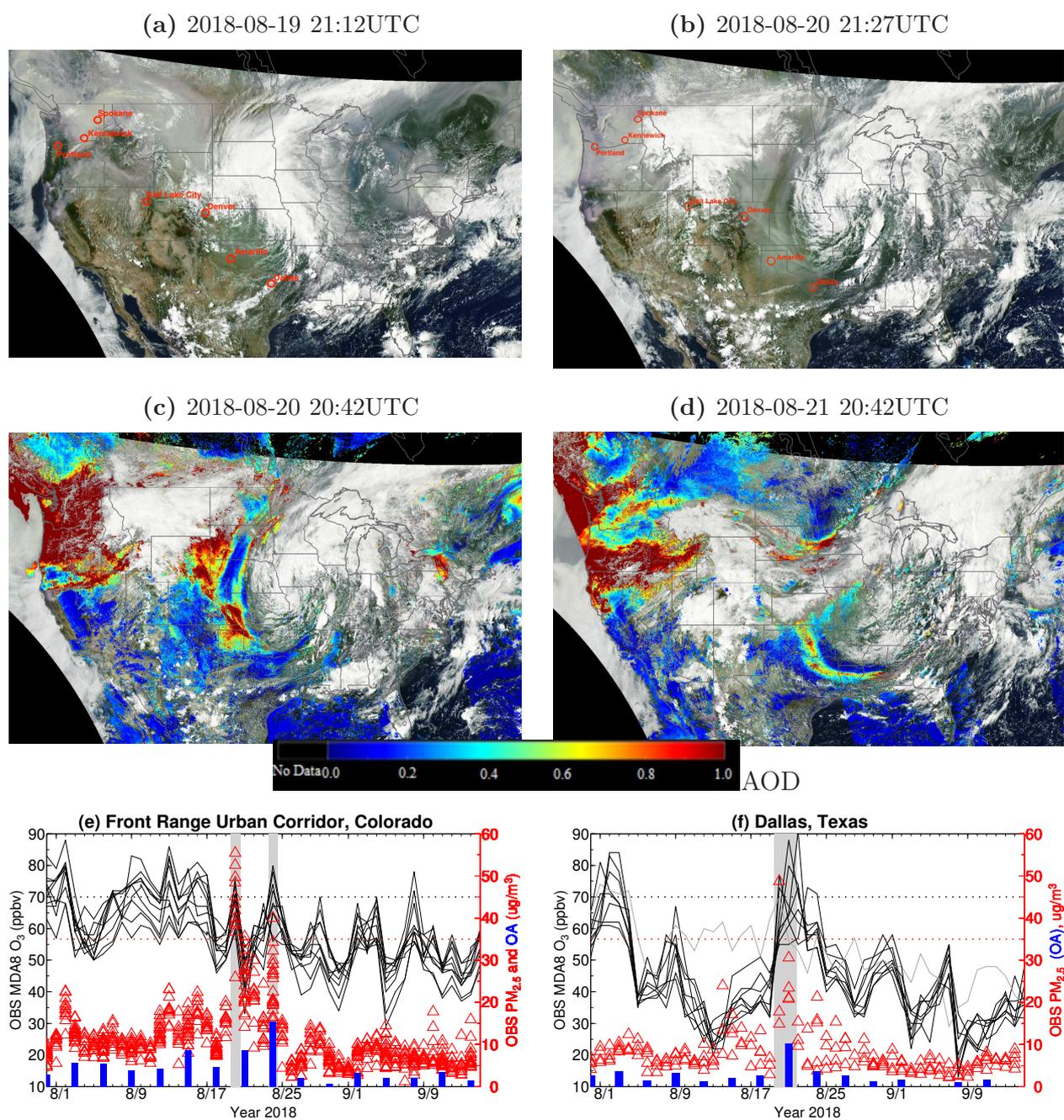


Figure 1. (a-b) GOES images on August 19 and 20, 2018. Cities referenced in the article are labeled. (c-d) Suomi-NPP AOD superimposed on the GOES images on August 20 and 21, 2018. (e-f) Time series of observed daily MDA8 O₃ (black lines) and 24-h PM_{2.5} (red triangles) at AQS sites in the Front Range 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.

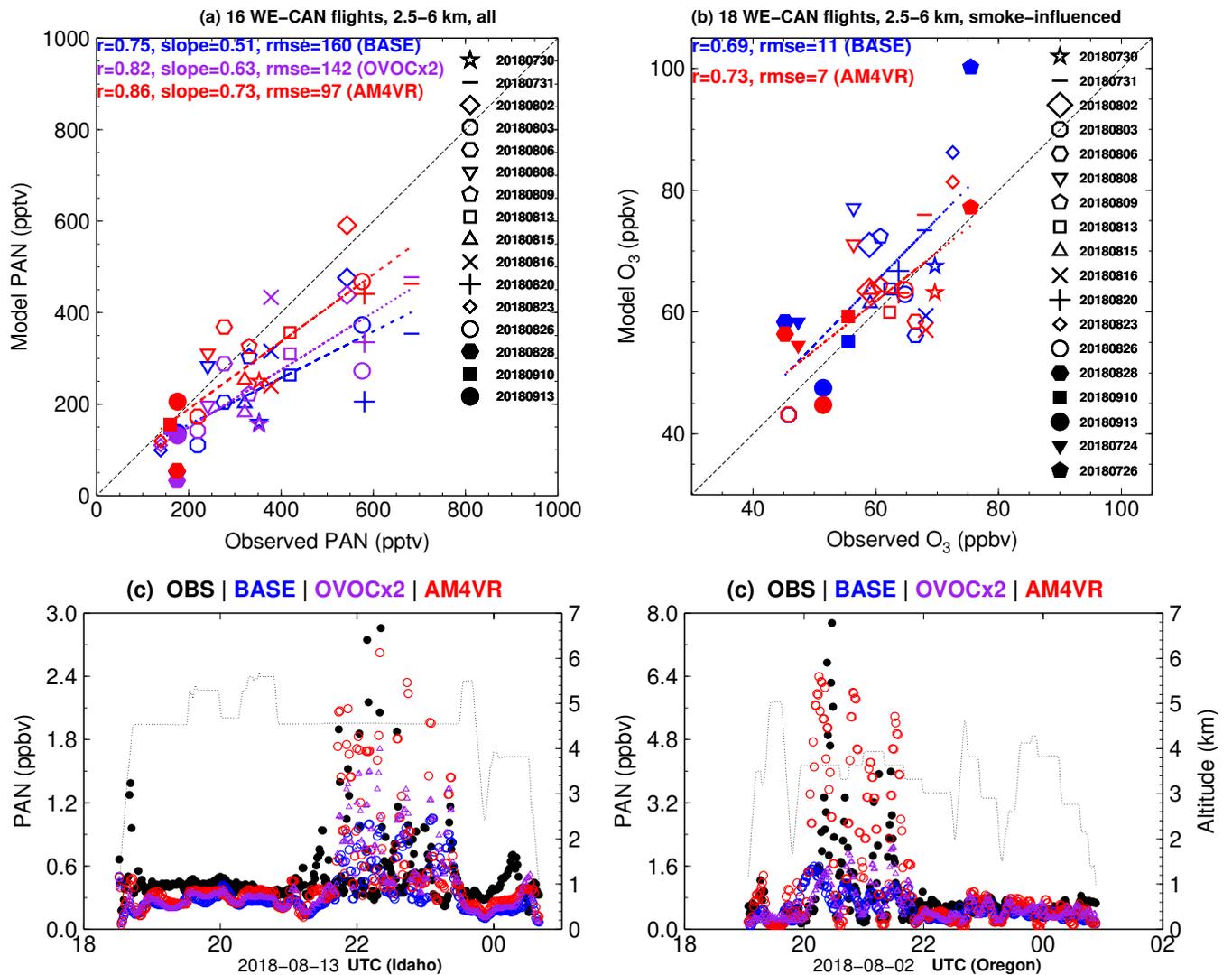


Figure 2. (a) Scatter plots of observed and simulated median mixing ratios of PAN during WE-CAN: each dot represents average of all data between 2.5-6 km altitude for each flight. Results are shown for BASE with BB emitting NO_y as 100% NO (blue), for doubling OVOC BB emissions (purple), and for AM4VR (red) with BB emitting NO (36%), HNO_3 (27%), and PAN (37%); (b) Same as (a) but for median O_3 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.

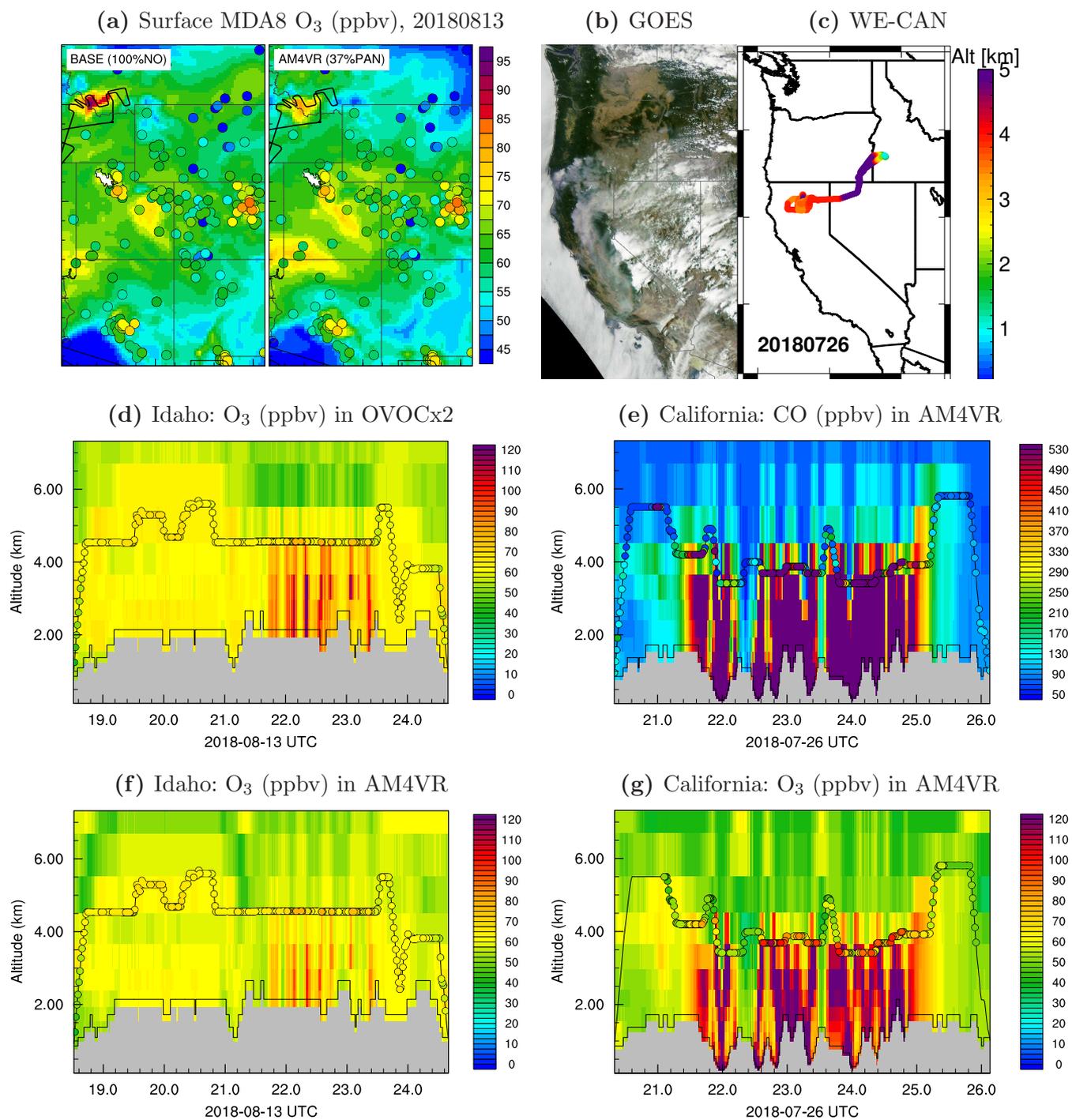


Figure 3. (a) Maps of surface MDA8 O₃ on August 13 from BASE (left) and AM4VR (right) simulations, with color-coded circles representing AQS observations. Thick black lines denote the flight track. (b,c) GOES image and WE-CAN flight on July 26. (d,f) Ozone observed on the August 13 flight superimposed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

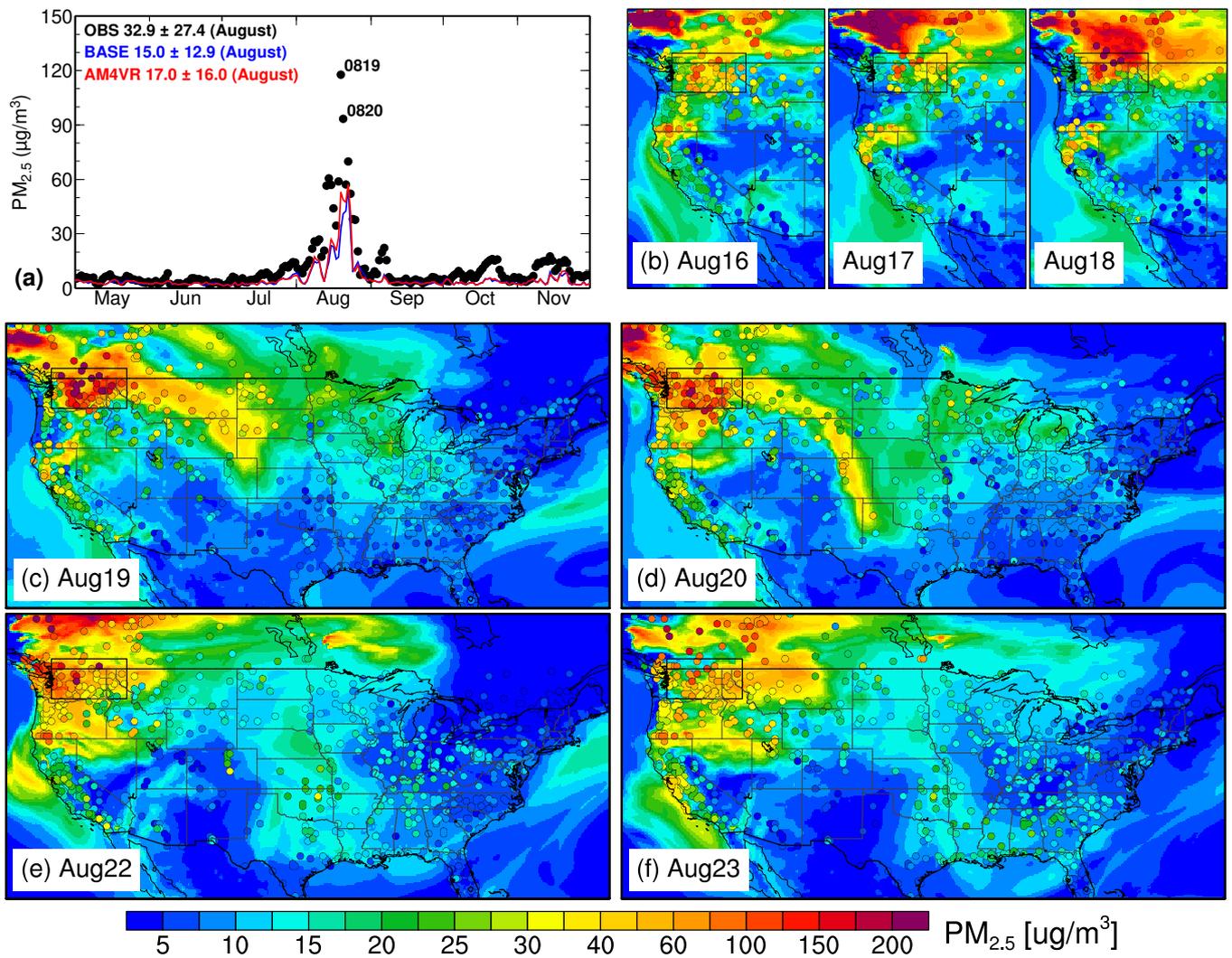


Figure 4. (a) Time series of 24-h mean surface $PM_{2.5}$ averaged over AQS sites in Washington state (box on map). (b-f) Maps of 24-h mean $PM_{2.5}$ from observations (filled circles) and AM4VR simulations (shading) on August 16-18 over the western US, and August 19-23 over the contiguous US.

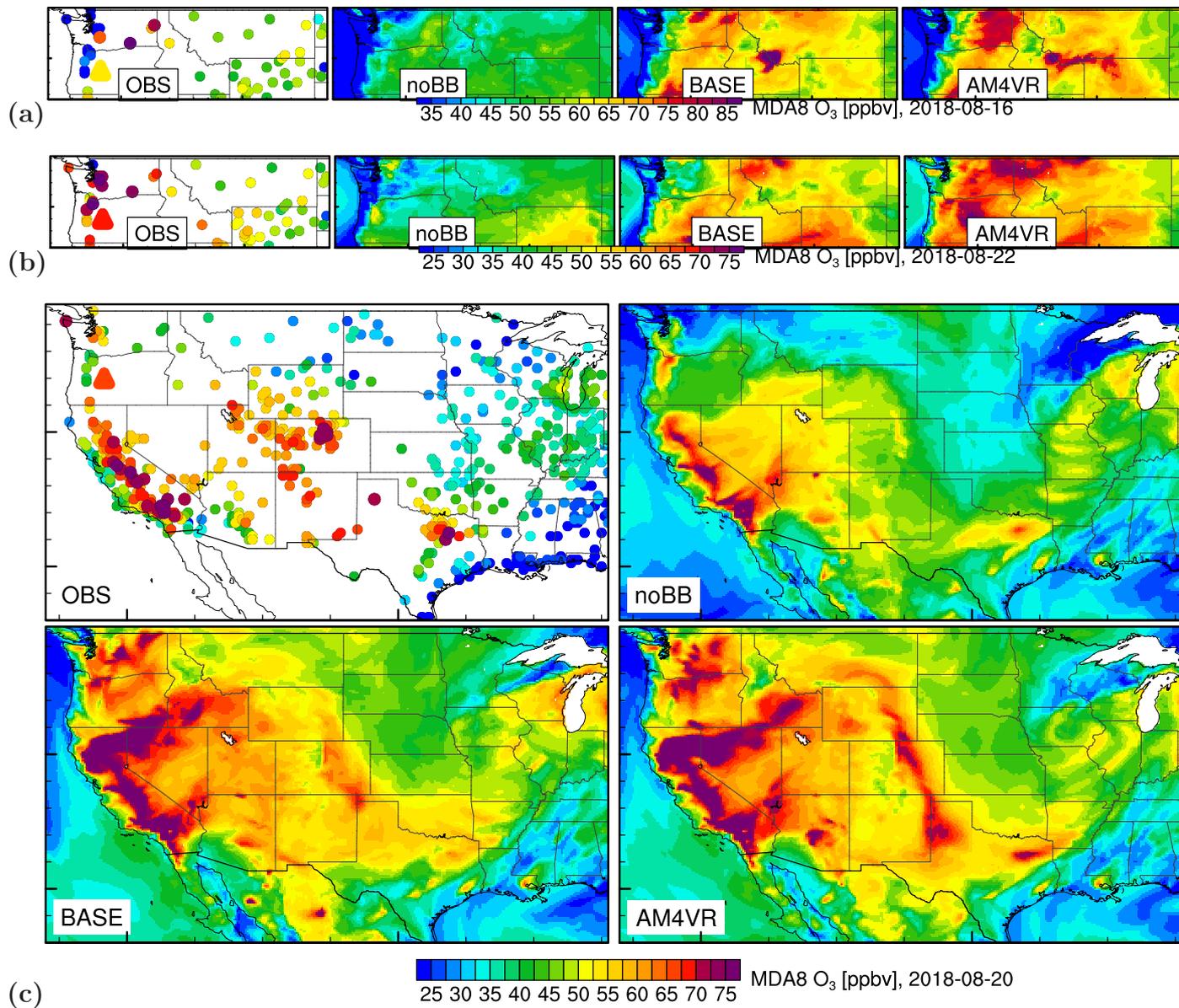
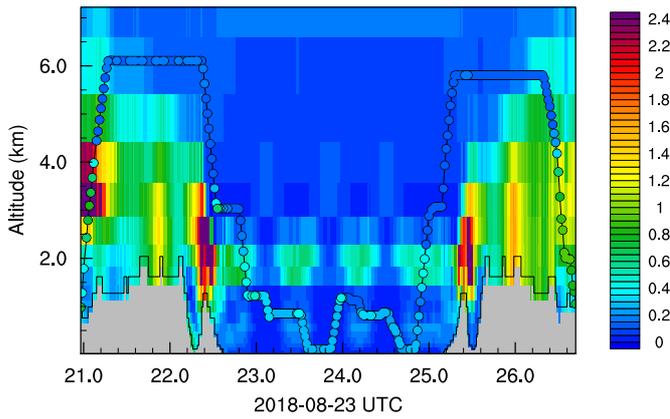
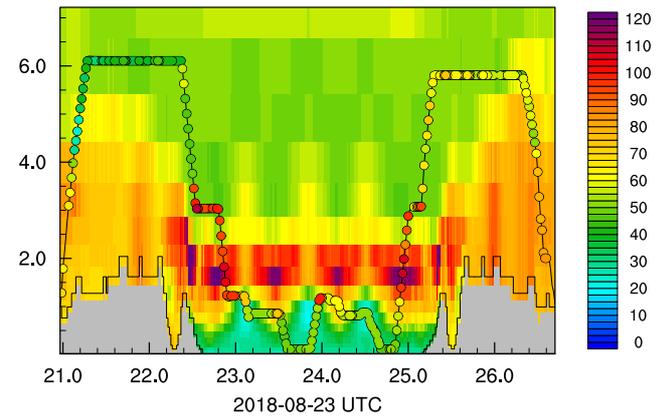


Figure 5. Surface MDA8 O₃ concentrations on August 16, 22 and 20 of 2018 from observations and model simulations with BB emissions of all NO_y and VOCs zero out (noBB), with BB emitting NO_y as 100% NO (BASE), and with AM4VR including the NO_y partitioning.

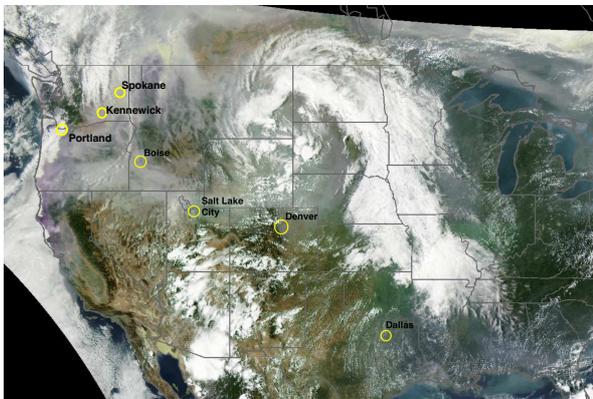
(a) PAN (ppbv) in AM4VR, $r=0.41$, $rmse=0.33$



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



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



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

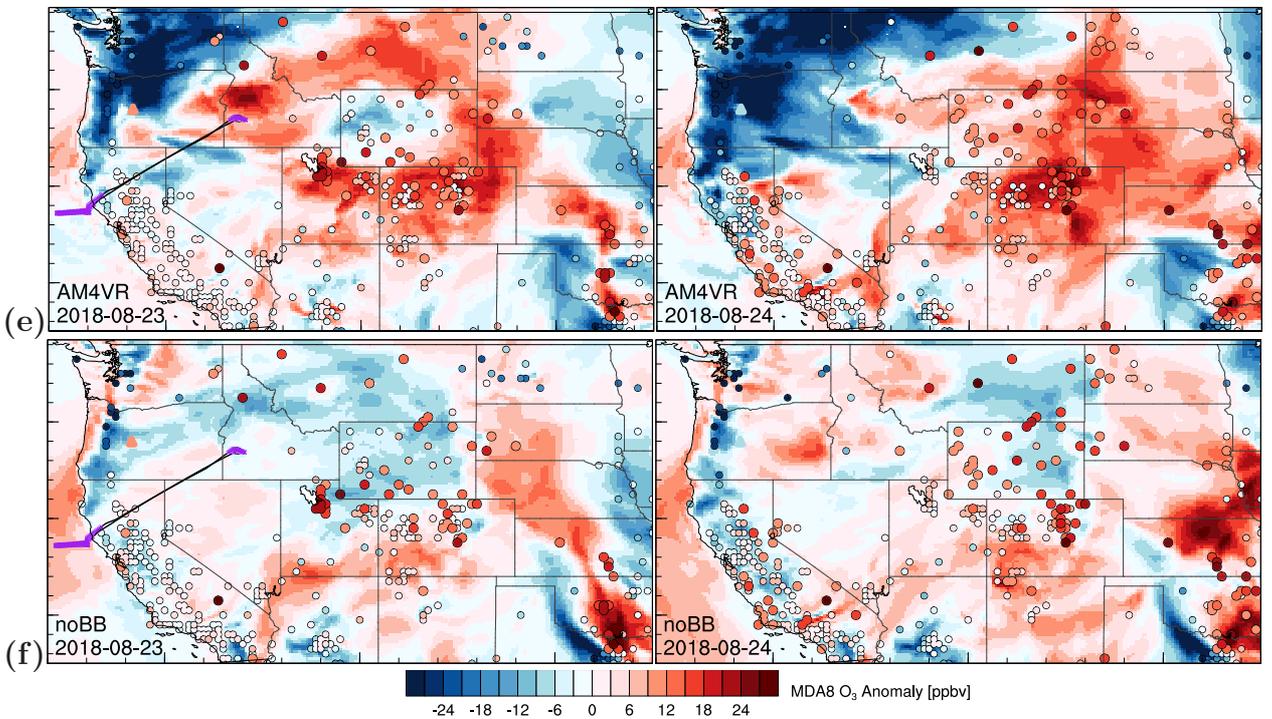
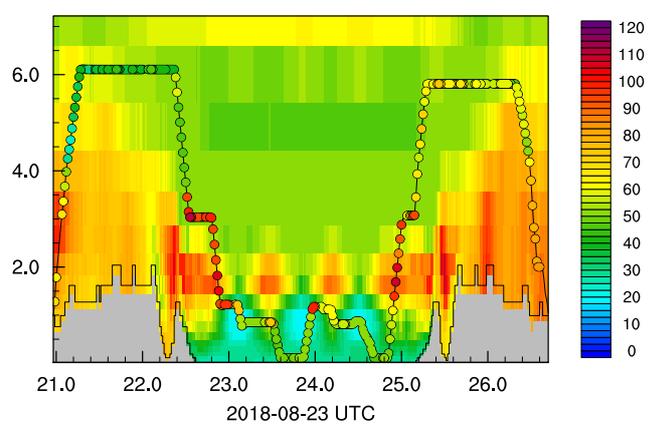


Figure 6. (a,b) Observed (filled circles) and AM4VR simulated PAN and O₃ for the August 23 flight; (c) GOES image; (d) Same as (b) but showing simulated O₃ from BASE. (e) Observed and AM4VR simulated surface MDA8 O₃ anomalies on August 23 and 24 (relative to August 22). (f) Same as (e) but showing noBB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