Table S1. Details of the open fires sampled in Western US during the 2018 WE-CAN campaign.

Fire names	Fire locations		Sampling dates/times	(UTC)	Acres burned (Acres)
	Latitude	Longitude	Starting	Ending	
Rattlesnake Creek Fire	45.334	-116.396	07-24 19:06	07-25 00:56	2,100
Carr Fire	42.882	-122.734	07-30 20:06	07-31 02:24	20,000
South Umpqua Complex	42.882	-122.734	07-30 20:06	07-31 02:24	13,168
Taylor Creek Fire	42.515	-123.583			24,965
Sharps Fire	43.467	-114.145	07-31 20:04	08-01 02:29	20,000
Cougar Creek Fire	47.851	-120.549	08-03 20:00	08-04 02:27	3,614
Kiwah Fire	44.823	-115.286			500
Rabbit Foot Fire	44.856	-114.307			600
Donnell Fire	38.349	-119.929	08-06 19:57	08-07 02:15	11,074
Ferguson Fire	37.652	-119.881			91,502
Dollar Ridge Fire	40.1	-110.96	08-09 18:55	08-10 01:45	59,250
Coal Hollow Fire	39.951	-111.403			17,969
Bear Trap Fire	39.2931	-109.874			N/A
Rabbit Foot Fire	44.856	-114.307	08-13 18:30	08-14 00:41	15,767
Goldstone Fire	45.117	-113.534			3,769
Wigwam Fire	45.153	-111.931			N/A
Monument Fire	44.968	-111.851			4,215
Rabbit Foot Fire	44.856	-114.307	08-15 20:00	08-16 01:56	26,294

Beaver Creek Fire	45.893	-113.528			1,000
Shellrock Fire	46.929	-111.741			300
Goldstone Fire	45.117	-113.534			4,000
Miriam Fire	46.61	-121.35	08-16 17:38	08-16 23:25	2,655
Sheep Creek Fire	40.773	-116.842	08-20 19:05	08-21 02:14	40,000
Mendocino Complex	39.24	-123.11	08-20 19:05	08-21 02:14	398,862
South Sugarloaf Fire	41.812	-116.324	08-26 18:56	08-27 02:14	200,692
Red Feather Prescribed Burn	40.852	-105.576	09-10 19:31	09-10 23:01	4,348
Silver Creek Fire	40.223	-106.655	09-13 19:12	09-13 23:29	5,973

Note: The acres burned represent the situation as of when the C-130 sampled the fire as documented in the InciWeb- Incident Information System. Details can be found in http://catalog.eol.ucar.edu/we-can/tools/missions.

Table S2. Speciation of lumped VOCs from WE-CAN observations, emissions inventories, and in the GEOS-Chem model

Lumped VOCs	Chemical formula	WE-CAN Observation	GFED4	GFAS	QFED
		VOC contributors			
Xylenes	C_8H_{10}[a]	o-Xylene, m-xylene, and p-Xylene	Xylenes	xylenes	xylenes
ALK4 (lumped $\geq$ C_4 alkanes)	C_4H_{10}[b]	n-Butane and i-Butane	n-Butane and i-Butane	n-Butane and i-Butane	n-Butane and i-Butane
	C_5H_{12}[b]	n-Pentane and i-Pentane	n-Pentane and i-Pentane	n-Pentane and i-Pentane	N/A
	C_6H_{14}[c]	n-Hexane and 3-Methylpentane	n-Hexane and i-Hexane	n-Hexane and i-Hexane	N/A

	C_7H_{16}[c]	2,4-Dimethylpentane, n-Heptane, 2-Methylhexane[b], 3-Methylhexane, 2,3-Dimethylpentane	Heptane	Heptane	N/A
	C_8H_{18}[c]	n-Octane, 2-Methylheptane, 2,2,4-Trimethylpentane, 2,3,4-Trimethylpentane, and 3-Methylheptane	N/A	N/A	N/A
	C_9H_{20}[c]	n-Nonane	N/A	N/A	N/A
PRPE (lumped $\geq C_3$ alkenes)	C_3H_6[c]	Propene	Propene	Propene	Propene
	C_4H_8[b]	Butenes	1-Butene, i-Butene, trans-2-Butene, and cis-2-Butene	1-Butene, i-Butene, trans-2-Butene, and cis-2-Butene	N/A
	C_5H_{10}[a]	Pentenes and Methylbutenes	1-Pentene and 2-Pentene	1-Pentene and 2-Pentene	N/A
	C_6H_{12}	N/A	Hexene	Hexene	N/A
	C_8H_{16}	N/A	Octene	Octene	N/A
RCHO (lumped $\geq C_3$ aldehydes)	C_3H_6O[b]	Propanal	N/A	N/A	N/A
	C_4H_8O[b]	Butanal	N/A	N/A	N/A

[a] Using observations from the proton-transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS).

[b] Using observations from the trace organic gas analyzer (TOGA).

[c] Using observations from the advanced whole air sampler (AWAS).

Table S3. Location and elevation of nine ground sites

Site location	Longitude	Latitude
Seattle, WA	-122.31	47.57
Boise, ID	-116.35	43.60

	-105.01	39.78
Denver, CO	-105.01	39.78
Stockton, CA	-121.27	37.95
Fresno, CA	-119.77	36.79
Reno, NV	-119.81	39.53
Chico, CA	-121.84	39.76
Missoula, MT	-113.99	46.86
Mt. Bachelor Observatory, OR[a]	-121.68	43.98

[a] The Mt. Bachelor Observatory (MBO) located at Deschutes, OR is a mountaintop site with an elevation of approximately 2.8 km.

Table S4. FIREX-AQ observations used in this analysis.

Formula	GEOS-Chem Species	Full Name	Instruments	Reported Uncertainty
C2H6	C2H6	Ethane	CAMS	2 %
C3H8	C3H8	Propane	**TOGA**	15 %
-	ALK4	Lumped $\geq C_4$ Alkanes	WAS	10 %
-	PRPE	Lumped $\geq C_3$ Alkenes	WAS	10 %
CH2O	HCHO	Formaldehyde	**CAMS**/ISAF	6 %
CH3CHO	ALD2	Acetaldehyde	**NOAA PTR**/TOGA	15 %
-	RCHO	Lumped $\geq C_3$ Aldehydes	**TOGA**	30 %
C6H6	BENZ	Benzene	**NOAA PTR**/TOGA	15 %
C7H8	TOLU	Toluene	**NOAA PTR**/TOGA	15 %
C8H10	XYLE	Xylenes	**NOAA PTR**/TOGA	15 %
C3H6O	ACET	Acetone	**NOAA PTR**/TOGA	15 %
CH3C(O)C2H5	MEK	Methyl Ethyl Ketone	**NOAA PTR**/TOGA	15 %
HCOOH	HCOOH	Formic acid	NOAA PTR/**NOAA CIMS**	30%
C2H4O2	ACTA	Acetic acid	**NOAA PTR**	15 %

Notes: We applied 0.78/0.22 and 0.65/0.35 ratios to the PTR-ToF-MS measurement to distinguish the isomers of acetone/propanal, and xylenes/ethylbenzene as we did in the WE-CAN. Measurements used for figures in Section 4 are in bold text.

Table S5. Model evaluation metrics of ground measurement sites for July-September 2018

Site	MB (base)	MB ($3 \times$ GFAS)	RMSE (base)	RMSE ($3 \times$ GFAS)	r (base)	r ($3 \times$ GFAS)

Seattle, WA	141.25	250.46	221.1	557.9	0.78	0.74
Boise, ID	-118	**-40.63**	129.4	**128.3**	0.74	0.74
Missoula, MT	-96.94	**-19.7**	115.2	**104**	0.83	**0.84**
Mt. Bachelor, OR	-107.7	**-85.04**	160	**142.3**	0.55	0.5
Reno, NV	-88.78	**-28.85**	120	**90.89**	0.67	0.65
Denver, CO	-34.97	**6.55**	54.44	85.91	0.72	0.66
Chico, CA	-117	**30.93**	141.3	224.6	0.71	0.69
Stockton, CA	-94.96	**-7.65**	133.1	240.9	0.39	0.36
Fresno, CA	-142	**-65.74**	174.8	**166.2**	0.52	0.48

Note: The 3 × GFAS run metrics are in bold text when it performs better than base run (GFAS). The units for MB (mean bias) and RMSE (root-mean-square error) are ppb, and *r* is unitless.

Table S6. Model evaluation metrics of ground measurement sites for the BB-impacted days in July-September 2018

Site	MB (base)	MB (3 × GFAS)	RMSE (base)	RMSE (3 × GFAS)	*r* (base)	*r* (3 × GFAS)
Seattle, WA	370.48	1041.36	501.45	1453.73	0.74	0.7
Boise, ID	-116.68	**7.07**	131.02	136.08	0.75	0.74
Missoula, MT	-118.8	**-0.29**	133.96	**121.15**	0.81	**0.83**
Mt. Bachelor, OR	-134.36	**-93.33**	187.81	**160.96**	0.51	0.44
Reno, NV	-114.3	**-4.97**	152.55	**111.3**	0.55	0.51
Denver, CO	-21.72	143.41	66.74	199.66	0.7	0.48

Site	MB (base)	MB (3 × GFAS)	RMSE (base)	RMSE (3 × GFAS)	r (base)	r (3 × GFAS)
Chico, CA	-123.22	**69.12**	151.55	255.4	0.65	0.62
Stockton, CA	-98.85	**37.63**	153.78	311.75	0.23	0.21
Fresno, CA	-169.59	**-38.59**	210.77	**201.91**	0.32	0.28

Note: The 3 × GFAS run metrics are in bold text when it performs better than base run (GFAS). The units for MB (mean bias) and RMSE (root-mean-square error) are ppb, and correlation r is unitless.

Table S7. Model evaluation metrics of ground measurement sites for the least BB-impacted days in July-September 2018

Site	MB (base)	MB (3 × GFAS)	RMSE (base)	RMSE (3 × GFAS)	r (base)	r (3 × GFAS)
Seattle, WA	104.78	124.64	129.02	156.49	0.66	**0.77**
Boise, ID	-119.9	**-106.51**	127.18	**116.76**	0.25	**0.27**
Missoula, MT	-61.28	**-51.39**	75.02	**67.16**	0.56	0.45
Mt. Bachelor, OR	-67.75	-72.61	105.44	108.47	0.16	**0.21**
Reno, NV	-64.18	**-51.88**	76.45	**65.45**	0.4	**0.46**
Denver, CO	-37.23	**-16.75**	52.05	**43.01**	0.63	**0.68**
Chico, CA	-98.88	**-80.94**	105.57	**84.24**	0.83	**0.89**
Stockton, CA	-89.94	**-66.14**	100.21	**86.2**	0.79	0.63
Fresno, CA	-108.82	**-98.33**	117.79	**108.7**	0.81	0.53

Note: The 3 × GFAS run metrics are in bold text when it performs better than base run (GFAS). The units for MB and RMSE are ppb, and correlation r is unitless.
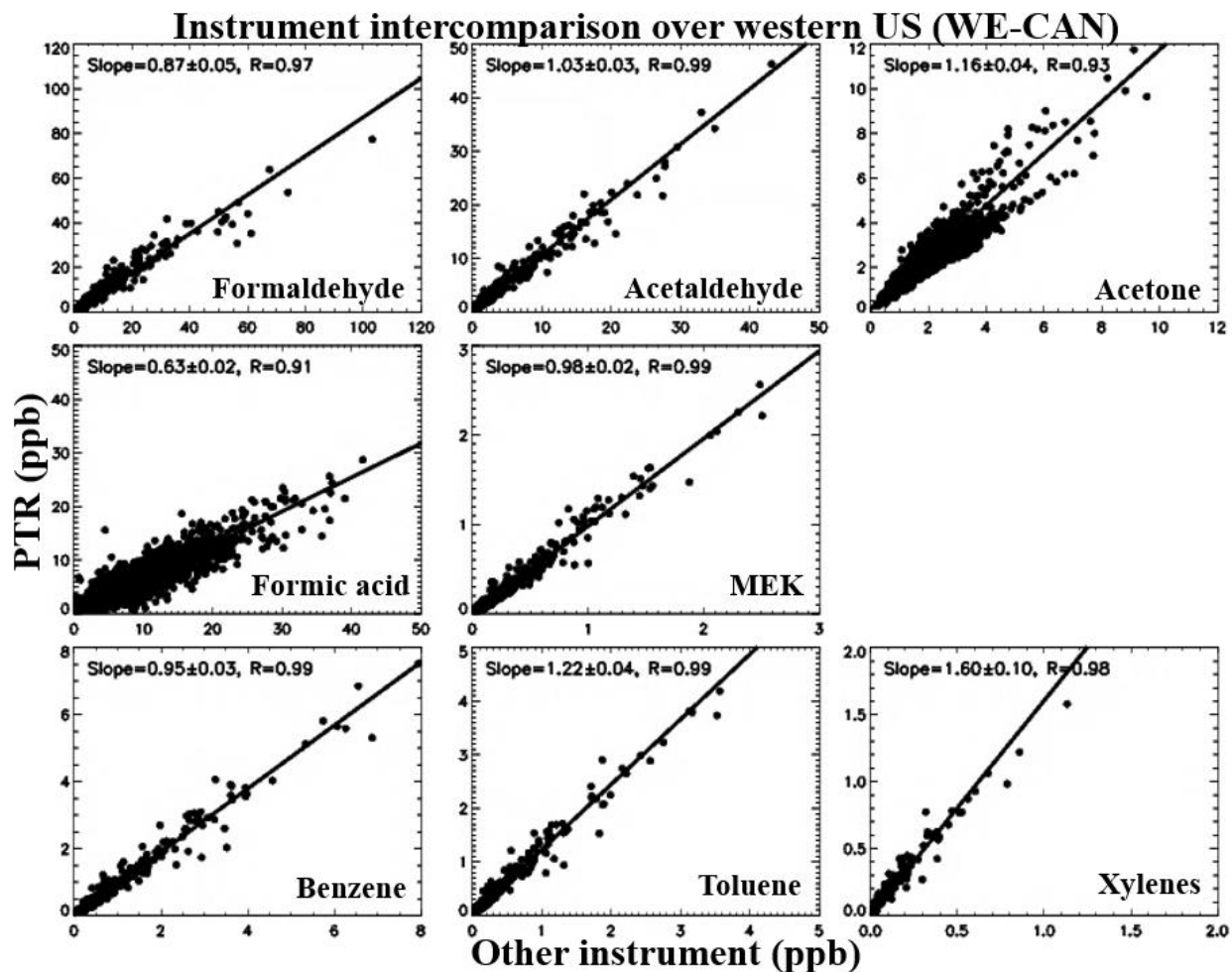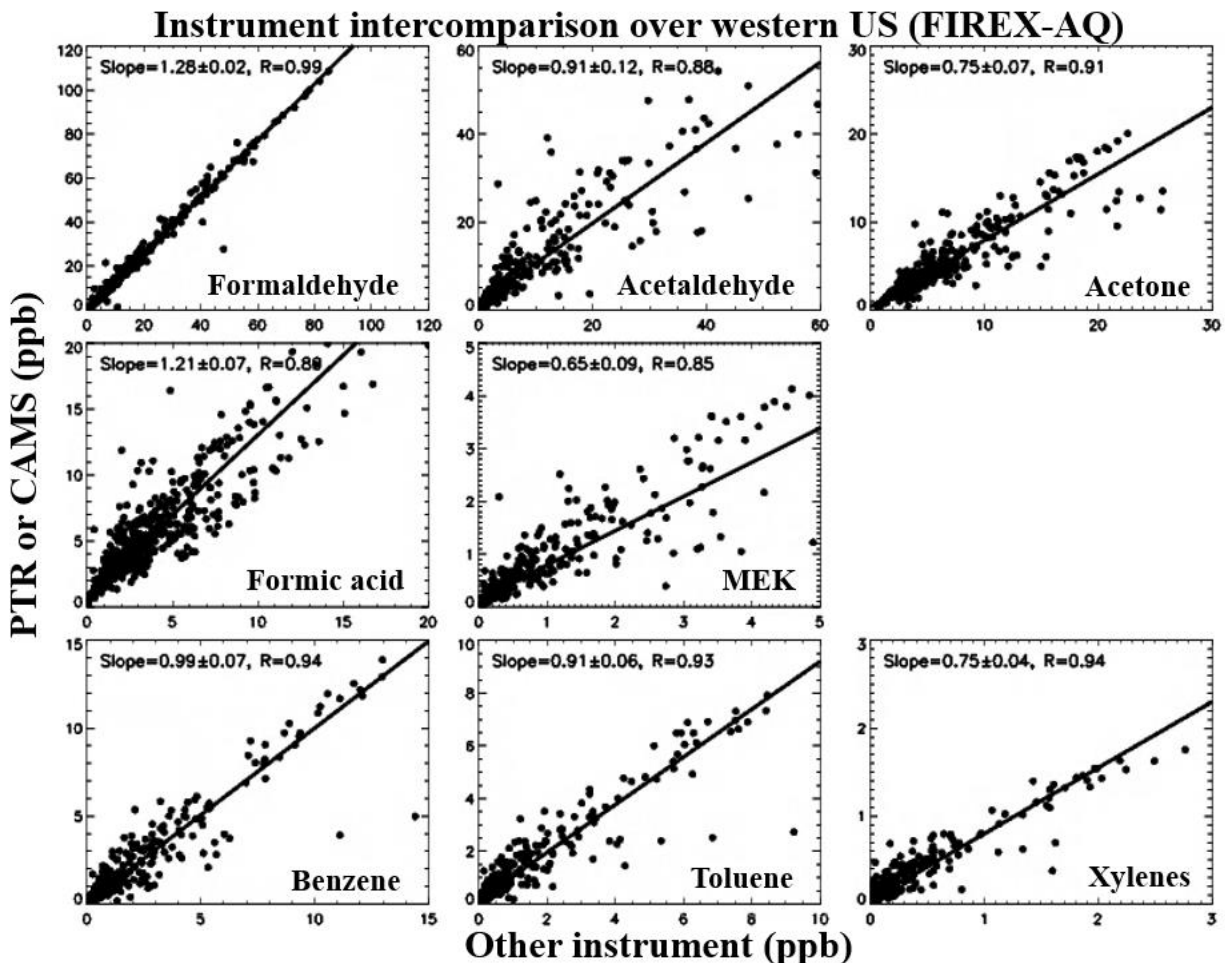
Figure S1a. Instrument intercomparison of VOC mixing ratios in the western US made on the NSF/NCAR C-130 aircraft during WE-CAN. PTR-ToF-MS is compared to co-deployed I-CIMS measurements for formic acid and TOGA for remaining VOCs. Observations are averaged over the corresponding sampling period of the TOGA instrument (using TOGA merge data files at https://www.air.larc.nasa.gov/cgi-bin/ArcView/firexaq?MERGE=1#TOGA.C130_MRG/). The acetone in TOGA is compared to 0.78 times PTR acetone + propanal measurements. The MEK in TOGA is compared to 0.8 times PTR MEK + butanal measurements. The sum of m-, o-, p-xylenes in TOGA is compared to 0.65 times PTR C_8 aromatics. Details are in Table 1.

Instrument intercomparison over western US (FIREX-AQ)

Figure S1b. Instrument intercomparison of VOC mixing ratios in the western US made on the NASA DC-8 aircraft during FIREX-AQ. CAMS (Compact Atmospheric Multispecies Spectrometer) is compared to co-deployed ISAF (In Situ Airborne Formaldehyde) for formaldehyde. PTR-ToF-MS is compared to co-deployed NOAA I-CIMS measurements for formic acid, and TOGA for remaining VOCs. Observations are averaged over the corresponding sampling period of the TOGA instrument (using TOGA merge data files at https://www-air.larc.nasa.gov/cgi-bin/ArcView/firexaq?MERGE=1#TOGA.DC8_MRG/). The acetone in TOGA is compared to 0.78 times PTR acetone + propanal measurements. The MEK in TOGA is compared to 0.8 times PTR MEK + butanal measurements. The sum of m-, o-, p-xylenes in TOGA is compared to 0.65 times PTR C_8 aromatics. Details are in Table 1.
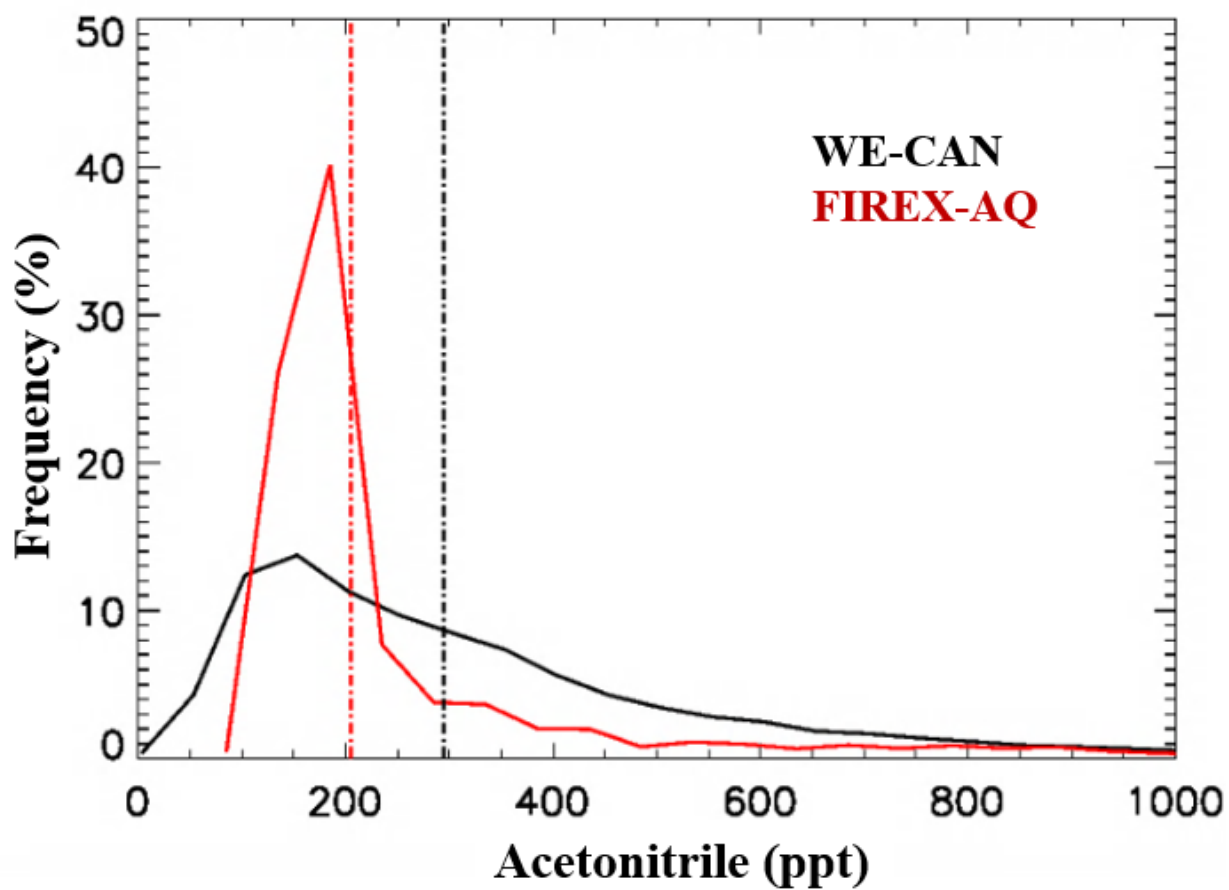
Figure S2. Comparison of observed acetonitrile histograms across fire-influenced campaigns for the western US (WE-CAN in black and FIREX-AQ in red). Vertical dashed lines mark the median for each campaign.
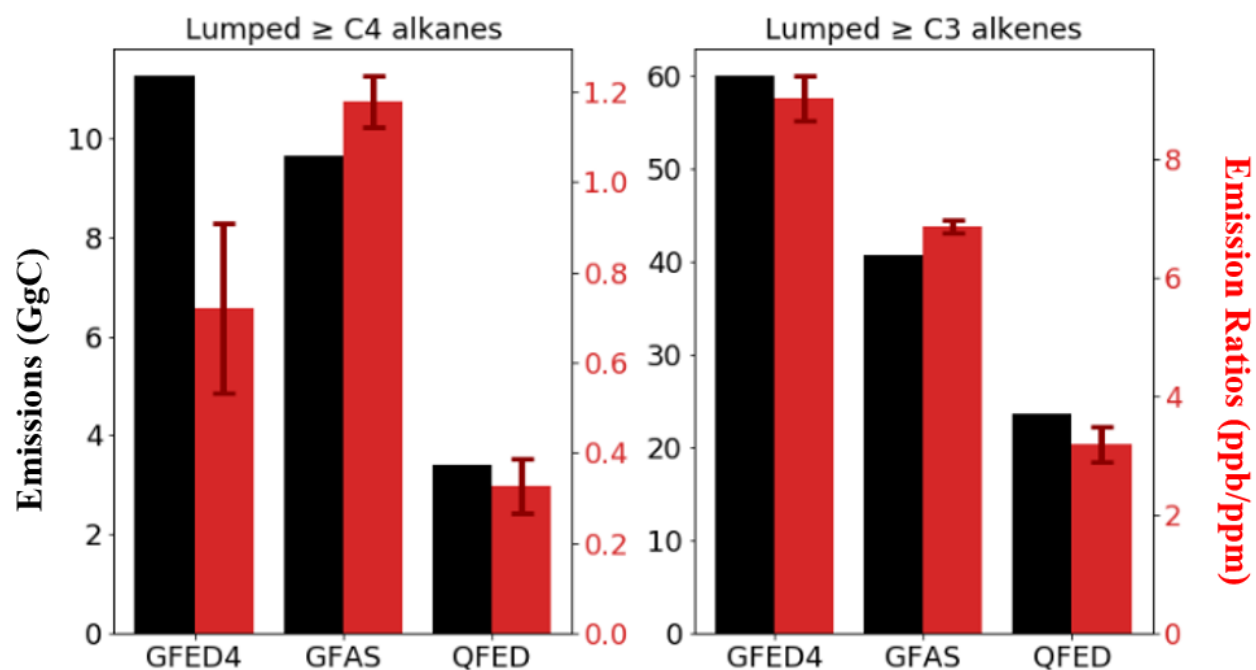
Figure S3. Biomass burning VOC emission estimates for the 2018 fire season (JJAS) (black) and emission ratios (red) with error bar (dark red) over the western US in 3 global emission inventories for lumped ≥ C4 alkanes and lumped ≥ C3 alkenes. The emission ratios are regionally averaged from each inventory and are calculated from the regression of VOC and CO emission estimates, with error bars representing 95 % confidence interval from the bootstrapping resampling of the regression.

VOC vertical profiles over western US (WE-CAN)
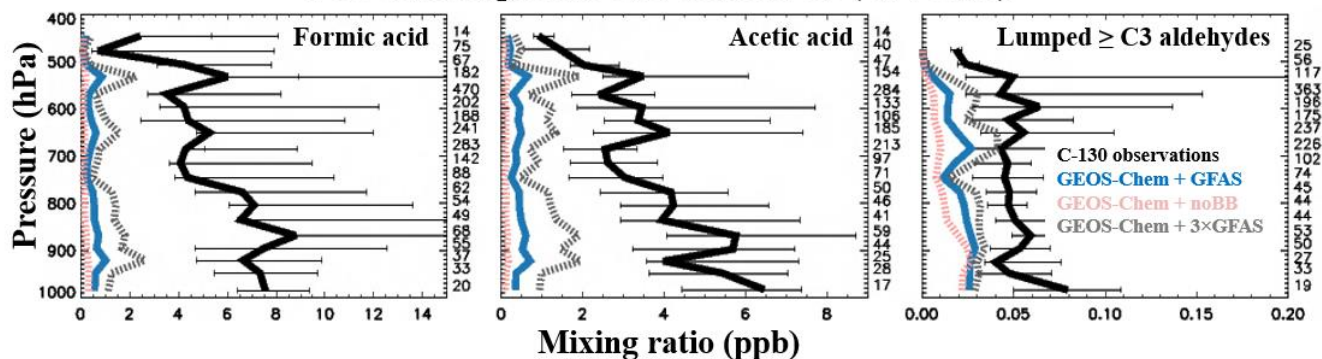
Figure S4. Median vertical profiles of VOC mixing ratios (formic acid, acetic acid, and lumped ≥ C3 aldehydes) in the western US during the WE-CAN aircraft campaign (July-September 2018). GEOS-Chem simulation driven by GFAS is compared to observations. Also shown are two model sensitivity tests with biomass burning emission turned off (noBB) and with tripling GFASv1.2 emission (3 × GFAS). Model results are sampled along the flight tracks at the time of flights; and observations are regridded to model resolution. Profiles are binned to the nearest 30 hPa. Horizontal bars show the 25th-75th percentile range of measurements in each vertical bin. The number of observations in each bin is given on the right side of each panel.

**CO vertical profiles over western US (low/no smoke for WE-CAN)**
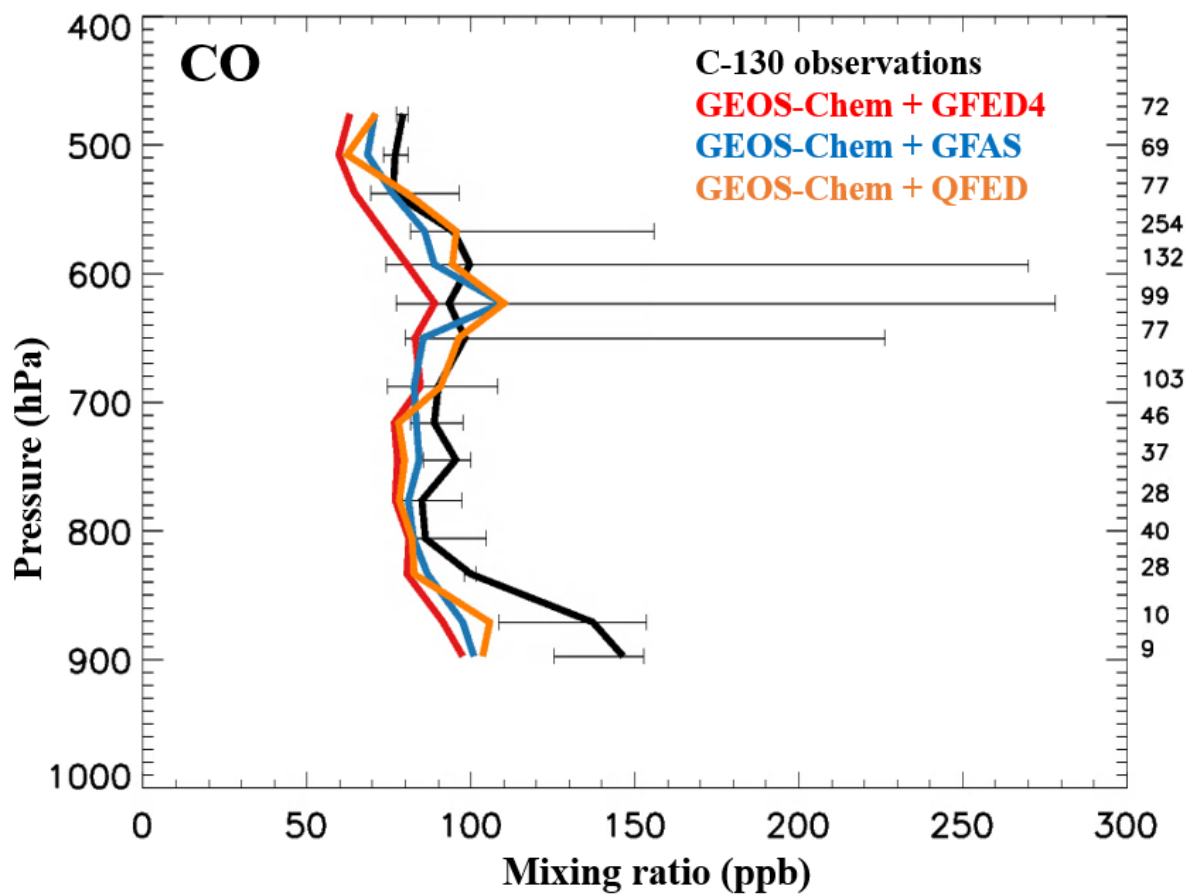
Figure S5. Median vertical profiles of CO mixing ratios in the western US for low/no smoke conditions in the WE-CAN aircraft campaign. GEOS-Chem simulations driven by three different biomass burning emission inventories (GFED4s, GFASv1.2, and QFED2.4) are compared to observations. Results are filtered to include only data coincident with the bottom 25th percentile of observed acetonitrile, where EnRs of CH_3CN to CO larger than 2.01 ppb ppm^{-1}, and where the number of datapoints are larger than 5. Model results are also sampled along the flight tracks at the time of flights; and observations are regridded to model resolution. Profiles are binned to the nearest 30 hPa. Horizontal bars show the 25th -75th percentile range of measurements in each vertical bin. The number of observations in each bin is given on the right side of each panel.

VOC vertical profiles over western US (WE-CAN)
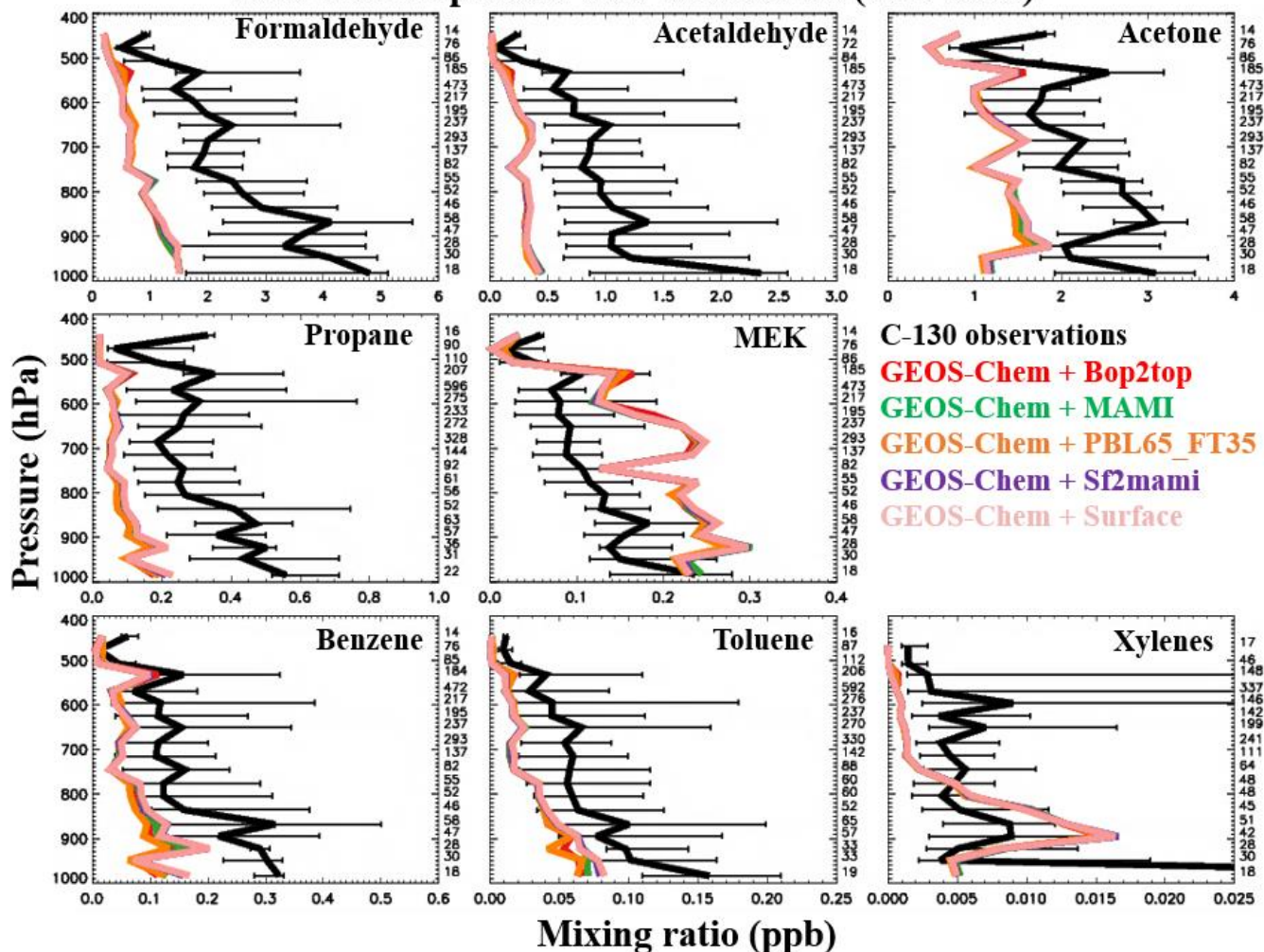
Figure S6. The median vertical concentration profiles of 8 VOCs observed during WE-CAN (black, solid) over the western US. Also shown are GEOS-Chem simulations driven by GFASv1.2 in five injection schemes: 1) releasing BB emissions evenly from bottom of the plume to the top of the plume (Bop2top, red); 2) emitting BB at the mean altitude of maximum injection (MAMI, green); 3) emitting 65% of BB emissions into planetary boundary layer and 35% into free troposphere (PBL65FT35, orange); 4) emitting BB evenly from the surface to the mean altitude of maximum injection (Sf2mami, purple); 5) emitting BB at surface (Surface, pink).
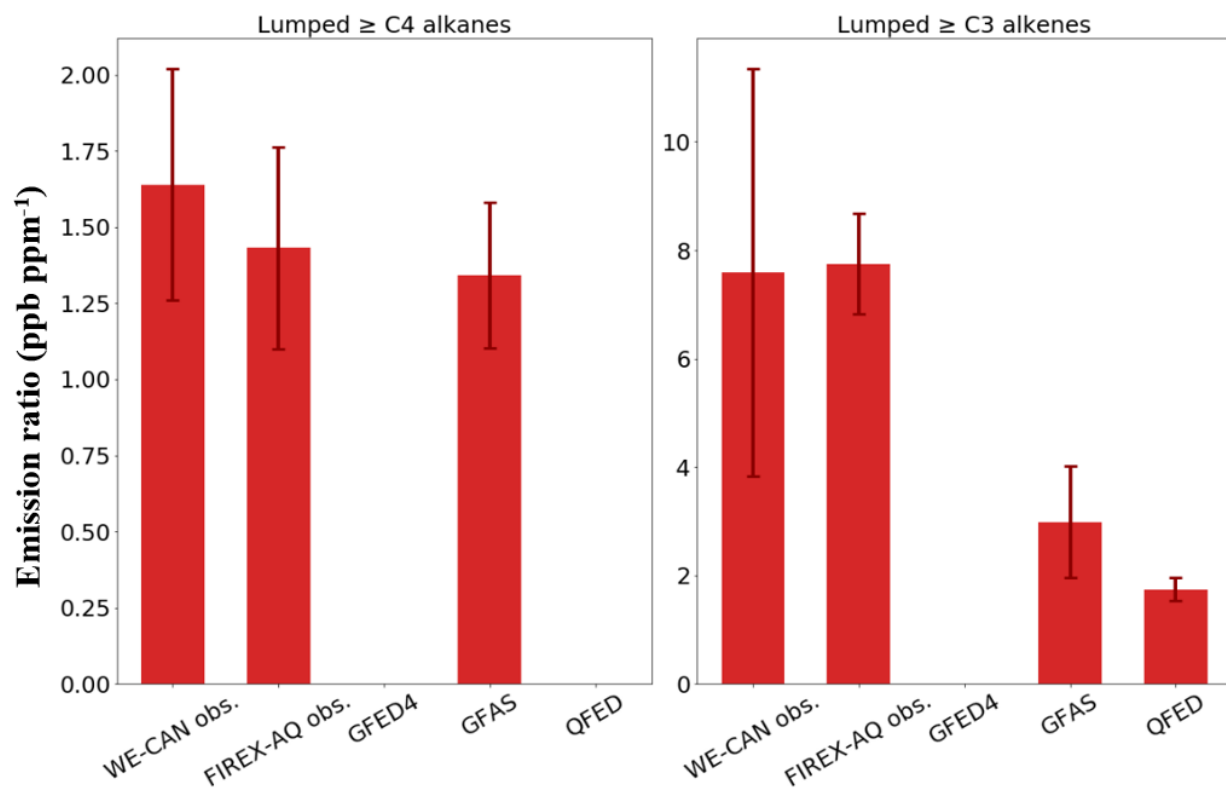
Figure S7. Biomass burning VOC emission ratios for western US wildfires observed on the C-130 during WE-CAN and the DC-8 during FIREX-AQ. Also shown are the emission ratios in GEOS-Chem simulations driven by three different BB emission inventories. Values of zero indicate that the species were not included in the BB emission inventory in the standard GEOS-Chem. Emission ratios are calculated from the reduced major axis regression (RMA) of VOC and CO, with error bars representing the 95% confidence interval from the bootstrapping resampling of the regression. R > 0.7 is used as the threshold in the RMA regression for ER calculations.

Toluene vs Benzene over western US (WE-CAN and FIREX-AQ)

Obs: slope = 1.01 ± 0.02, intercept = -0.68 ± 0.02
GFAS: slope = 0.93 ± 0.02, intercept = -1.05 ± 0.04

Obs: slope = 0.89 ± 0.03, intercept = -0.52 ± 0.05
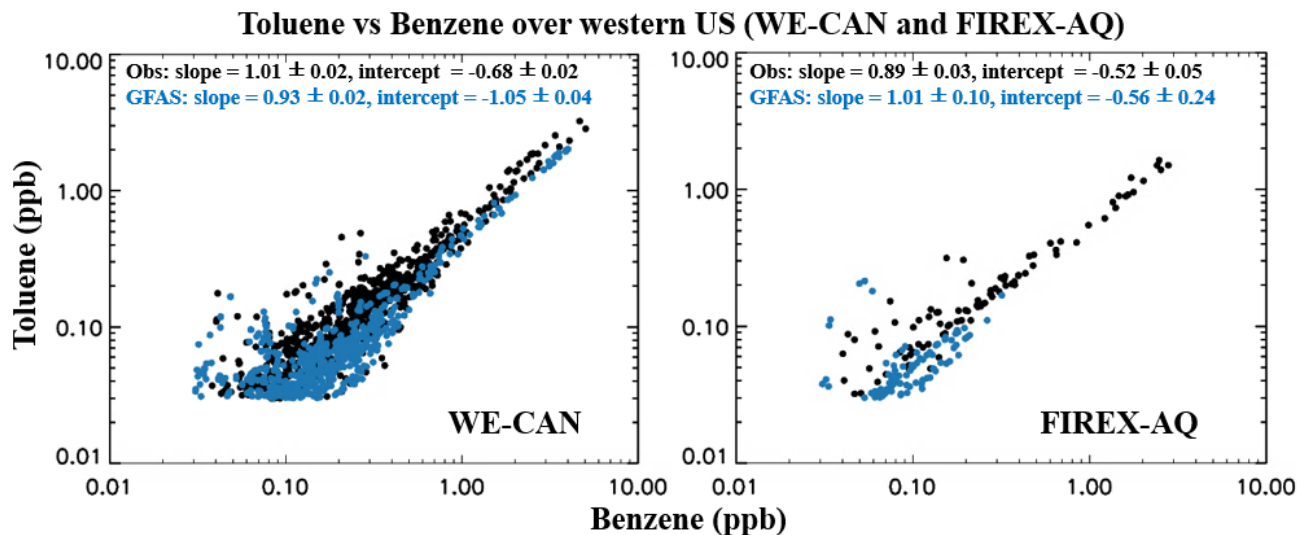GFAS: slope = 1.01 ± 0.10, intercept = -0.56 ± 0.24

Figure S8. Relationship between benzene and toluene in the western US during WE-CAN (left) and FIREX-AQ (right). Data are plotted on a log-log scale, with observations in black and corresponding GEOS-Chem + GFAS simulations in blue. Model results are sampled along the flight tracks at the time of flights; and both the observations and the model outputs are regridded to model resolution (5 min and 0.25° × 0.3125°). The regression parameters shown represent the best fit of the data using the reduced major axis regression, corresponding to the relationship between $\log_{10}$(benzene) and $\log_{10}$(toluene).

VOC vertical profiles over western US (FIREX-AQ)

DC-8 observations
GEOS-Chem + GFAS
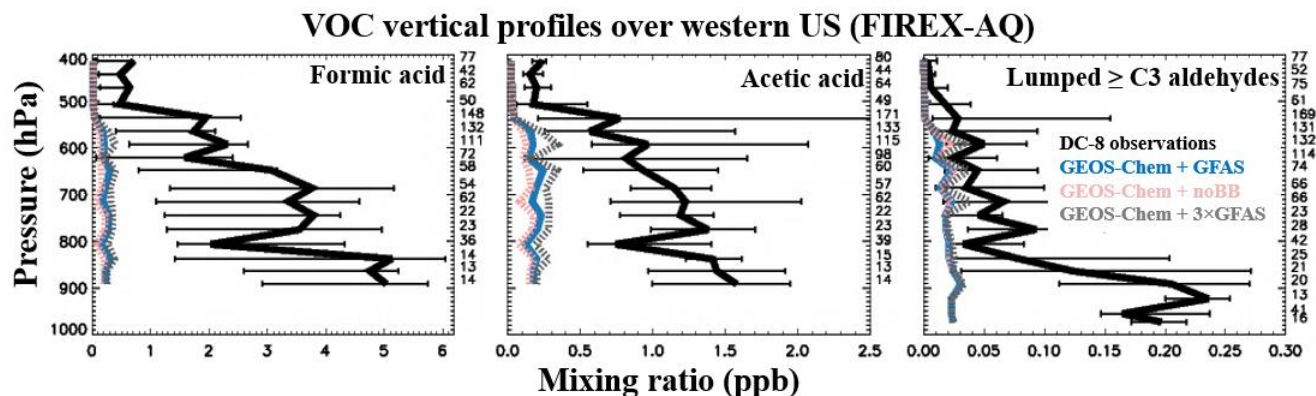GEOS-Chem + noBB
GEOS-Chem + 3×GFAS

Figure S9. Median vertical profiles of three observed VOC mixing ratios in the western US during the FIREX-AQ aircraft campaign (July-September 2019). GEOS-Chem driven by GFASv1.2 is compared to observations. Also shown are two model sensitivity tests with biomass burning emission turned off (noBB) and with tripling GFASv1.2 emission (3 × GFAS). Model results are sampled along the flight tracks at the time of flights; and both the observations and model outputs are regridded to the model resolution. Profiles are binned to the nearest 30 hPa. Horizontal bars show the 25th-75th percentile range of measurements in each vertical bin. The number of observations in each bin is given on the right side of each panel. Results are filtered to include only data where the number of datapoints for the pressure bin is larger than 10.
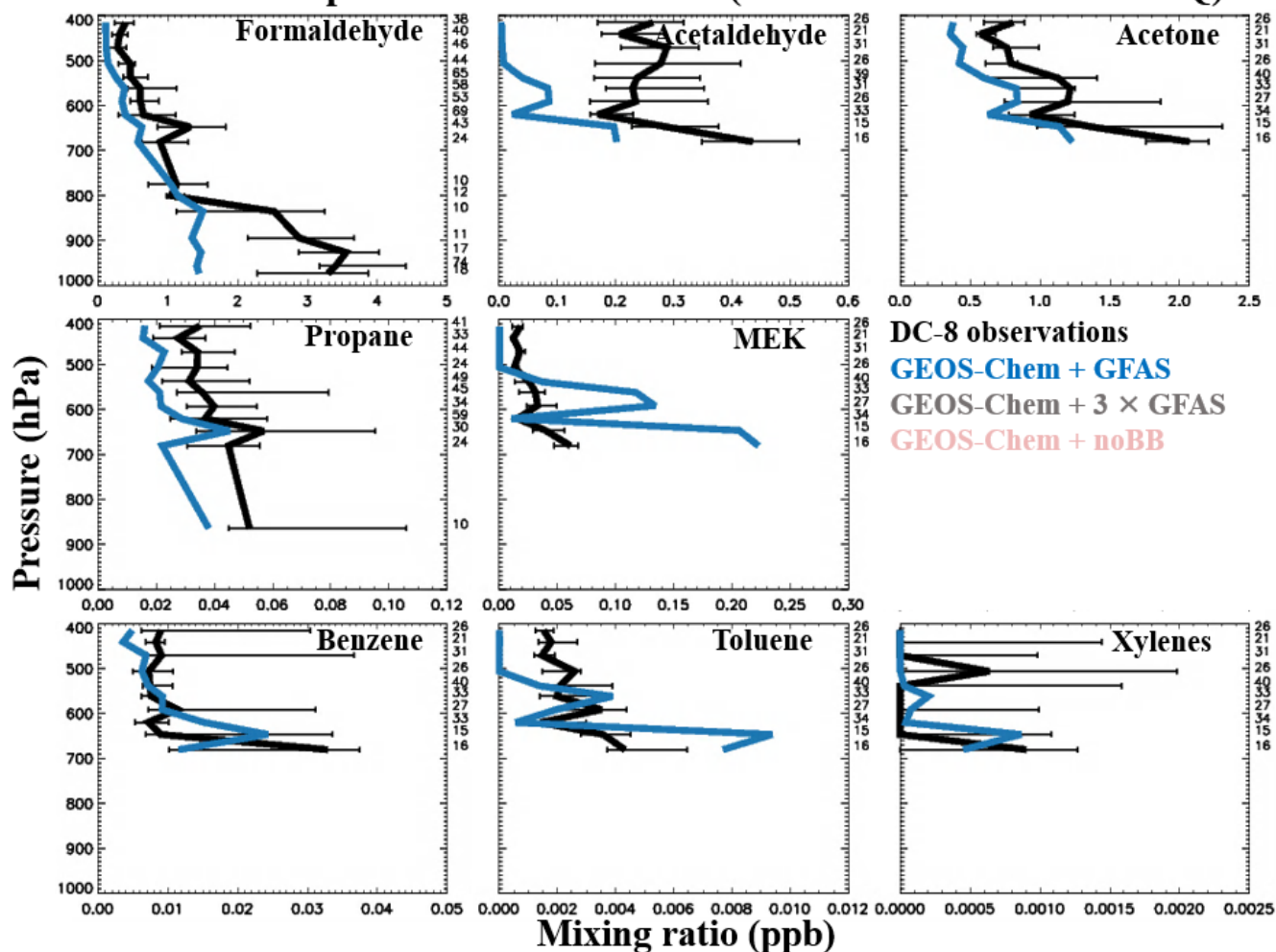
15

Figure S10. Median vertical profiles of observed VOC mixing ratios in the western US for low/no smoke conditions sampled in FIREX-AQ. Observations are compared to GEOS-Chem simulation driven by GFASv1.2. Results are filtered to include only data coincident with the bottom 25th percentile of observed acetonitrile, where $\Delta CH3CN/\Delta CO$ larger than 2.01 ppb ppm^{-1}, and where the number of datapoints of each pressure bin are larger than 5. Model results are also sampled along the flight tracks at the time of flights; and both observations and model outputs are regridded to model resolution. Profiles are binned to the nearest 30 hPa. Horizontal bars show the 25th-75th percentile range of measurements in each vertical bin. The number of observations in each bin is given on the right side of each panel.