Supporting Information for AGU Publication Geophysical Research Letter

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

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Text S1: WE-CAN observations and sampling of AM4VR simulations

The WE-CAN aircraft campaign focused on near-source aging of smoke plumes with physical ages less than 6 h (< 185 km from the centroid of the active burned area) [*Lindaas et al., 2020; Juncosa Calahorrano et al., 2021; Permar et al., 2021*]. There are a total of 16 research flights based out of Boize, Idaho and 3 educational flights based out of Broomfield, Colorado, during July 24 to September 13 in 2018 (**Fig.S1**). PAN was not measured on the July 24 and 26 flights.

In this study, we use WE-CAN aircraft measurements to evaluate chemical composition in the near-fire smoke plumes, including CO, PAN, O_3, and VOCs [Flocke et al., 2019; Weinheimer et al., 2019; Campos T. 2019; Apel et al., 2020; Permar et al., 2021]. The 1-min merged WE-CAN data are used in this study. AM4VR calculates atmospheric chemistry and physics and land every 10 min [Lin et al., 2024]. For comparison with WE-CAN data, three-dimensional (3D) chemical fields are archived from the model every 3 h. The three hourly average model fields are then linearly interpolated to the 1-min merged flight tracks in space and time. Due to the different temporal resolution of observational data and model outputs, the timing and location of wildfire plumes are not expected to match exactly in the two datasets. This may explain some of the observations–AM4VR discrepancies when the aircraft performed wildfire plume transects, such as during 21–24 UTC on August 13 and 20–22 UTC on August 2 (Fig.2 in the main article).

Text S2: Comparison of simulated CO and VOCs with WE-CAN data

Figure S2 shows comparisons of the average campaign profiles for carbon monoxide (CO), formaldehyde (HCHO), acetaldehyde (CH_3CHO), acetone (CH_3COCH_3), and propane (C_3H_8) between WE-CAN observations and AM4VR simulations. During the WE-CAN campaign, HCHO, CH_3CHO, and CH_3COCH_3 were measured by both a proton-transfer time-of-flight mass spectrometer (PTR-ToF-MS) and Trace Organic Gas Analyzer (TOGA). TOGA measured ambient air for ~30s every 100s, while PTR-ToF-MS measured at 2 and 5 Hz continuously

(Permar et al., 2021). The different sampling frequencies partly explain why the average campaign profiles for CH_3CHO and CH_3COCH_3 determined from TOGA are lower than those from PTR-ToF-MS. Point-to-point comparisons by aggregating PTR-ToF-MS into the TOGA sampling periods show that HCHO, CH_3CHO, and CH_3COCH_3 measurements from the two instruments agree well within instrument uncertainty (<30%) in WE-CAN emissions transects and in campaign averages (Permar et al., 2021; Jin et al., 2023). Simulated CO and VOCs mean profiles in AM4VR are biased low against observations from all instruments. The mean bias (MB) is -27% for CO, -43% for HCHO, -73% for CH_3CHO, -48% for CH_3COCH_3 and -62% for C_3H_8 against TOGA. Similar biases are found in the GEOS-Chem model driven by a suite of BB emission inventories [L. Jin et al., 2023], including GFED4s used by AM4VR in the present study. These biases likely reflect the combined effects of significant underestimation of primary VOC emissions from biomass burning, unimplemented VOCs in the current model chemical mechanisms, and model deficiencies in representing or resolving complex chemical and physical transformations in concentrated smoke plumes.

Table S1: List of nudged AM4VR experiments for 2018

Experiments	**BB NO_y emissions**	**BB VOC emissions**
BASE	100% as NO	HCHO, CH_3CHO, CH_3COCH_3, MEK (C_4H_8O), CH_3OH, C_2H_5OH, C_2H_6, C_3H_8, C_4H_{10}, C_2H_4, C_3H_6, isoprene (C_5H_8), and monoterpenes ($C_{10}H_{16}$).
AM4VR	36% NO, 37%PAN, 27% HNO_3	As in BASE
OVOCx2	100% as NO (as in BASE)	Doubling HCHO, CH_3CHO, and CH_3COCH_3 emissions, others as in BASE
noBB	Zero out*	Zero out*

*Emissions of all gases from fires, including NO_y, VOCs, CO, SO_2, H_2, and NH_3, are zero out in the noBB experiment. Note that emissions of primary aerosols (OC and BC) from fires remain the same in all four experiments. With the same BB aerosol emissions and nudging, we maintain similar meteorology and atmospheric physics and focus our discussion on the impact of NO_y and VOC emissions on ozone photochemistry.

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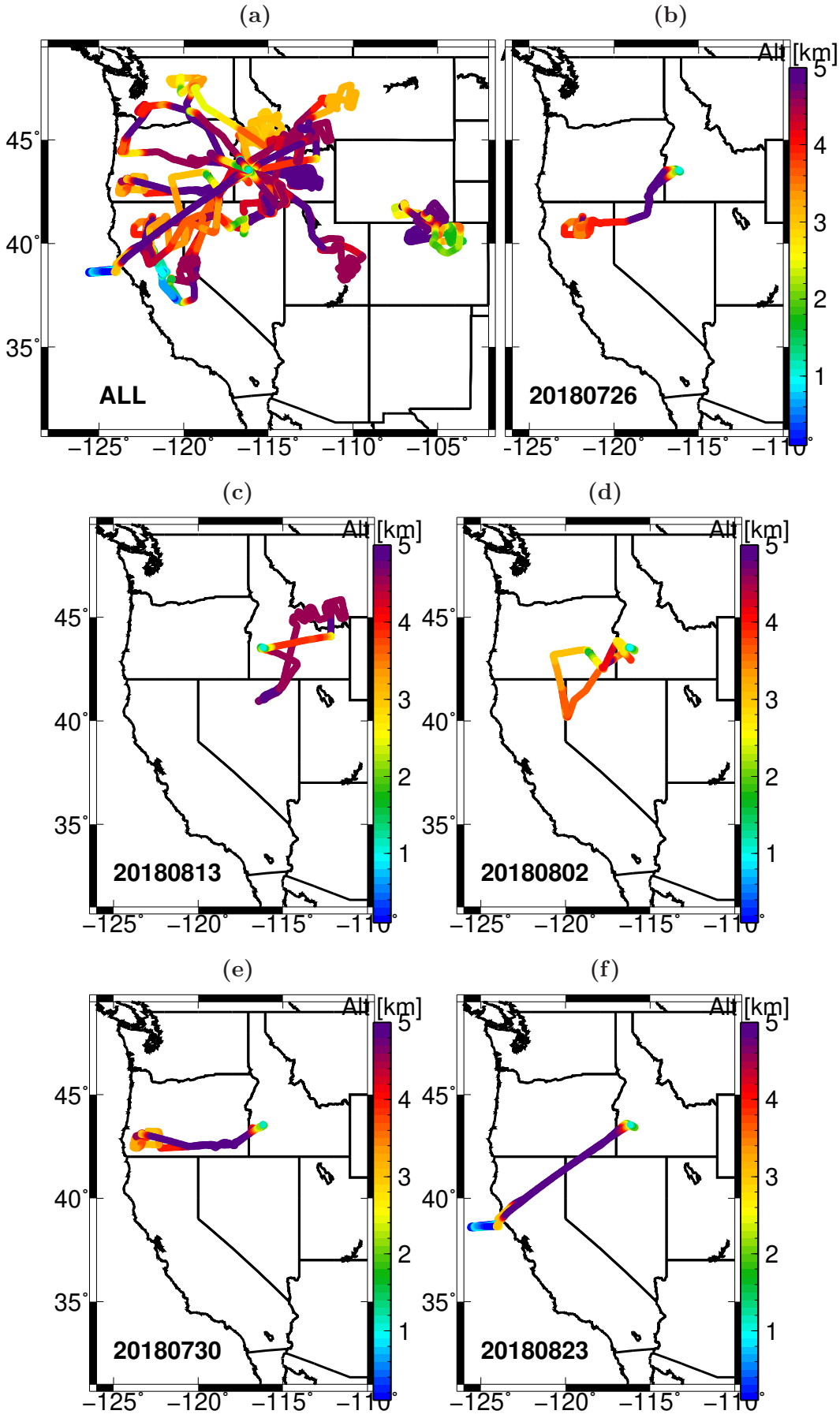


Figure S1. The WE-CAN flight tracks: (a) All; (b-f) July 26, August 13, August 02, July 30, and August 23, 2018.

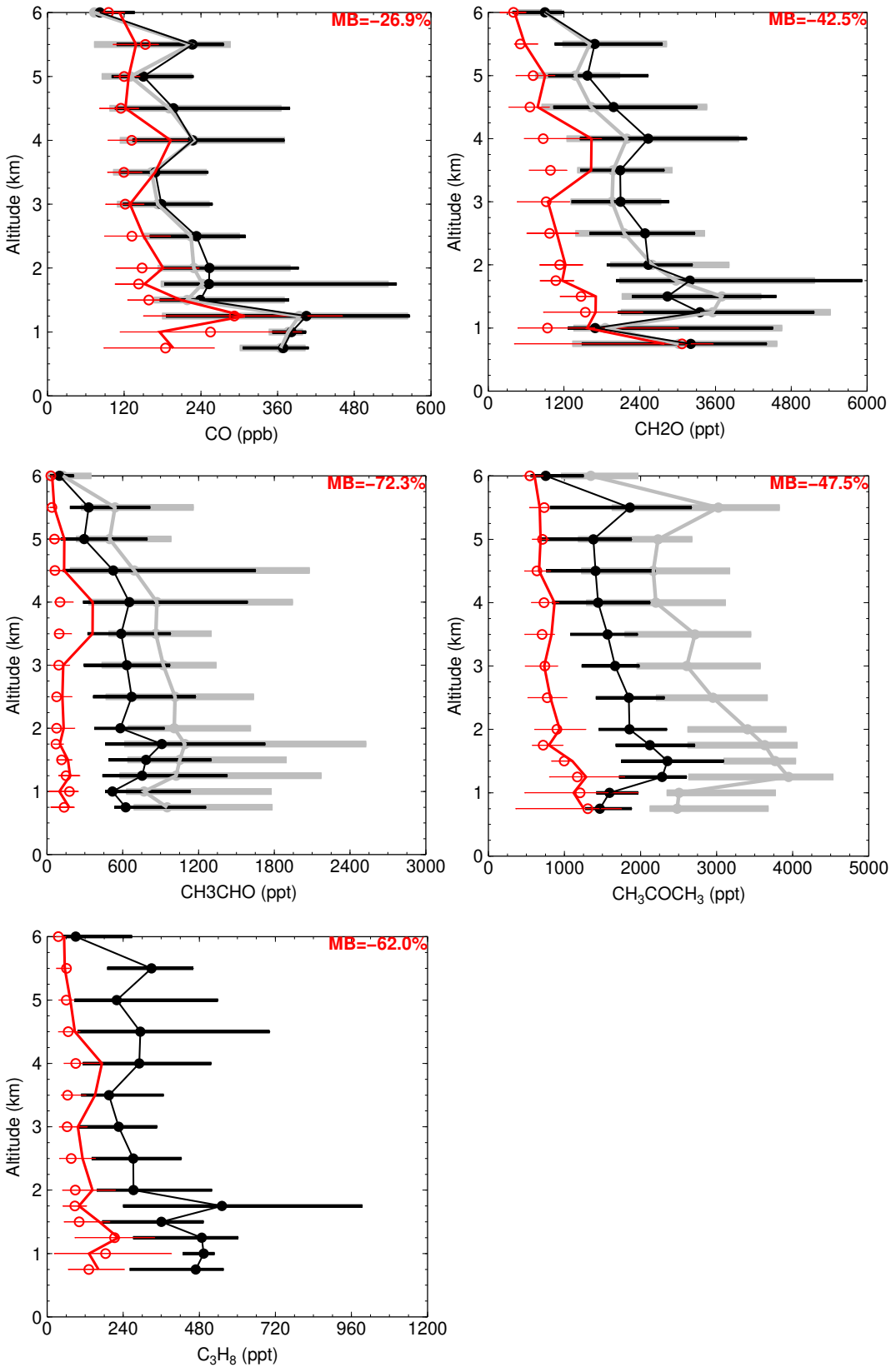
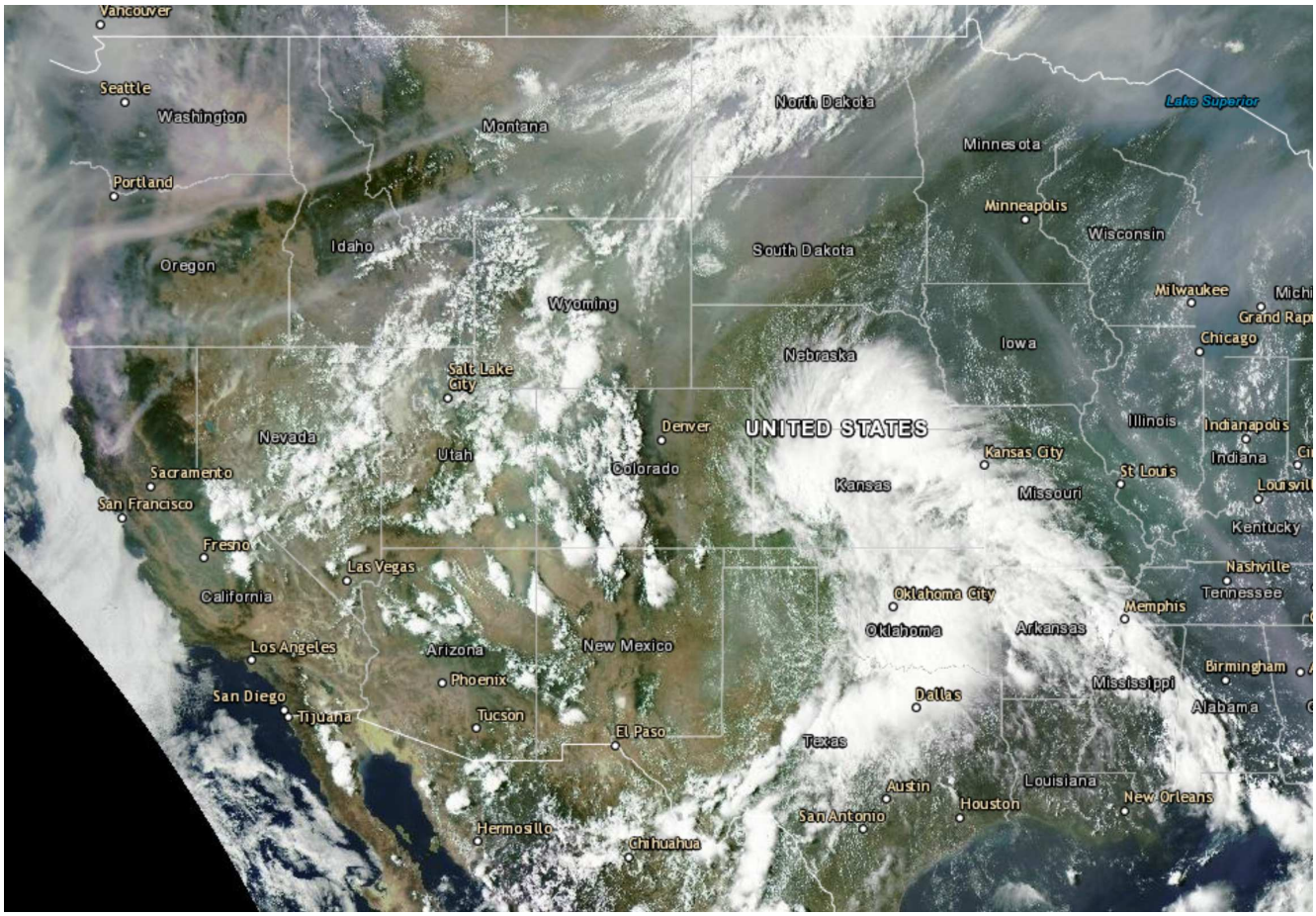


Figure S2. Average vertical profile of CO, HCHO, CH_3CHO, CH_3COCH_3, and C_3H_8 from observations (black/gray) and AM4VR simulations (red) during the 2018 WE-CAN campaign. The circles represent the median value and the horizontal bars represent the 25th-75th percentile range. The red lines represent the model means. For CO, black represents PICARRO observations and gray for QCL observations. For VOCs, black represents TOGA observations while gray denotes PTR-ToF-MS observations (Text S1). Model mean bias (MB) against TOGA measurements are reported.

(a) GOES 2018-08-13 21:32UTC



(b) Surface MDA8 O_3 2018-08-13

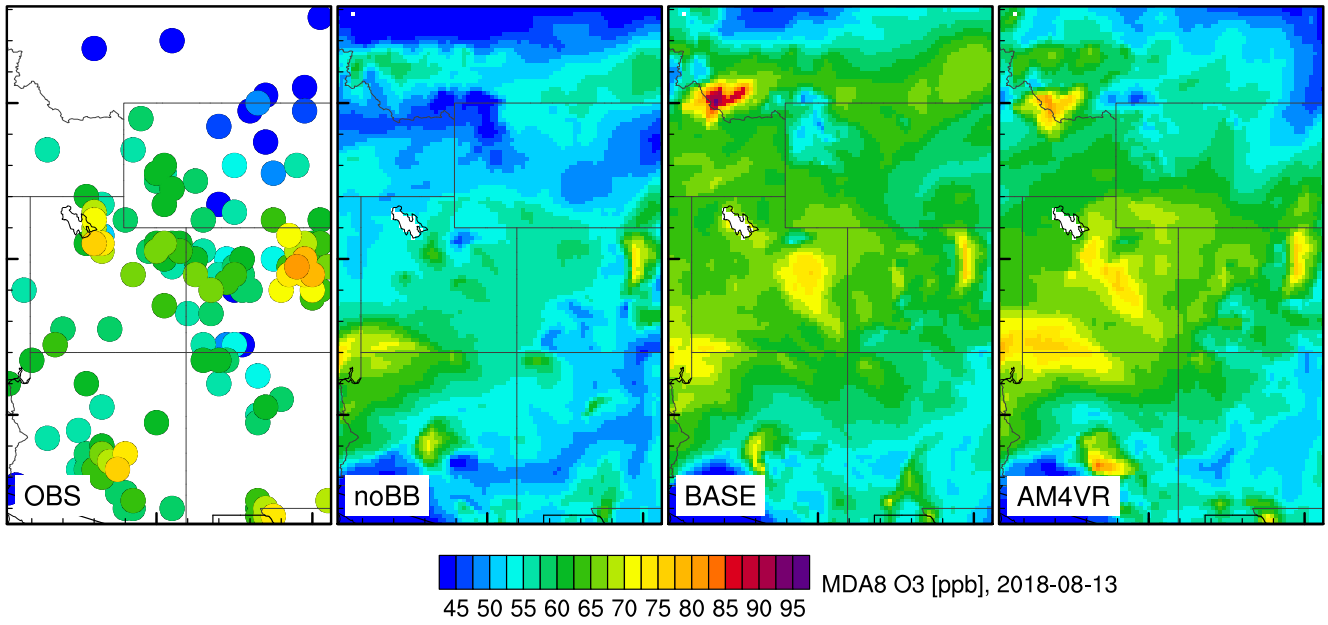


Figure S3. (a) The GOES image showing the presense of smoke in Salt Lake City on August 13, 2018. (b) Surface MDA8 O_3 concentrations on August 13, showing that AM4VR with the NO_y partitioning improves upon BASE in representing the MDA8 O_3 enhancement (10 ppbv) in aged smoke over Salt Lake City. The O_3 exceedance in Denver was primarily due to O_3 produced from regional anthropogenic emissions, as evidenced from a small difference (< 2 ppbv) between the noBB and AM4VR experiments.

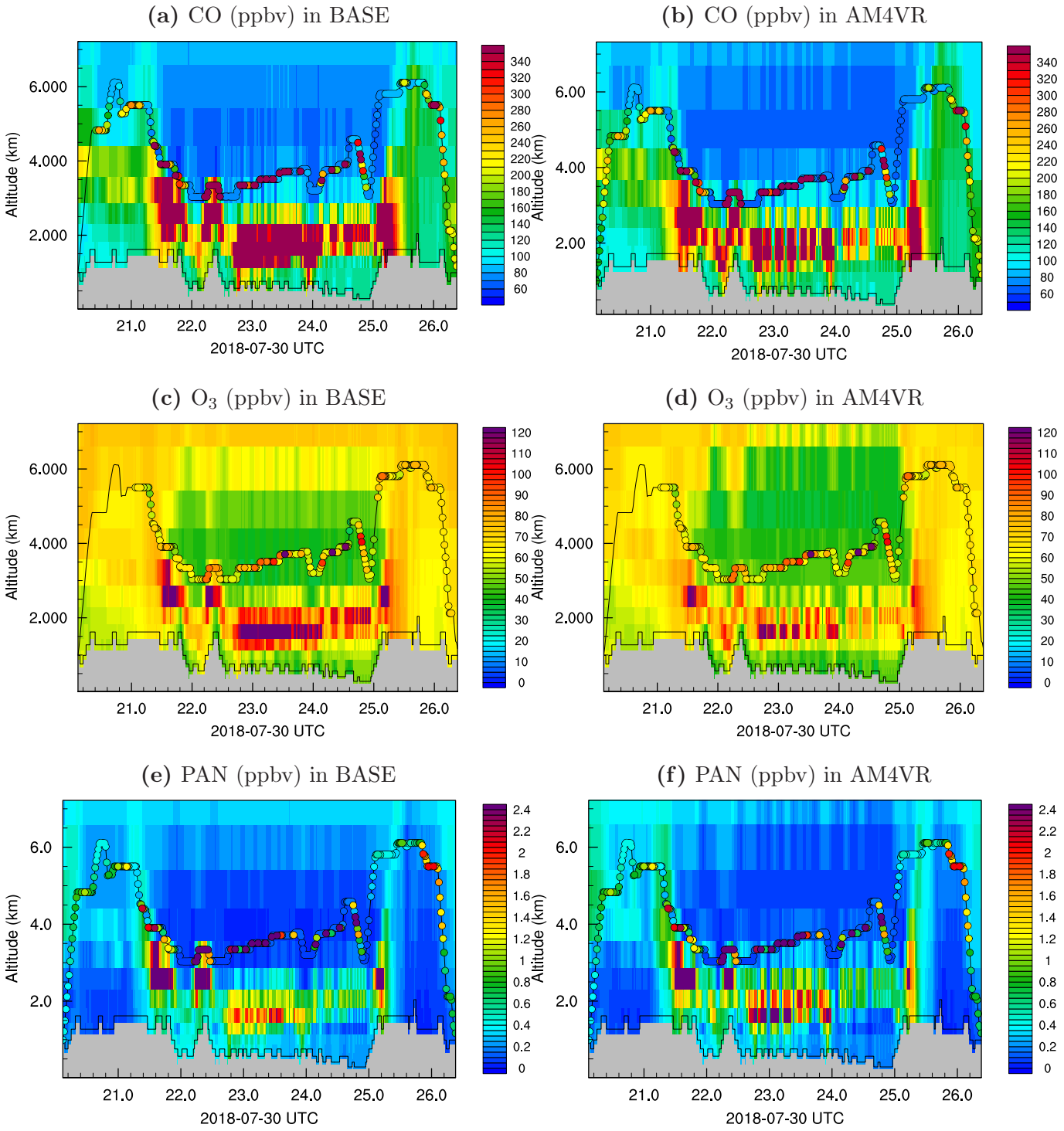


Figure S4. Comparisons of CO, O_3, and PAN mixing ratios from the BASE (100%NO) and AM4VR (37% PAN) experiments for the July 30 flight over Oregon (Fig.S1e). The color-coded circles represent WE-CAN observations.

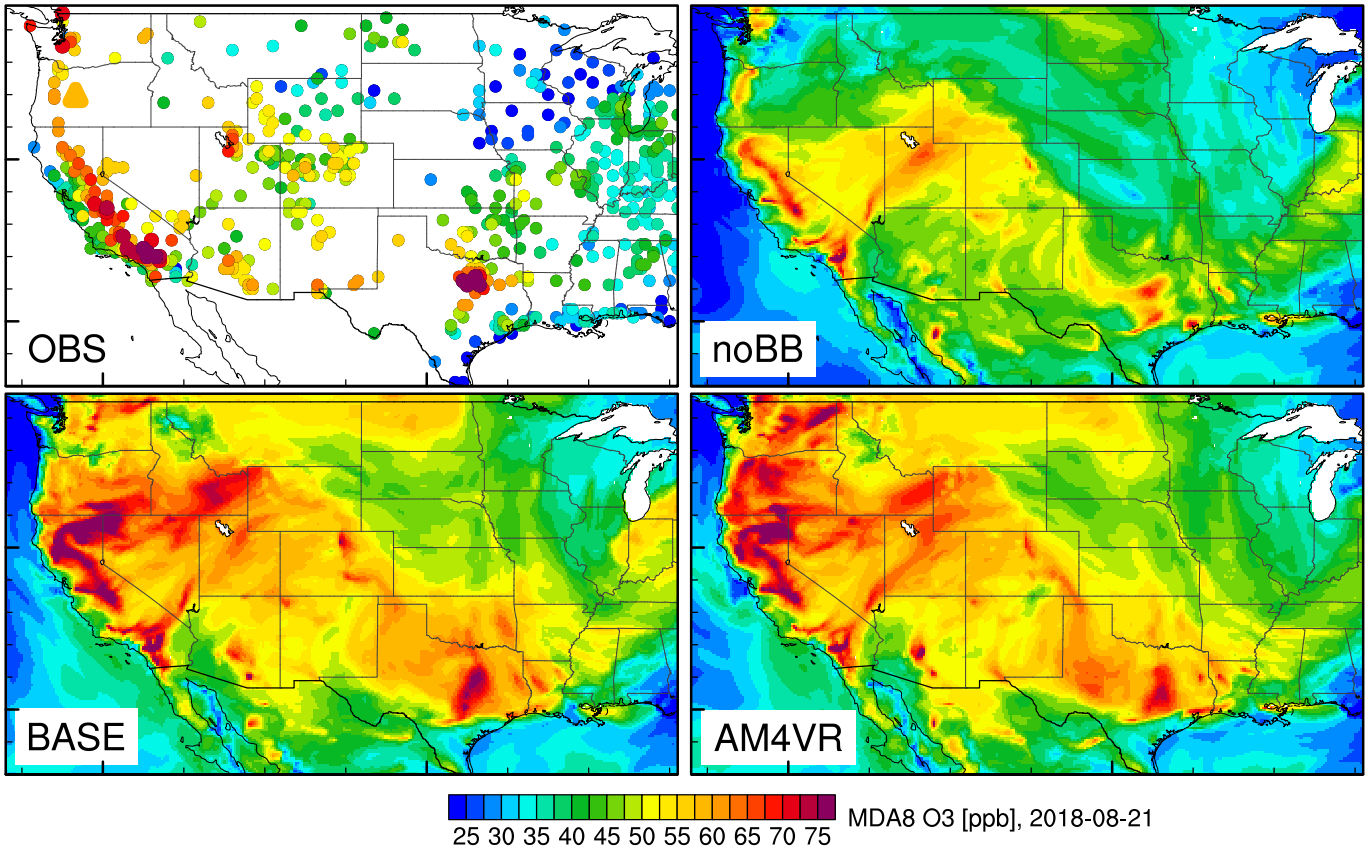


Figure S5. Surface MDA8 O_3 concentrations on August 21 of 2018 from observations (OBS) and model simulations with BB emissions of all NO_y and VOCs zero out (noBB), with BB emitting NO_y as 100% NO (BASE), and with AM4VR including the NO_y partitioning. Over the Dallas region, BASE simulates 5 ppbv higher MDA8 O_3 than noBB; including the NO_y partitioning does not significantly enhance O_3 relative to BASE. These results suggest that mixing of NO_x-rich urban pollution and VOC-rich wildfire smoke facilitated ozone formation in Dallas for this case.

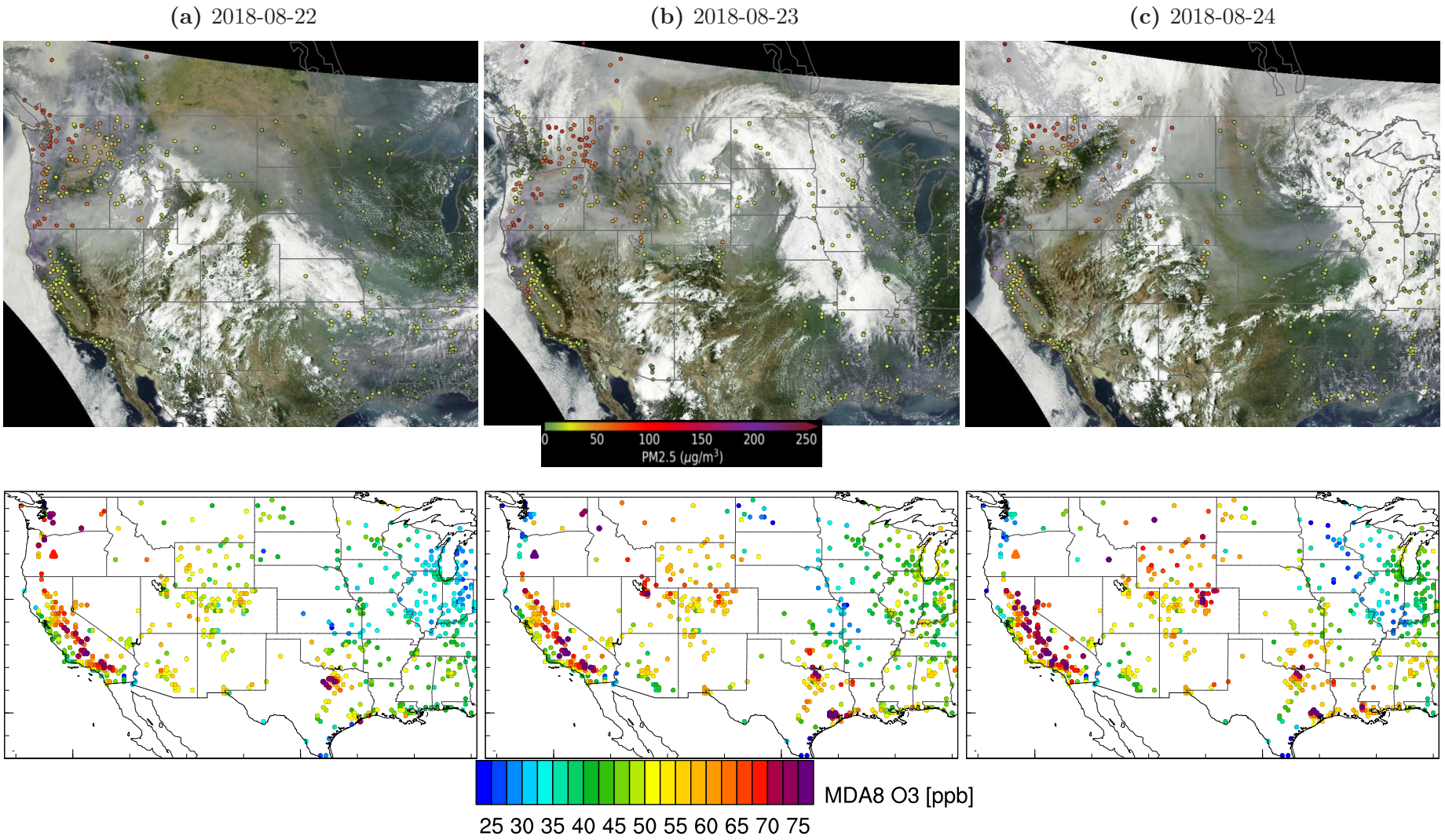


Figure S6. (Top) Surface 24-h mean $PM_{2.5}$ observations superimposed on the GOES GeoColor images at 21:42UTC on August 22, 23 and 24, 2018. The images were produced from NOAA AerosolWatch (https://www.star.nesdis.noaa.gov/smcd/spb/aq/AerosolWatch/). (Bottom) Surface daily MDA8 O_3 observations for the corresponding days.