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Supplement of

Formaldehyde evolution in US wildfire plumes during the Fire Influence on Regional to Global Environments and Air Quality experiment (FIREX-AQ)

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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 name, plumes sampling date, and sampling circuits	**Lagrangian sampling patterns (transects >3)**	**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 Hills	√	√	√
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 O_3 mixing ratios, OH uncertainty due to O_3 variation, total OH uncertainty, and estimated OH of the 12 plumes

Plume sampling date	O_3 mixing ratios (mean±std, ppb)	OH uncertainty due to O_3 variability $\times 10^6$ (molecules cm^{-3})	Total OH uncertainty $\times 10^6$ (molecules cm^{-3})	Estimated OH $\times 10^6$ (molecules cm^{-3})
20190725	32.0±5.7	0.31	0.59	1.69
20190729	51.2±1.6	0.15	0.60	0.34
20190802	55.5±6.7	0.51	0.70	5.34
20190803	88.2±18.6	1.51	1.76	1.90
20190803	43.7±19.2	1.55	1.62	2.19
20190806	58.3±4.3	0.36	1.10	2.57
20190807	60.4±23.5	1.42	1.50	2.09
20190812	50.6±2.3	0.14	0.23	1.10
20190812nighttime	47.5±0.8	0.05	0.46	-0.45

20190813	56.1±4.4	0.26	0.72	0.86
20190816	63.1±6.5	0.34	0.33	1.67
20190830	74.4±17.3	2.04	1.71	4.83

Table S4. Mean and standard deviation of nHCHO production and loss rates of the 12 analyzed plumes.

Plume sampling date	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

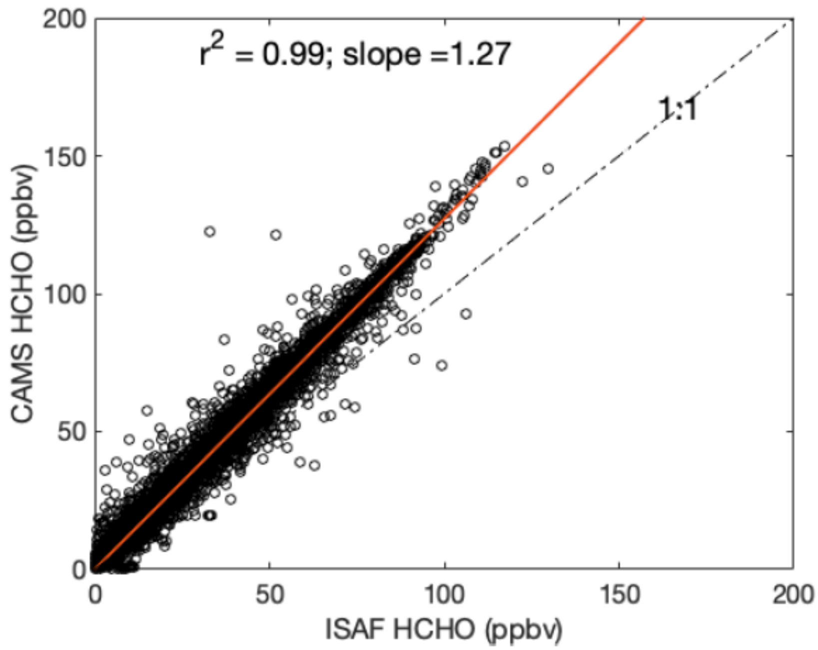

Figure S1. A scatter plot of 1-s average CAMS vs. ISAF HCHO measurements for western US wildfire flights and one eastern US wildfire flight during FIREX-AQ. CAMS HCHO measurements correlates well with ISAF HCHO measurements with a slope of 1.27 and an r^2 = 0.99.

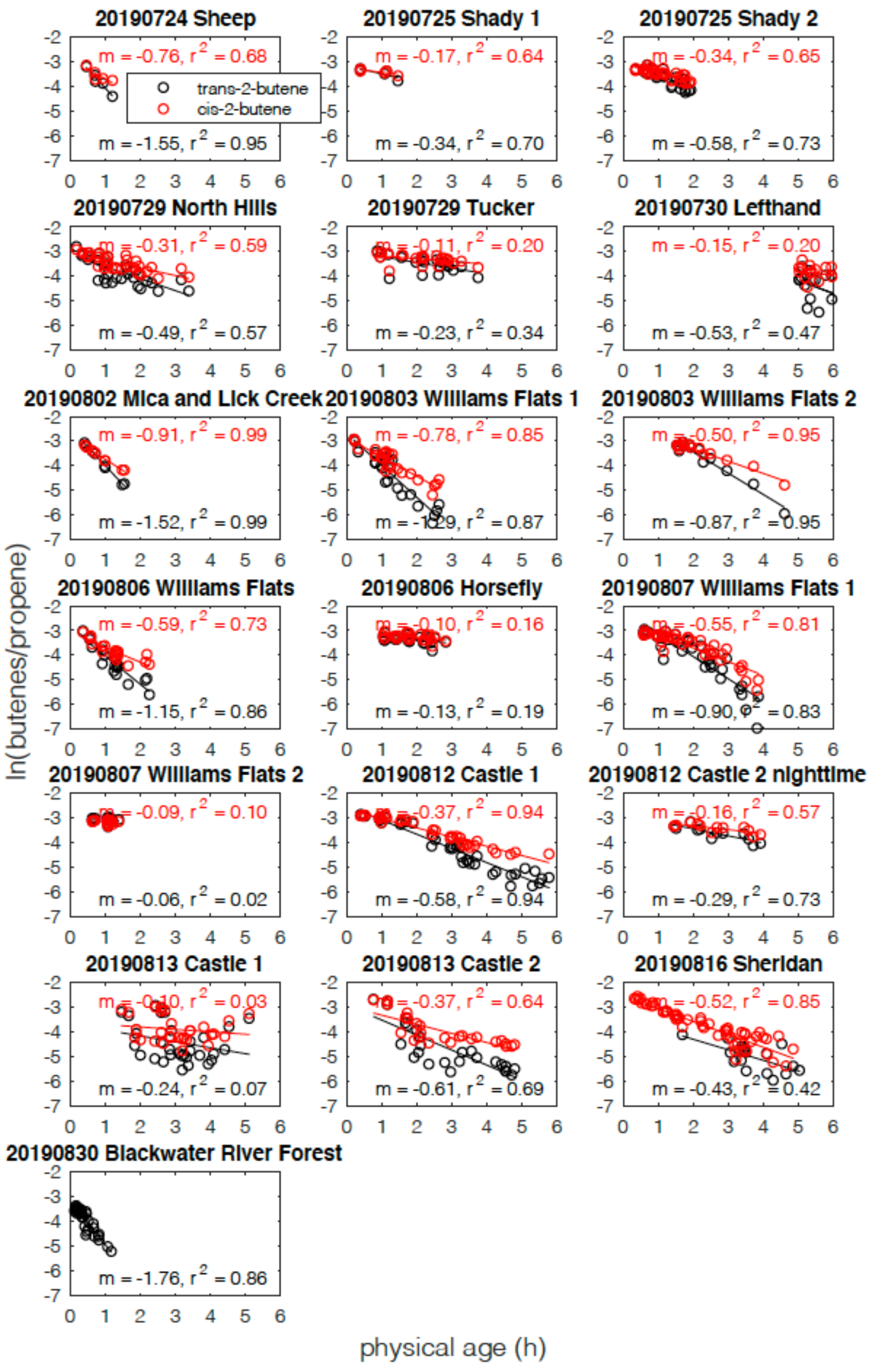

Figure S2. Natural logarithms of cis-2-butene to propene ratios (red circles) and trans-2-butene to propene ratios (black circles) vs. physical age for 18 western US and 1 eastern US wildfire plumes that met selection conditions a) in Sect. 2.3. 25 July Shady 3 plume was not plotted because of the unavailability of iWAS data. The plumes with good correlations ($r^2 \geq 0.57$) between natural logarithms of the butenes/propene ratios and physical age and with sufficient data (data points > 8) are selected for this analysis. 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.

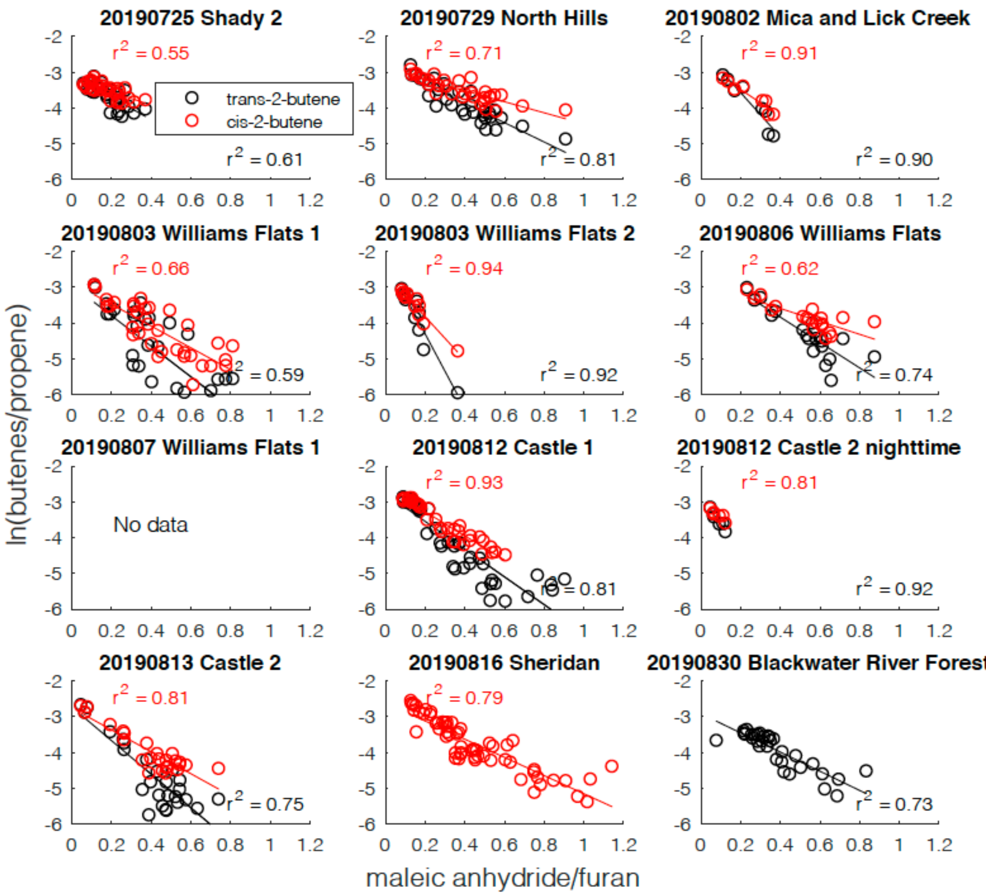

Figure S3 A scatter plot of ln (trans-2-butene/propene) and ln (cis-2-butene/propene) vs. maleic anhydride/furan for the plumes analyzed. No PTRMS data are available for 07 August plume.

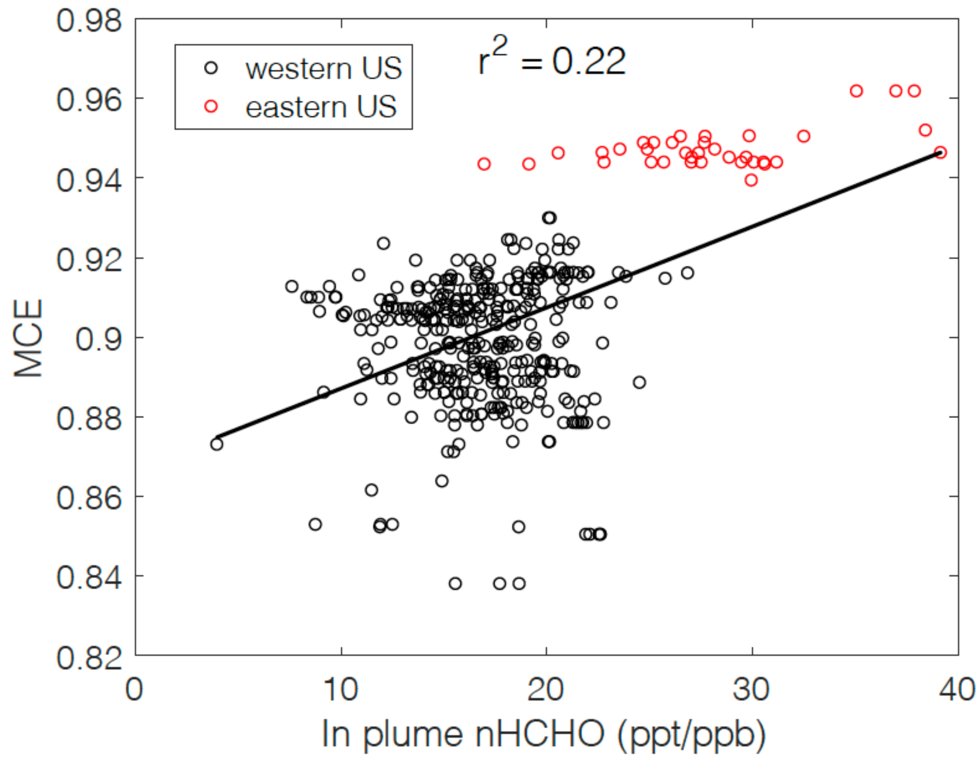

Figure S4. A scatter plot of nHCHO vs. modified combustion efficiency (MCE) for the 12 plumes analyzed. The slightly positive correlation is due to the eastern US wildfire plume that had higher MCE and in plume nHCHO than western US wildfire plumes.

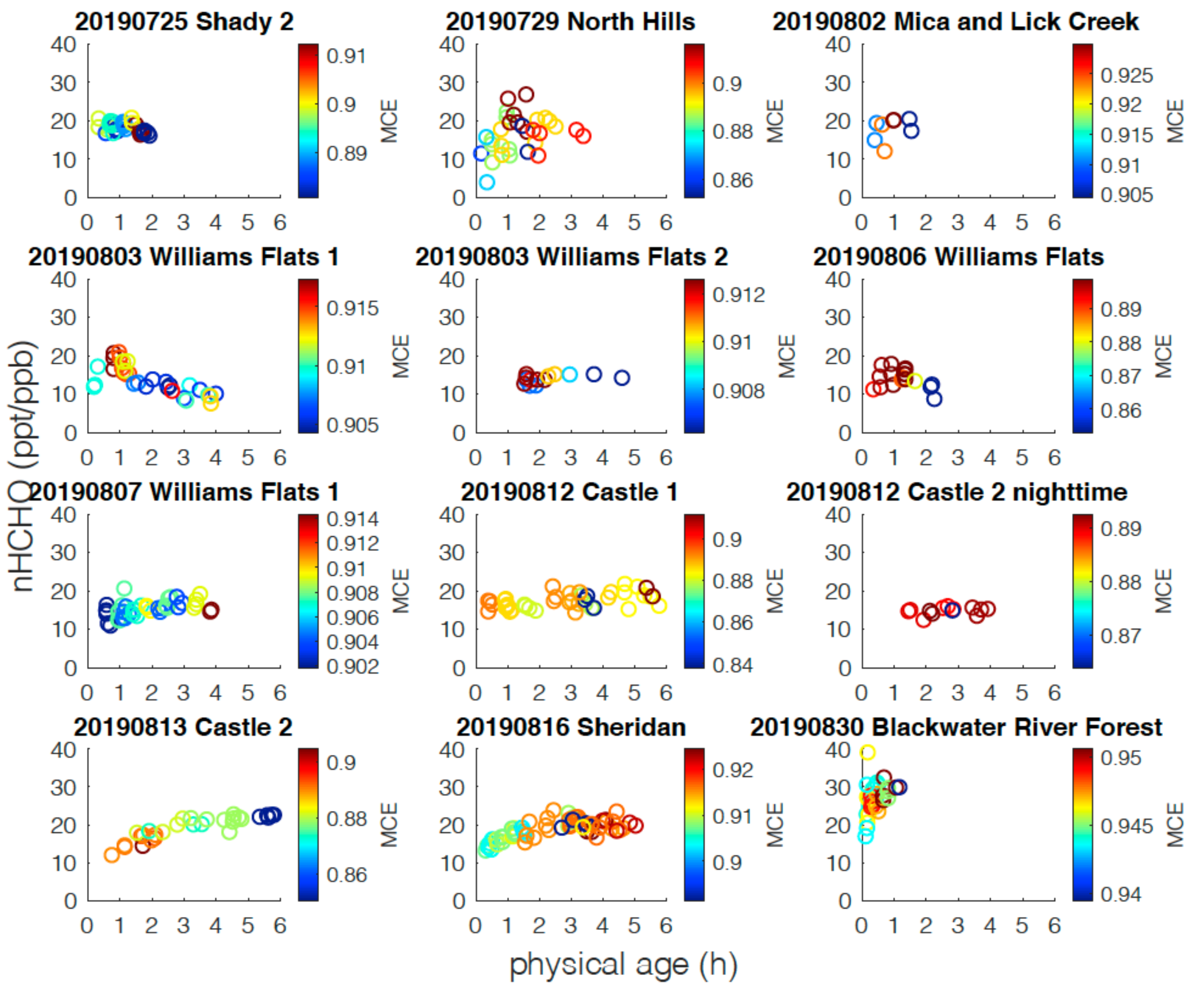

Figure S5. Trends of nHCHO against physical age for the 12 analyzed plumes, colored by MCE.

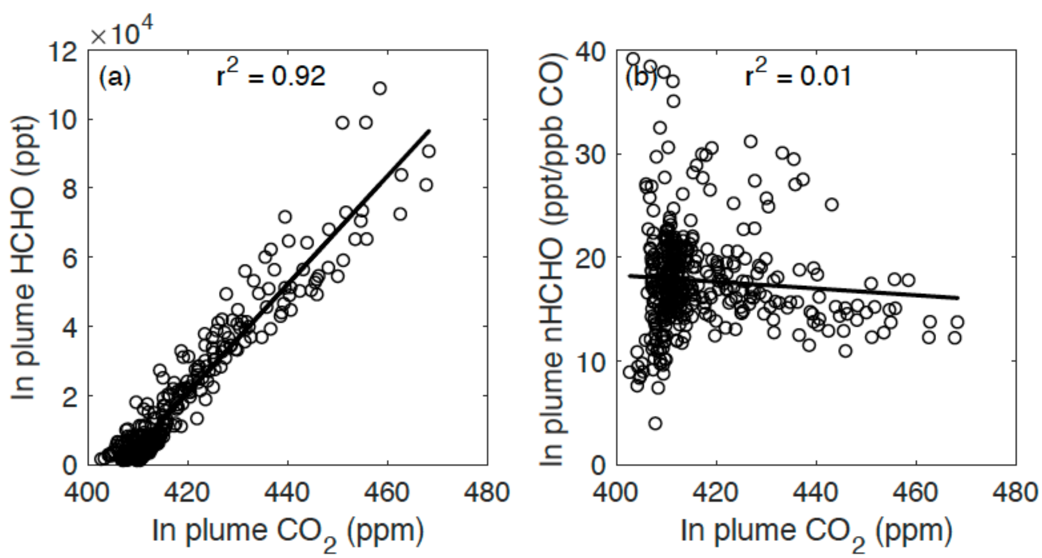

Figure S6. (a) A scatter plot of in plume HCHO vs. CO_2; (b) A scatter plot of in plume nHCHO vs. CO_2 for the 12 plumes. The slight decreased nHCHO at higher CO_2 concentrations can be due to the general increased nHCHO and decreased CO_2 trends with physical age. The CO_2 concentrations for each plume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

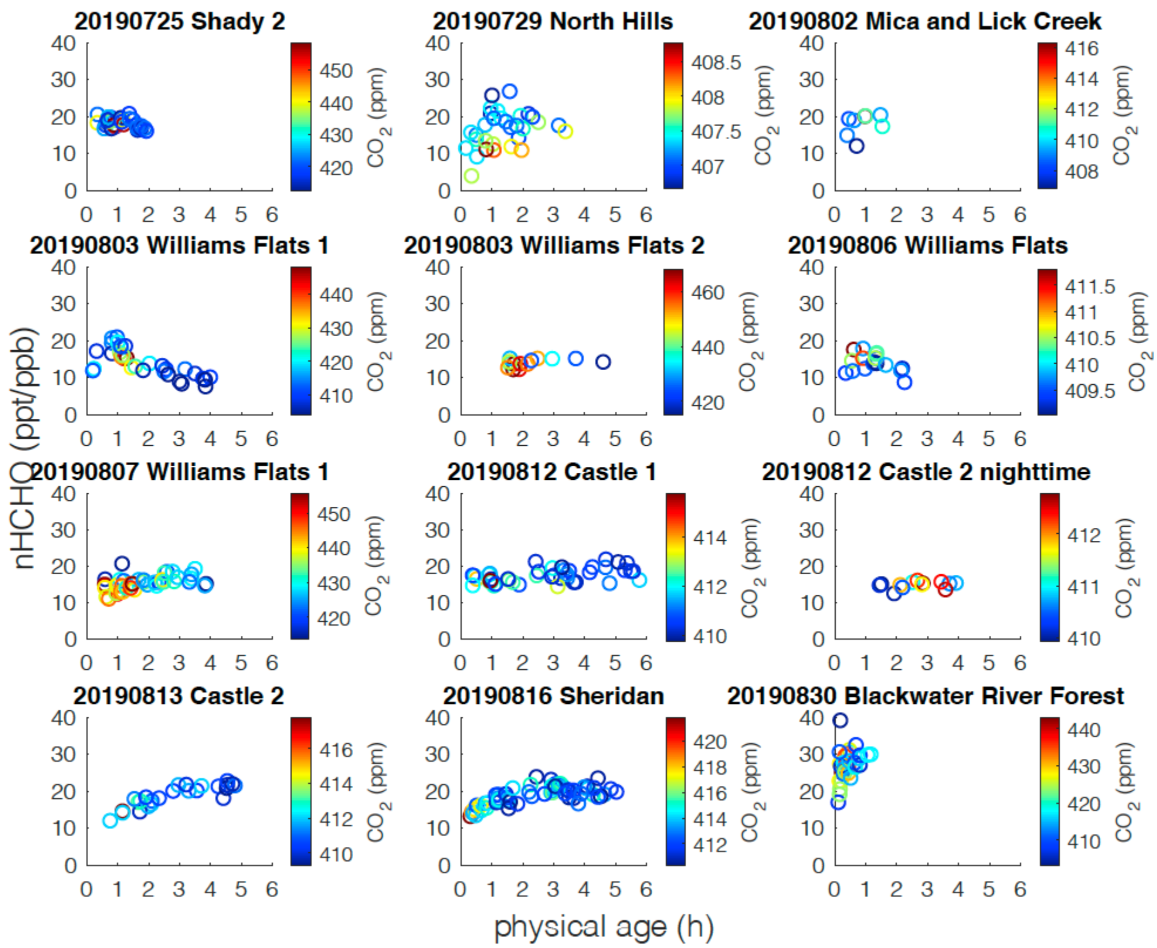

Figure S7. Trends of nHCHO against physical age for the analyzed 12 plumes, colored by CO_2 concentrations, the variability of which is used as an approximation of FRP variability.

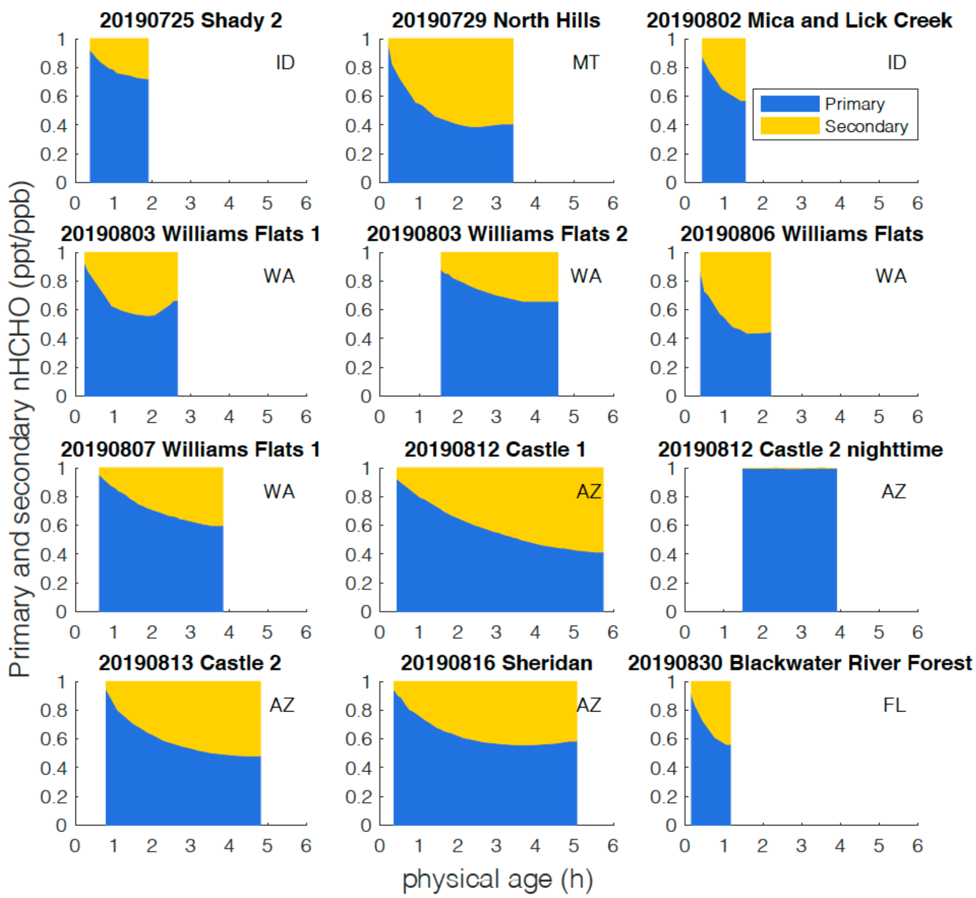

Figure S8. Fraction of primary and secondary nHCHO vs. plume physical age for the 12 plumes. The fraction of primary nHCHO is estimated by assuming nHCHO and the loss rate of nHCHO were constant between emission and the closest observation. The slight increase in primary nHCHO fraction with physical age for the 20190803 Williams Flats 1 may be due to the uncertainty in the polynomial fit of the observed nHCHO, the nHCHO loss rate calculation, Lagrangian plume assumption, or emission variation.

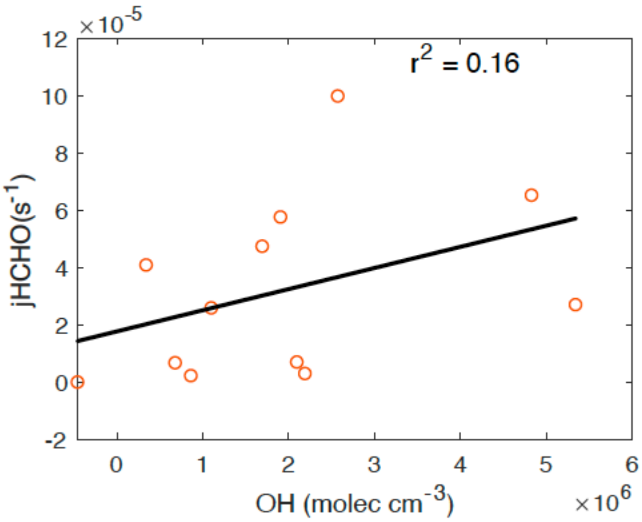

Figure S9 A scatter plot of photolysis rate of HCHO vs. average OH concentrations.

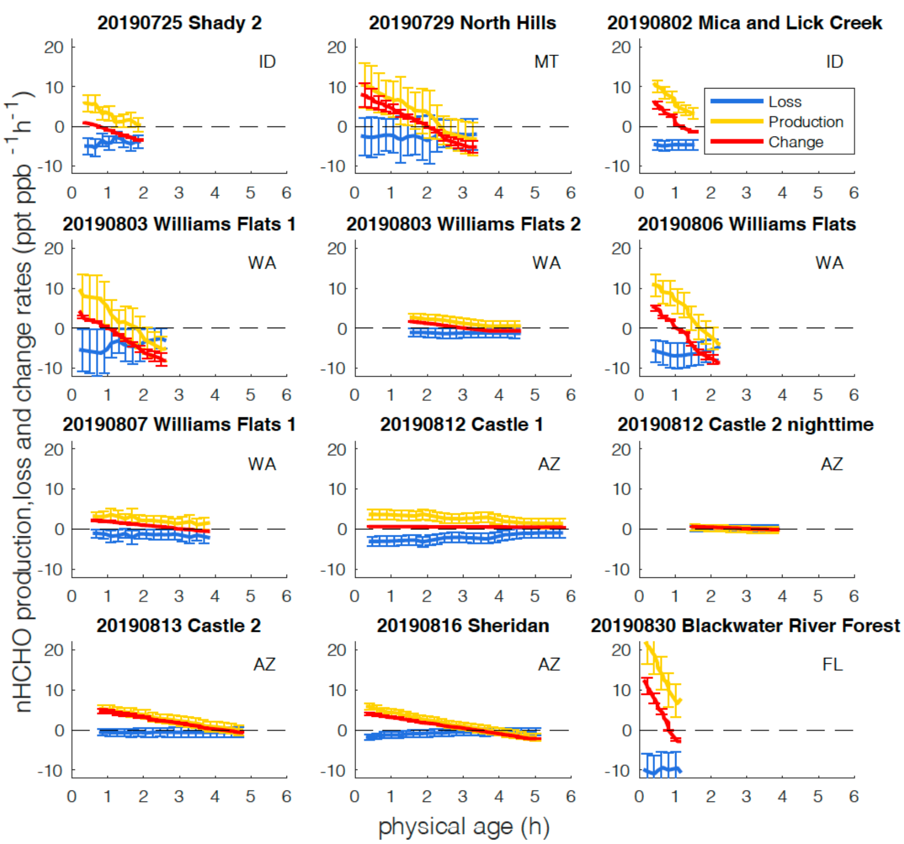

Figure S10 nHCHO production (gold), loss (blue) and change (red) rates with physical age for the 12 plumes. The uncertainty (red error bars) in nHCHO change rate is estimated from the difference between measured nHCHO and the polynomial fit. The uncertainty (blue error bars) in nHCHO loss rate is estimated from the uncertainty in OH estimation and the difference between the loss rate calculated from the measured photolysis rates and temperature dependent reaction rate coefficient and the loss rate calculated from the interpolation of the average photolysis rates and reaction rate coefficient. The uncertainty (gold error bars) in nHCHO production rate is the combined uncertainty in nHCHO loss rate and change rate. The uncertainty accounts for the majority of the negative calculated nHCHO production rates. The negative nHCHO production rate at the end of the 0803 Williams Flats 1 plume cannot be not fully accounted by the estimated uncertainty. This may be due to emission variation or uncertainties in the Lagrangian plume sampling assumption for air masses downwind away from the source.

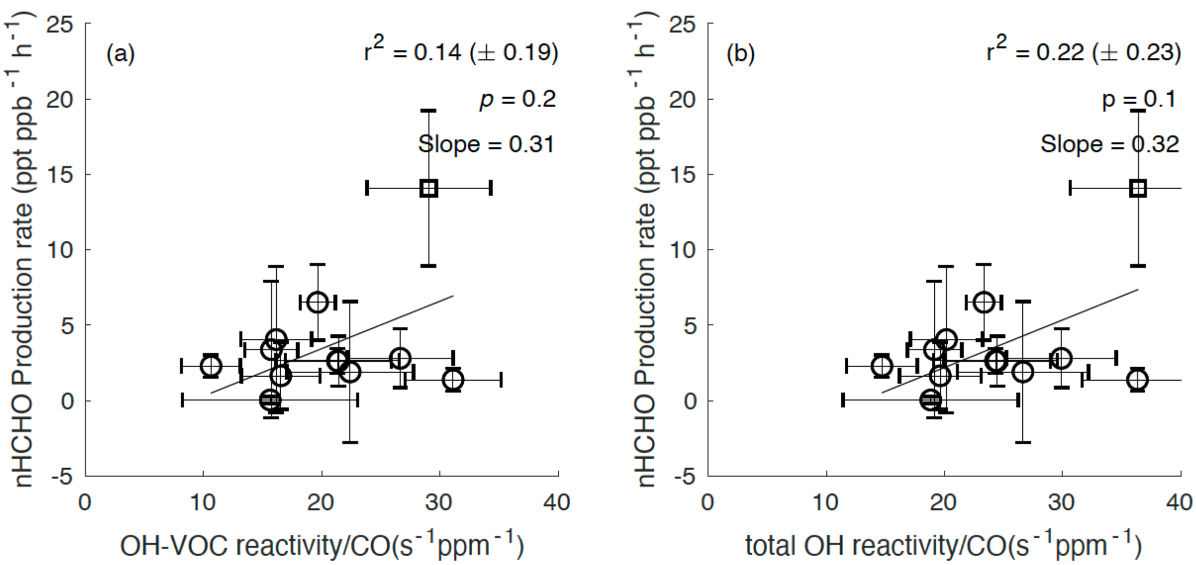

Figure S11. (a). Average nHCHO production rate vs. normalized OH-VOC reactivity (OH-VOC reactivity /CO) for the 12 plumes including 11 western US wildfire plumes (circles) and 1 eastern US wildfire plume (square). Unweighted bivariate linear regression was applied to fit the data. The unweighted (or equally weighted) bivariate linear regression yields a slope = 0.31, $r^2 = 0.14 \pm 0.19$, and $p = 0.2$ for the 12 wildfire plumes. (b) Average secondary nHCHO production rate vs. total OH reactivity/CO for the 12 plumes including 11 western US wildfire plumes (circles) and 1 eastern US wildfire plume (square). An unweighted (or equally weighted) bivariate linear regression yields a slope = 0.32, $r^2 = 0.22 \pm 0.23$, and $p = 0.1$ for the 12 wildfire plumes.