Supplementary material:

Table S1. VOC species used in F0AM box model to calculate OH reactivity

Alkanes	**Alkenes/Alkynes**	**Aromatics**	**Oxygenated**
Methane	Ethyne	Benzene	Formaldehyde
Ethane	Ethene	Toluene	Methanol
Propane	Propene	Ethylbenzene	Acetaldehyde
n-Butane	1-Butene	o-Xylene	Acetone
i-Butane	cis-2-Butene	m-Xylene	Propanal
n-Pentane	trans-2-Butene	p-Xylene	MVK
i-Pentane	i-Butene	Furan	Methacrolein
n-Hexane	1-Pentene	Furfural	Hydroxyacetone
2-Methylpentane	cis-2-Pentene	2-Methylfuran	Glycolaldehyde
3-Methylpentane	trans-2-Pentene	3-Methylfuran	Formic Acid
n-Heptane	2-Methyl-1-butene	Dimethyfuran	Acrolein
2,2-Dimethyl-butane	3-Methyl-1-butene	5-Methylfurfural	Ethanol
n-Octane	Isoprene	Catechol	Glyoxal
n-Nonane	α-Pinene	Guaiacol	Methyglyoxal
n-Decane	Limonene	Creosols	MEK
Cyclohexane	β-Pinene	Syringol	Butanal
		Furanone	2-Methylpropanal
		Phenol	Methyl Acetate
		Cresol	Ethyl Formate

	Benzaldehyde	2,3-Butanedione
	Styrene	2-Methyl-3-buten-2-ol (MBO)

Table S2. Wildfire plume selection conditions. Conditions to select the plumes suitable for analyzing the evolution of HCHO in wildfires based on iWAS merge data. For example, the 0807 Williams Flats plume 2 was not selected due to lack of iWAS data for most of the sampling plume and thus there were not enough data for appropriate VOC decay. The plumes in shaded grey area meet our selection conditions and are used in our analysis.

Wildfire plumes sampling circuits	**Lagrangian sampling patterns (transects >3)**	**Elevated concentrations above background (max 1s HCHO > 600 ppt)**	**Appropriate VOC ratios decay with physical age ($r^2 \geq 0.57$)**	**Sufficient data with appropriate VOC decay (data numbers ≥ 8)**
20190724 Sheep	√	√	√	×
20190724 Shady	×	√	√	×
20190725 Shady 1	√	√	√	×
20190725 Shady 2	√	√	√	√
20190725 Shady 3	√	√	√	×
20190729 North Hill	√	√	√	√
20190729 Tucker	√	√	×	√
20190730 Tucker	√	×	√	√
20190730 Lefthand	√	√	×	√
20190802 RidgeTop	×	√	√	√
20190802 Mica and Lick Creek	√	√	√	√

20190803 Williams Flats 1	√	√	√	√
20190803 Williams Flats 2	√	√	√	√
20190806 Williams Flats	√	√	√	√
20190806 Horsefly	√	√	×	√
20190807 Williams Flats 1	√	√	√	√
20190807 Williams Flats 2	√	√	×	×
20190808 Williams Flats aged	×	√	×	√
20190808 Williams Flats PyroCb	×	√	√	√
20190812 Castle1	√	√	√	√
20190812 Castle 2 nighttime	√	√	√	√
20190813 Castle1	√	√	×	√
20190813 Castle 2	√	√	√	√
20190815 Sheridan	×	√	×	√
20190816 Sheridan	√	√	√	√
20190830 Blackwater River Forest	√	√	√	√

√ : meet the condition.

× : does not meet the condition.

Table S3. Mean and standard deviation of nHCHO production and loss rates of the 12 plumes.

Plumes	nHCHO production rate (mean±std, ppt/ppb/hr)	nHCHO loss rate (mean±std, ppt/ppb/hr)
20190725	2.8±2.0	4.1±0.7
20190729	3.4±4.5	2.5±0.5
20190802	6.5±2.5	4.7±0.1
20190803	0.6±1.9	3.1±1.0
20190803	1.4±0.8	1.2±0.1
20190806	4.0±4.9	6.1±0.6
20190807	2.3±0.7	1.5±0.3
20190812	2.6±0.8	2.1±0.8

20190812N	0.0±0.2	-0.2±0.0
20190813	2.6±1.7	0.6±0.0
20190816	1.6±2.2	0.8±0.4
20190830	14.1±5.2	10.0±0.4

Table S4. Mean and standard deviation of O_3 concentrations and the uncertainty in OH estimation due to O_3 variation of the 12 plumes

Plumes	O_3 mixing ratios (mean±std, ppb)	OH estimation uncertainty due to O_3 variation (molec cm-3)
20190725	32.0±5.7	0.31×10^6
20190729	51.2±1.6	0.15×10^6
20190802	55.5±6.7	0.51×10^6
20190803	88.2±18.6	1.51×10^6
20190803	43.7±19.2	1.55×10^6
20190806	58.3±4.3	0.36×10^6
20190807	60.4±23.5	1.42×10^6
20190812	50.6±2.3	0.14×10^6
20190812nighttime	47.5±0.8	0.05×10^6
20190813	56.1±4.4	0.26×10^6
20190816	63.1±6.5	0.34×10^6
20190830	74.4±17.3	2.04×10^6

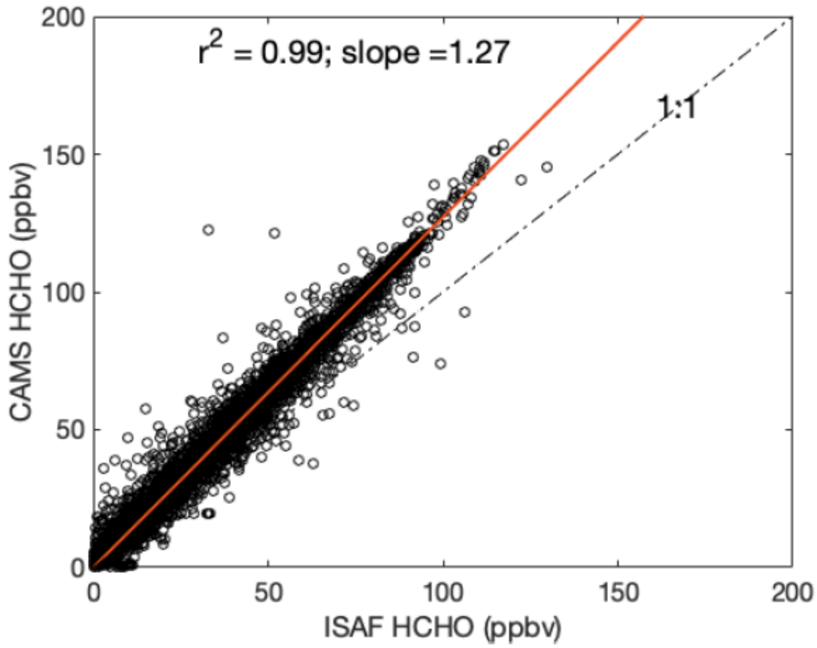

Figure S1. A scatter plot of 1-s average CAMS vs. ISAF HCHO measurements for western US wildfire flights and one eastern US wildfire flight during FIREX-AQ. CAMS HCHO measurements well correlates with ISAF HCHO measurements with a slope of 1.27 and an r^2 = 0.99.

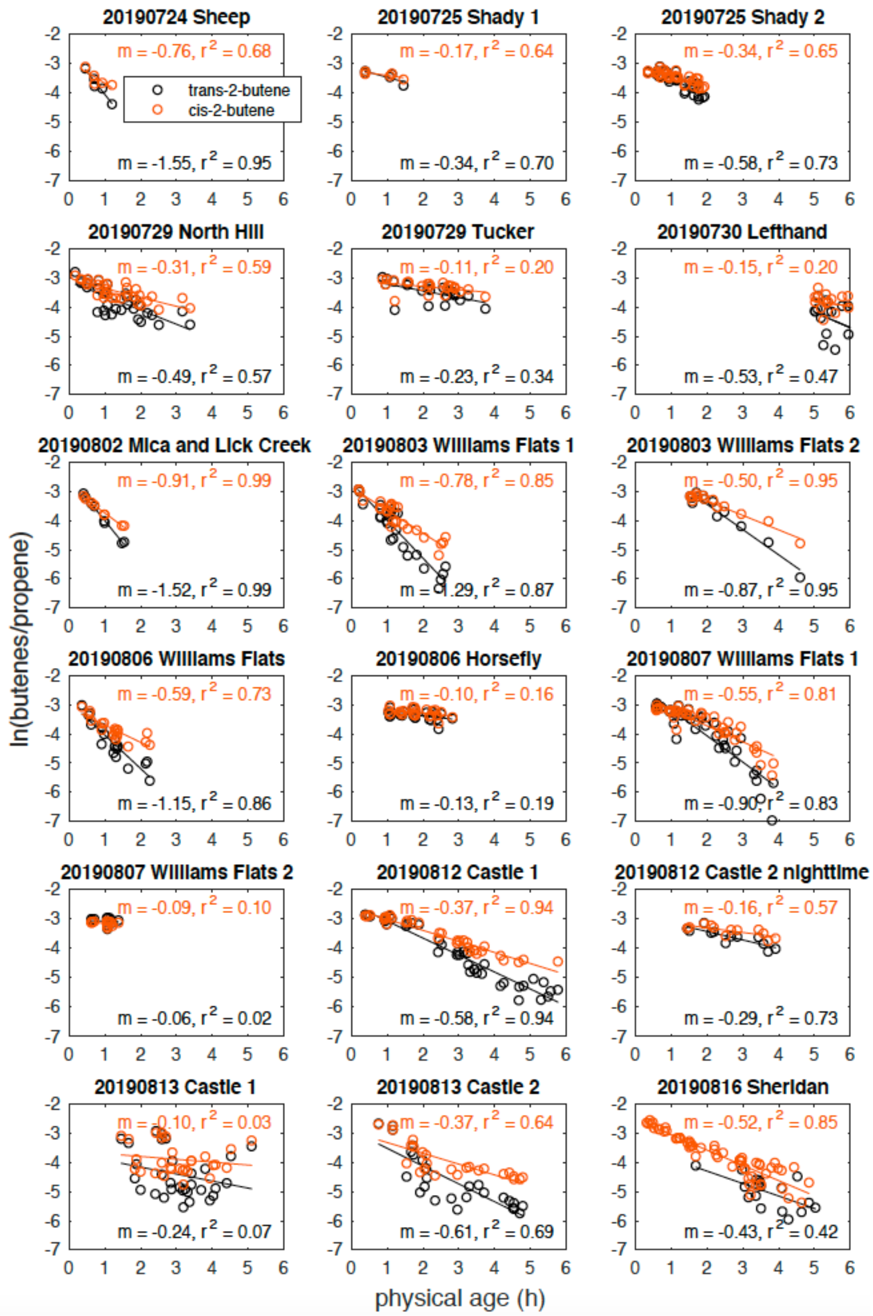

Figure S2. Natural logarithms of cis-2-butene to propene ratios (red circles) and trans-2-butene to propene ratios (black circles) vs. physical age for 18 western US wildfire plumes that met selection conditions a) and b) in Sect. 2.3. 25 July Shady 3 plume was not plotted because of the unavailability of iWAS data. The slopes of the linear fits to the data (m, shown on the plots) reflect the oxidation by OH and O_3 and are used to calculate the average OH concentrations with average

O_3 concentrations and reaction coefficients. The eastern US wildfire plume not plotted here is displayed in Fig. 2.

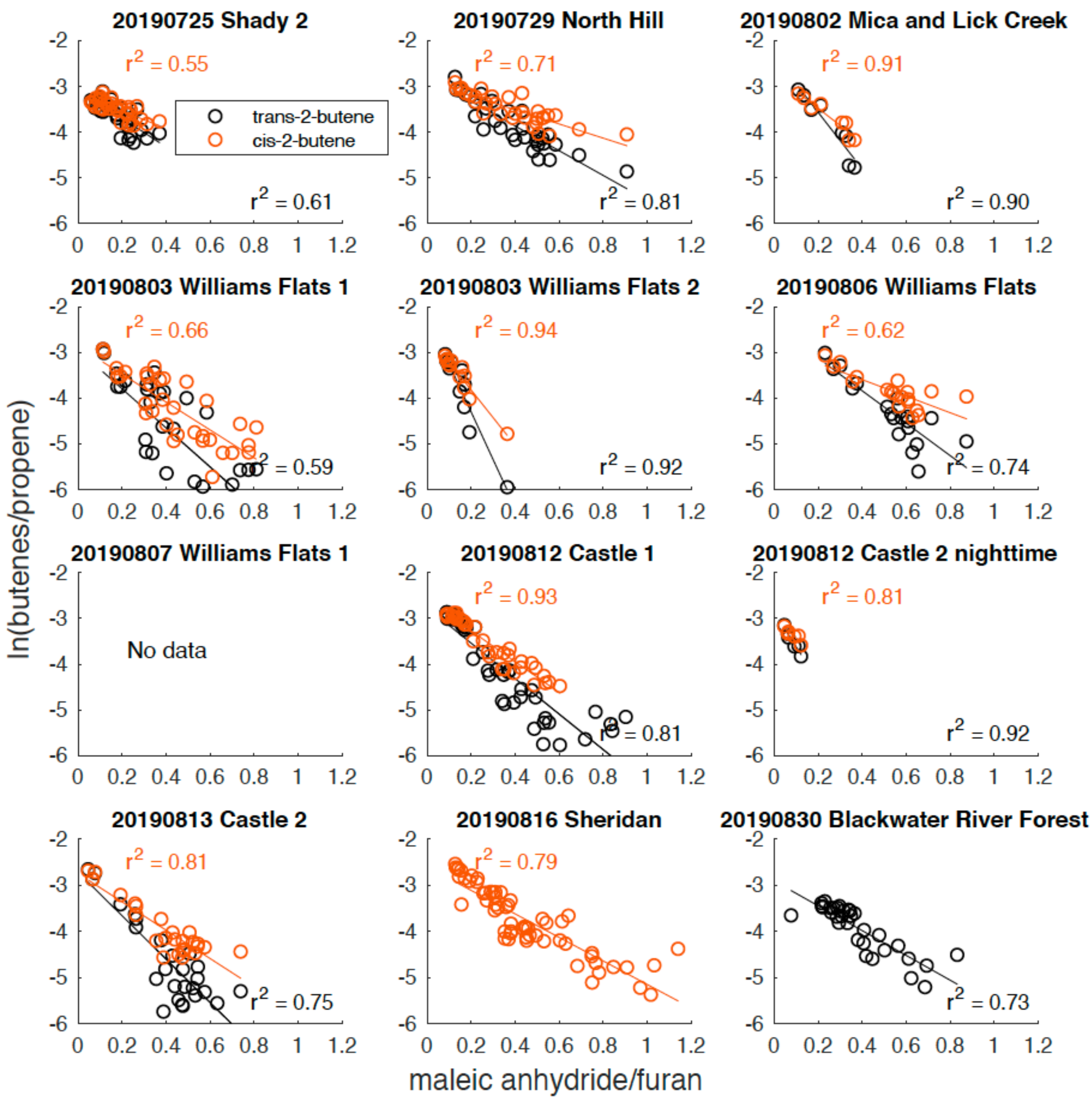

Figure S3 A scatter plot of ln (trans-2-butene/propene) and ln (cis-2-butene/propene) vs. maleic anhydride/furan for the plumes analyzed. No PTRMS data are available for 07 August plume.

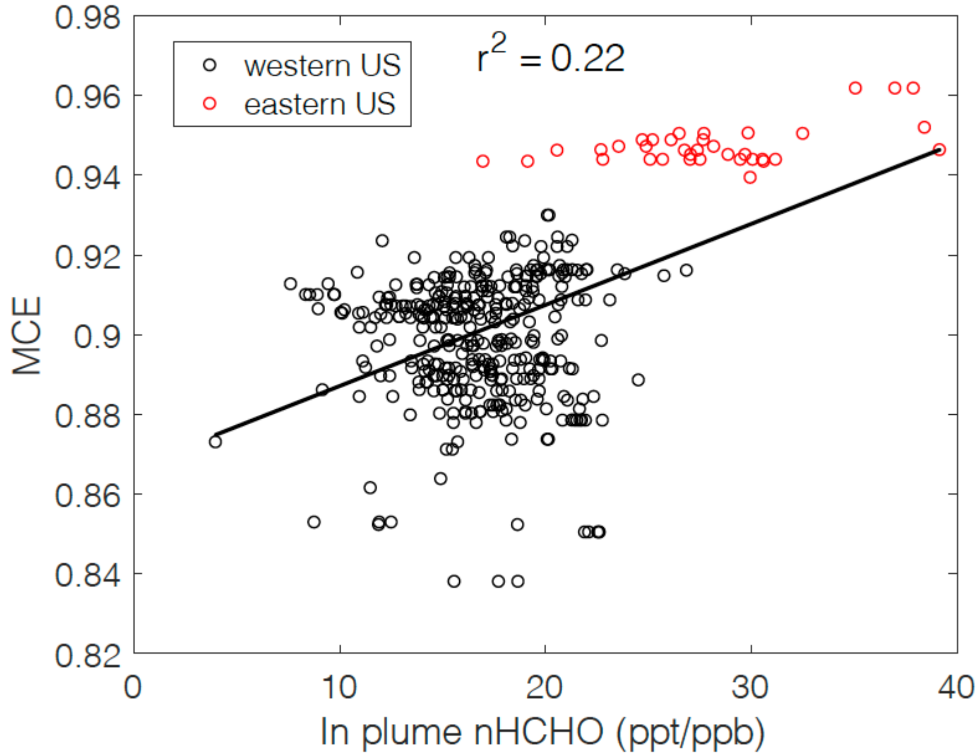

Figure S4. A scatter plot of nHCHO vs. modified combustion efficiency (MCE) for the 12 plumes analyzed. The slightly positive correlation is due to the eastern US wildfire plume that had higher MCE and in plume nHCHO than western US wildfire plumes.

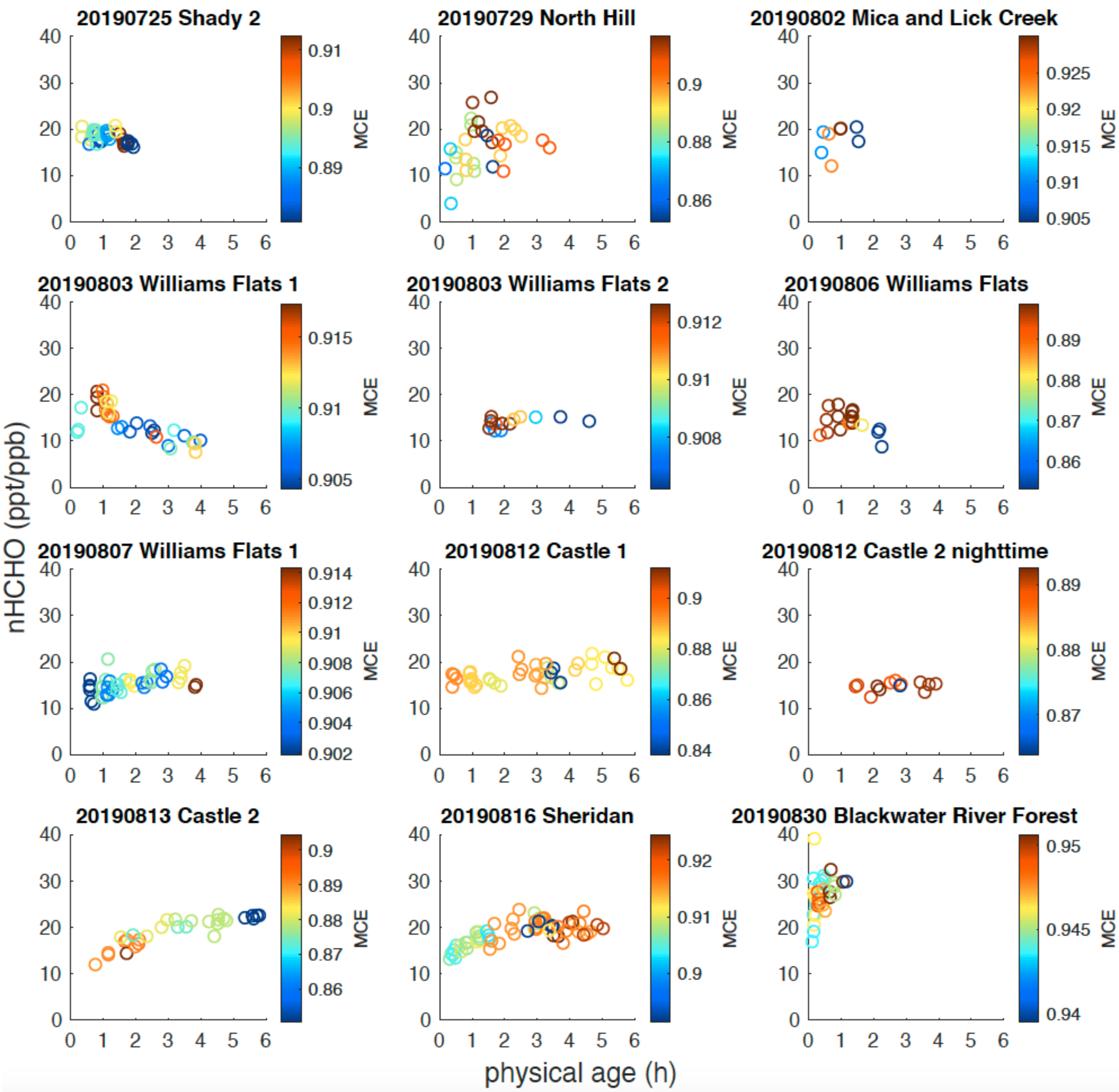

Figure S5. Trends of nHCHO for the 12 plumes analyzed color-coded by MCE.

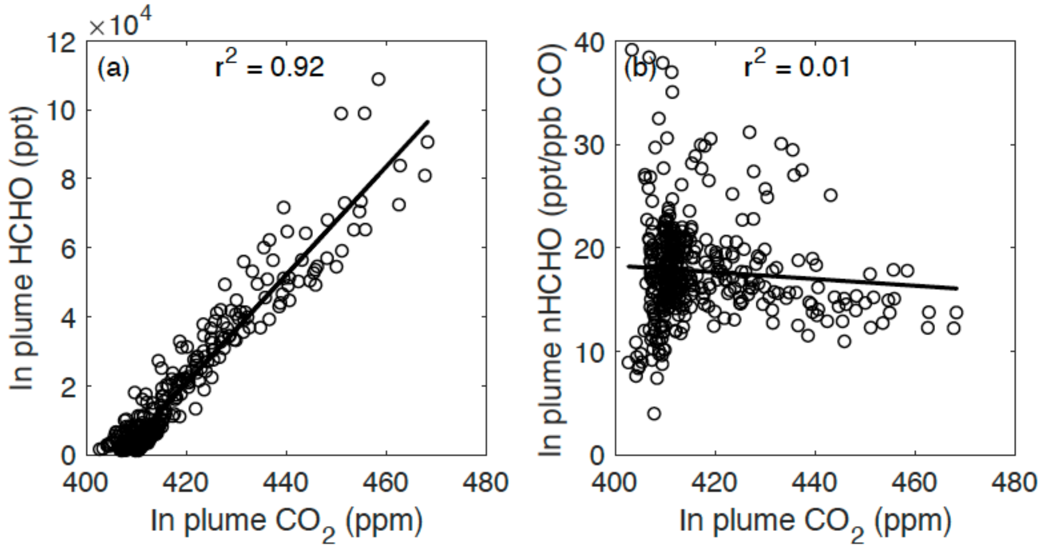

Figure S6. (a) A scatter plot of in plume HCHO vs. CO_2; (b) A scatter plot of in plume nHCHO vs. CO_2 for the 12 plumes. The slight decreased nHCHO at higher CO_2 concentrations can be due to the general increased nHCHO and decreased CO_2 trends with physical age. The CO_2 concentrations for each plume are provided in Figure S7.

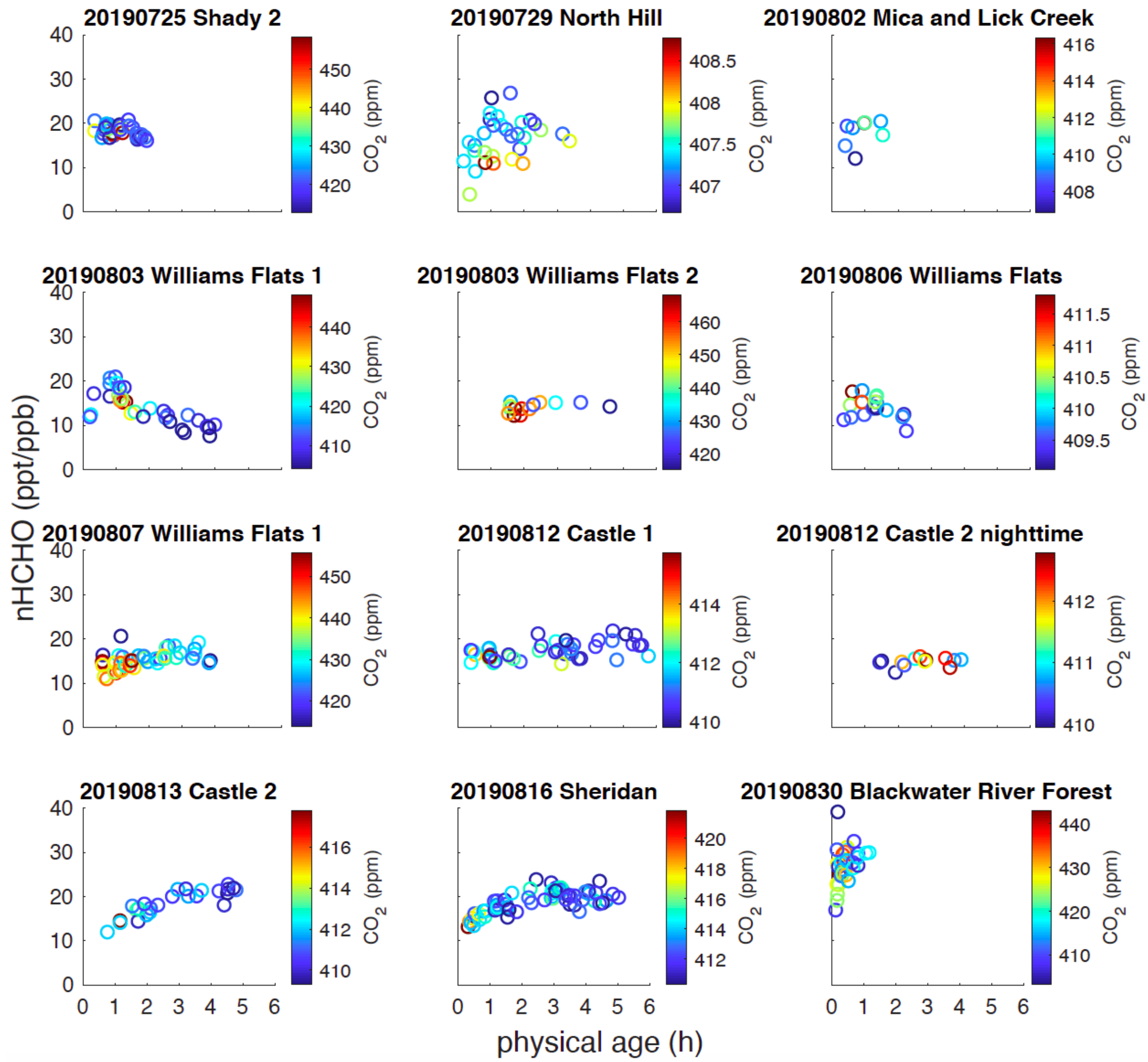

Figure S7. Trends of nHCHO for the 12 plumes analyzed color-coded by CO_2 concentrations, the variability of which is used as an approximation of FRP variability.

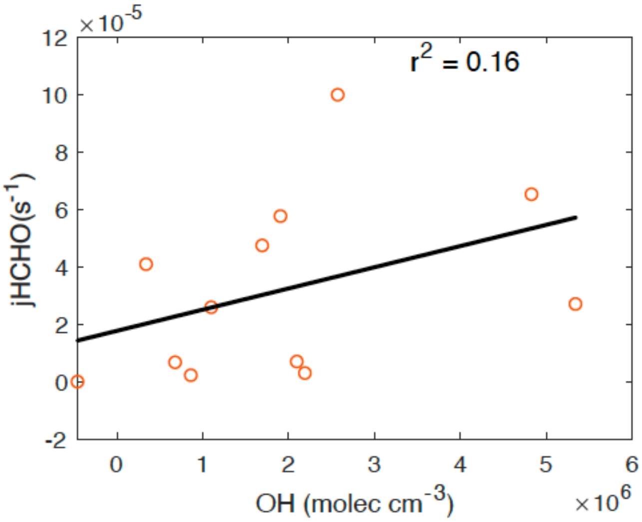

Figure S8 A scatter plot of photolysis rate of HCHO vs. average OH concentrations.